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Global Risk-Based Management of Chemical Additives II

Risk-Based Assessment and Management Strategies

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Founded by Otto Hutzinger

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Volume 23

The Handbook of Environmental Chemistry

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Global Risk-Based Management of Chemical Additives II

Risk-Based Assessment and Management Strategies

Volume Editors: Bernd Bilitewski · Rosa Mari Darbra ·
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In Memoriam Otto Hutzinger 1933–2012

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Aims and Scope

Since 1980, *The Handbook of Environmental Chemistry* has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry,* there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry,* the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of*

Environmental Chemistry provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Editors-in-Chief

Volume Preface

This second volume of this book, *Global Risk-Based Management of Chemical Additives*, presents the results obtained after 3 years of research conducted during the EC funded RISKCYCLE project (Risk-based management of chemicals and products in a circular economy at a global scale).

The main objective of this project was to establish and coordinate a global network of European and international experts and stakeholders from worldwide countries to assess the risks of hazardous chemicals and additives contained in different daily products. The transport of these compounds is given at a global scale, increasing their potential damage to the environment and citizens all over the world.

In the first part of this book, different models related to the assessment of the potential risk posed by the chemical additives are presented. These models come from different fields of expertise: toxicology, risk assessment, chemicals fate and exposure, life cycle assessment, economics, etc. The potential benefits of the different models as well as their drawbacks are analyzed in order to select some of them for the application to particular case studies.

Some aspects related to the chemicals regulations are also reviewed, especially those affecting the European new chemicals legislation, such as REACH (regulation concerning the Registration, Evaluation, Authorizations and restriction of Chemicals). Some socioeconomic aspects are also treated in relation to the need of chemicals for the society.

In the second part, specific case studies in which the aforementioned models have been applied are presented. The results of such application as well as their reliability are discussed. Toxicological studies in Italy, risk assessment of electronic waste in China, or disposal of bearing lamps in India are some examples of selected scenarios.We hope that the scientific community finds in this book a source of information and inspiration to continue the research on chemical additives contained in products around the world.

Finally, we would like to thank all the authors who have contributed to this book, for their effort in gathering the information and elaborating the different chapters. We are also grateful that the advisory board of the project was helping us to keep realism in the project discussions. We would like to mention especially Dr. Jürgen Büsing, scientific officer from the Commission DG Research, for his help and his guiding comments.

Georges Deschamps
EC Project Officer

B. Bilitewski, R.M. Darbra, D. Barceló
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Introduction

D. Barceló, R.M. Darbra, B. Bilitewski, V. Grundmann, and A. Zehm

Abstract Chemicals are part of different daily products due to the characteristics that they provide to them. However, their release into the environment during the end of the product's life can affect harmfully the environment and the citizens. The worldwide transport of these chemicals at a global scale increases this negative potential effect. In this sense, initiatives such as the RISKCYCLE project (risk-based management of chemicals and products in a circular economy at a global scale) are trying to assess the risks of these substances in a circular economy.

This second volume of the book presents the results obtained during the RISKCYCLE project, paying special attention to a set of selected additives in the diverse industrial sectors (i.e., PFOS, DEHP, Pb). Different methodologies have been used to analyze aspects such as the fate, human and environmental exposure, and toxicity of these compounds. Case studies have been developed to assess their risk in developing countries such as China or Vietnam. The findings have been presented in the different RISKCYCLE workshops as well as at the final conference in Dresden.

Finally, some research gaps have been identified which will provide the framework for future work in the field of the chemicals and the environment.

Keywords Chemical risk, Environment, Global scale, Human health

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This book includes the results of a Coordination Action funded by the European Union called RISKCYCLE (risk-based management of chemicals and products in a circular economy at a global scale). This project (n. 226552) started the 1st of September of 2009 and ended on the 31st of August 2012. Its main objective was to establish and coordinate a global network of European and international experts and stakeholders from worldwide countries (e.g., European countries, China, India, Brazil, Vietnam) to assess the risks of hazardous chemicals and additives contained in different daily products.

In order to accomplish with the aforementioned aim, during the first year of project, an extensive research on the different chemical additives used in six industrial sectors was conducted: plastics, textiles, electronics, lubricants, leather, and paper. A list of selected chemical additives was identified for each sector and used as a study basis for the rest of the project. This is the case of the decabromodiphenyl ether (BDE) used in electronics as a flame retardant or the triclosan used in the textile as a biocide. The results of this investigation were presented in the first volume of this book (Global Risk-Based Management of Chemical Additives I: Production, Usage and Environmental Occurrence). This volume also included a section of case studies related to the selected additives in different countries (i.e., Denmark, Vietnam, Brazil, India). The main outcomes of the first part of the project are summarized below:

- There exists a very wide range of chemical compounds used as additives in final products.
- The role of the chemical additives in order to provide the final characteristics of the products is essential.
- These additives can be applied during different stages during the product production (e.g., manufacture, finishing process).
- At the end of the product's life, the chemicals can be released into the environment with potential harmful effects to humans and ecosystems.
- Information regarding emission, fate, exposure, and toxicity of these chemicals is scarce, especially at the end of the product's life.
- Assessing the environmental risks associated with additives along the whole product's life cycle at a global scale is an issue of paramount relevance, which requires the development of proper methodologies and effort to gather information.

This last outcome was the starting point for the work to be done during the second part of the project. At this point, the different work packages focused on their topics, that is, in environmental fate, toxicology, risk assessment, life cycle assessment, and socioeconomic issues. The objective was to apply the different methodologies related to these fields of knowledge to the selected substances in order to assess the potential risk that they can pose to the human health and the environment.

In part I of this second volume, a review of these different methodologies has been conducted. The potential benefits of the different models as well as the drawbacks are analyzed in order to select the most suitable of them for the application to particular case studies. In addition, also in this part, some aspects related to the chemicals regulations are also reviewed, especially those affecting the European new chemicals legislation, such as REACH (regulation concerning the Registration, Evaluation, Authorizations and Restriction of Chemicals). Some socioeconomic aspects are also treated in relation to the need of chemicals for the society.

On the other hand, in part II of this volume, a set of case studies are introduced. The application of the selected methodologies inside each one of the foresaid disciplines (e.g., risk assessment, life cycle assessment) to specific cases and countries is presented here. The results of such application are discussed as well as their reliability. Toxicological studies in Italy, risk assessment of electronic waste in China, or disposal of bearing lamps in India are some examples of selected scenarios.

All the data gathered during the RISKCYCLE project as well as the results have been presented in the book but at the same time to different international events such as the four international workshops organized by the RISKCYCLE project:

- 1st Riskcycle Workshop: Risk-based Management of Chemicals and Products in a Circular Economy at a Global Scale. Hanoi (Vietnam), 3–6 May, 2010
- 2nd Riskcycle Workshop: Risk of Chemical Additives and Recycled Materials. Shenyang (China), 15–19 November, 2010
- 3rd Riskcycle Workshop: Environmental and Health Risks of Chemical Additives and Recycled Materials. Rio de Janeiro (Brazil), 2–6 May 2011
- 4th Riskcycle Workshop: Sustainable Waster Management. New Delhi (India), 12–13 October

In addition, the RISKCYCLE team also organized a conference in Dresden in May 2012 where the main outcomes of the project were presented to and discussed with the public. Apart from this, other dissemination activities have been carried out during the project such as contributions to other conferences and workshops, exchange of students, publications in scientific journals, and training courses on different methodologies among the partners.

At the end of the project, a set of research gaps to be taken into consideration for the future have been identified such as the lack of data about chemicals in products as well as their emission to the environmental compartments, the need to assess the risk of chemical mixtures and not the chemicals by themselves, or the necessity of optimizing the current legislation on chemicals.

As it can be seen, after 3 years of research, several gaps have been identified and showed the need to continue the research on the chemicals contained in products and transported worldwide. This is the future aim of the RISKCYCLE consortium.

Part I

Methodologies for the Global Management Strategies

Life Cycle Assessment of Additives: Methodology and Data

Ester van der Voet, Lauran van Oers, Tomas Rydberg, Jenny Westerdahl, and Henrik Fred Larsen

Abstract Life cycle assessment (LCA) is a useful tool to assess impacts of cradle-to-grave chains of products/services. In the Riskcycle framework, the focus is on additives. Additives are usually minor constituents of products, but depending on their specific properties they can be important in the total scope of impacts of such products. In the LCA literature, additives are hardly visible. Most case studies of products containing additives do not mention them. The reasons for this are unclear, but are at least partly due to the fact that information on additives is not included in standard LCA databases. This is true for both life cycle inventory (LCI) and life cycle impact assessment (LCIA) databases. Therefore, it is difficult to conclude whether or not additives indeed are important contributors to environmental impacts over the life cycle.

In the Riskcycle project, we have addressed these knowledge gaps for two categories of materials: plastics and paper (printed matter). Case studies have been conducted for products containing those materials (Larsen, 2012, Case study on printed matter, Hdb Env Chem; van Oers and van der Voet, 2012, LCA case study cushion vinyl floor covering and DEHP, Hdb Env Chem). A coherent attempt has been made to derive LCIA factors for toxicity for a large number of plastics- and paper-related additives (Åström et al., 2012, Are chemicals in products good or bad for the society? – the economic perspective, Hdb Env Chem. doi:10.1007/698_2012_184). In this chapter, we summarize and generalize these findings and try to establish a coherent framework for LCA studies of products containing

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additives. In this framework, we distinguish three relevant levels that have to be part of such LCA studies: the product level, the material level and the additive level. We also establish the relation of LCA toxicity assessments with risk-based approaches.

Keywords Additives, Life Cycle Assessment, LCI data, LCIA data, Plastics, Paper

Contents

1 Introduction

Additives form a part of the life cycle of many materials and therefore many products, wherein the materials are applied. Additives sometimes pose a risk to human and environmental health. Therefore, it may be expected that in life cycle assessment (LCA) studies this will show.

van Oers and van der Voet [1] did a literature review on published LCA case studies on plastics and additives, with the purpose of establishing the importance of additives in the life cycle of plastics and plastic products. To their surprise, they found that additives are not often even mentioned in LCA case studies. The literature survey resulted in 110 LCA case studies of plastics and plastic products. In about 25 of those, additives are mentioned. In none of the articles, the plastic additives are mentioned as an important issue in the life cycle impacts of plastics. For printed matter/paper the overall picture is about the same as described by Larsen [2] in this volume on printed matter case studies.

The reason for this apparent lack of importance regarding additives in LCAs is not obvious. Speculation leads to various possibilities:

- Additives do not contribute significantly to the life cycle impacts of plastics and paper products, and therefore do not come out in the results.
- Life cycle inventory (LCI) data on additives may be incomplete.
- The life cycle impact assessment (LCIA) may be restricted to one or a few impact categories, where additives do not contribute much.
- Life cycle impact characterization factors may be missing for a lot of additives.

Those possible explanations are investigated in this chapter. We will shortly describe the LCA methodology in Sect. 2. We will review case studies on plastics and printed matter/paper in Sect. 3. In Sect. 4 we will address the data situation for LCI databases and LCIA characterization factors. In Sect. 5 we will come to some conclusions and recommendations.

2 Life Cycle Assessment

LCA is a methodology out of the Industrial Ecology toolbox. It is designed to specify and compare the environmental impacts of cradle-to-grave chains of products or services. It is standardized by ISO [3] and has the following methodological steps:

1. Goal and scope definition, where the goal of the study is defined, the eventual alternatives that will be considered are given, the system boundary is determined and the processes within the product- or service-system are defined.
2. LCI, where the system is quantified in a strict format of linked processes. Each process is described in terms of the physical inputs and outputs, both economic (raw materials, materials, products) and environmental (extractions from and emissions to the environment). Out of the total, an ecological profile is compiled listing and adding up all extractions and emissions of the system. An important methodological issue is allocation: how to deal with multi-output processes? This issue is especially important when dealing with waste management processes and will be dealt with below.
3. LCIA, where the ecological profile is translated into a number of impact categories. These can be defined at “midpoint” level (acidification, toxicity, global warming, land use) or at “endpoint” level (human health, ecosystem health). Here, the main debate is on how to translate individual emissions and extractions into impact potentials for the different impact categories. For additives, the toxicity-related impact categories are important and also belong to the most difficult and controversial ones.
4. Interpretation of the results, which includes both the evaluation of the results in terms of the goal and scope as defined before and the assessment of the robustness of the results in terms of uncertainties and data gaps.

Coming back to the question of why additives do not show up in LCA case studies, this may be linked now with the various steps in the LCA procedure, especially to the LCI and the LCIA.

In the LCI, we have to rely on databases that are more or less incomplete. In general, production data are best covered, but even there may be gaps. Data on consumption and use processes are scarce in general – for additives, these use processes may be important since additives may leach out or evaporate from products in use. On waste treatment the data situation is also not very good. Average waste treatment processes out of LCI databases are not usable – these describe emissions out of municipal waste treatment in general. Sometimes specific processes or spreadsheet calculators are added for materials, such as plastics or paper, but whether additives are recognizable in them is to be doubted.

Another LCI-related issue is allocation. This is especially relevant to waste treatment options: when waste is recycled or used to generate energy, there is a multi-output process which needs to be dealt with. The waste then is no longer considered a waste, but a resource, and waste treatment is becoming a production process as well. What part of the emissions to allocate to the waste treatment service and what part to the secondary material or other co-product is then open to debate. ISO allows for various options. Whether additives are even visible in such processes is, again, doubtful.

In LCIA, emissions are translated into impact potentials for several impact categories. Additives may be expected to contribute to toxicity impact categories. Toxicity, however, is a complicated category with a great many specific substances contributing to it via a great many different pathways and mechanisms. In the LCA community, this is very much a category in development, and for a great many substances, such impact factors are still missing. This may also contribute to the invisibility of additives.

In the next section, we will investigate for two materials, plastics and paper, which possible explanations are correct for the invisibility of additives in LCA case studies.

3 LCA and Additives in Plastics and Printed Matter/Paper

In Sect. 3.1, we will address plastics, and in Sect. 3.2 printed matter/paper. Based on the literature and on our own work we will try to identify causes of the absence of additives.

3.1 Plastics

3.1.1 LCI Data

Van Oers et al. [4] conducted a review of over 30 LCI databases to assess the data situation on additive production and use. They came to the following conclusions:

- Data on additive production are mostly absent in LCI databases. Some data are available for metals production and for bisphenol-A, but even for widely used additives such as phthalates and brominated flame retardants, production data are not available.
- Data on plastic resins and the conversion of resins into materials or (half) products are present in most databases. Surprisingly, these data do not include additives. Neither the (compound) plastics nor the conversion processes take the inclusion, and thus possible emissions, of additives into account. Even more disturbing is that this is not clear to users of the database, which lead to the

suspicion that LCA case studies on plastics or plastic products have been performed without authors realizing additives are not included.
- No LCI data for the use of plastics and plastic products are available.
- In some databases, material-specific data are present for various waste treatment options. Plastics generally are among the materials included. However, no specific data on additives are found. In case of incineration, organic additives break down and therefore are not expected. In case of landfill, some leaching of evaporation would be probable, but cannot be found in the data.
- Data on plastics recycling are very poor.

In all, it would appear that including additives in LCA case studies on plastic(s) (products) is not possible by using standard LCI databases. Specific efforts must be made to supplement missing data in all stages of the life cycle.

3.1.2 LCIA Data

The data situation for additives in LCIA seems to be somewhat better than for the LCI [4]. Characterization factors exist for a number of additives and for a number of impact categories. Nevertheless, the list is nowhere near complete. Especially for the impact categories of human toxicity and ecotoxicity, impact factors are missing. Approaches exist to calculate such factors based on substance characteristics. In this volume, LCIA factors are derived for a large number of additives based on such approaches [5]. The lack of such factors, therefore, seems to be less of a problem for including additives in LCA case studies than the lack of LCI data.

3.1.3 LCA Case Studies

As mentioned before, additives do not come out as contributing to life cycle impacts in any of the 110 case studies reviewed. From the above, it is clear that a straightforward LCA case study using a standard LCI database would indeed not show additives, because they are not present in these databases. The fact that the plastics data are aggregate data masks any omissions, implying it is possible that case study performers were unaware of it. For example the studies on (waste treatment) of plastic packaging [6–12], plastic cup studies [13, 14] and some studies on automotive parts [15, 16] do not mention additives at all.

About a quarter of all papers do include additives, mostly phthalates (DEHP), but also pigments (TiO_2), and stabilizers (lead). These are mainly articles about developing LCIA impact assessment factors, not case studies. Of the case studies, only the comparative LCAs of flooring and window frames, and a few of the LCAs of the waste treatment options mention additives. However, for the latter most articles only give qualitative information on additives. In the LCAs about PVC containing flooring ([17, 18, 39]) and window frames [19] the production of additives is taken into account. However, only Potting and Blok [18] and Asif et al. [19] also refer to emissions of additives, like DEHP and lead stabilizers. In their papers, additives do not appear to contribute to life cycle impacts.

To test the assumption whether additives indeed do not contribute to any significant amount to life cycle impacts of plastics, Van Oers and Van der Voet [1] conducted a case study on PVC flooring, appearing in this volume as well. They conclude that additives can indeed contribute to life cycle impacts, and therefore more attention should be paid to additives. Closing the data gaps therefore seems to be a very important issue.

3.2 Printed Matter/Paper

For printed matter/paper we see about the same picture as for plastics but the number of case studies is far less.

3.2.1 LCI Data

Besides additives like phthalates and bisphenol-A mentioned for plastics, but also used in printing inks, other additives like pigments, siccatives and biocides also miss usefull inventory data to a high degree. As described by Larsen [2], a review of the relatively few existing case studies on printed matter shows that inventory data on additives are missing to a high degree. That this kind of data are difficult to find in existing databases is confirmed by a running case study on printed matter/paper performed at DTU (part of the EU project LC-Impact). In this ongoing project it has, however, been possible to find LCI data on a few additives like alkyd resin and kaolin, but only for carbon black as regards pigments. Looking at recycling of paper, which is of special focus in RiskCycle, recent ongoing research on additives/impurities in food packaging based on recycled paper [20, 21] could contribute with valuable LCI data in future case studies.

3.2.2 LCIA Data

As regards LCIA of additives the toxicity-related impact categories, i.e. ecotoxicity and human toxicity, are important. In order to quantify the potential (eco)toxic impacts of additives the emitted amount and a characterization factor (impact potential per kg emitted) for each is needed. As described above data on emissions, being part of the LCI data, are missing to a high degree. For characterization factors the picture is slightly better due to newer LCIA models like USEtox covering more than 2,000 substances, and specific initiatives on calculating characterization factors for additives in printed matter like in Larsen et al. [22]. Anyway, most of these factors have a low quality (are interim) due to lack of good and sufficient fate and effect data on which they are depend.

3.2.3 LCA Case Studies

As described by Larsen [2] only about ten case studies on printed matter (including paper) have been reported so far and almost all of them focus on energy consumption and do not include additives at all, or only to a very limited degree. Even a most recent Finish LCA study on different printing technologies [23] focus on energy (and material) consumption and only includes toxicity-related impact categories (i.e. human toxicity, terrestrial ecotoxicity and freshwater ecotoxicity) for the case study on a photobook (electrophotography/digital printing). The LCIA method used in this case is one of the newest, i.e. ReCiPe (www.lcia-recipe.net (version November 2009)) but the study only includes cradle to consumer (no "end of life" or recycling included). The resulting LCA impact profiles in the Finish case study shows dominance of the paper production together with the packaging material (plastic) for the photobook and transport to the consumer. Regarding the toxicity-related impact categories only the normalized impact potential for "Freshwater ecotoxicity" is significant and mainly related to metal emissions from plastic production. No other contribution from emissions of chemicals used (e.g. additives) are mentioned in the study, which is probably due to the general lack of inventory data and lack of characterization factors for toxicity contributing chemical emissions in available LCA databases.

Anyway, one of the recent and most comprehensive LCA studies on printed matter [22, 24] focus on the importance of chemical emissions as compared to emissions related to energy, and actually include toxic impacts from chemical emissions like printing ink, of which some components may accumulate in recycled paper.

The results of this case study shows that paper production contribute significantly (about 30% of total) to the impact profile but is not at all dominating like in former studies (60–80% of total) focusing on energy consumption and only including chemicals/additives and potential toxic impacts to a limited degree. Even though recycling of paper is included in this study there is no special focus on the additives/impurities in the recycled paper. However, the study shows that potential toxic impacts from the production and use of chemicals like pigments, solvents, metals, AOX and biocides may play a very significant role in the impact profile of printed matter. As for plastics, it therefore seems most probable that the inclusion of potential (eco)toxic impacts from additives/impurities could change future impact profiles of printed matter/paper case studies strongly. Filling the data gap on LCI and characterization factors regarding printed matter and paper-related additives is therefore highly relevant for the future possibilities to significantly improve the comprehensiveness and reliability of case studies on printed matter/paper.

4 Approach Taken in Case Studies to Estimate Missing Data

4.1 LCI Data

4.1.1 Plastics

In the case study on PVC flooring, process descriptions are based on the Ecoinvent database, version 2.2 [37]. Production data for DEHP are missing and are added, based on data from Potting and Blok [18] and processes from the ecoinvent database. Process descriptions for the production of stabilizers and other materials are missing as well, but are not further elaborated. In the ecoinvent database also emissions of DEHP are lacking. Therefore additional estimates for the emission of DEHP during production, use and waste disposal are estimated, based on several MFA studies ([25–27, 38]).

Waste treatment technologies for incineration and landfill of PVC are present in the ecoinvent database. The material specific burdens for the waste treatment are calculated by a supporting spreadsheet. Necessary data for the calculation of the burden are, e.g. element composition, water content, energy content, degradability in landfill, etc. Note that the Ecoinvent waste management model estimates emissions based on the element composition and some general characteristics of the materials (like degradability). Detailed characteristics, like the mobility of DEHP from PVC, are not taken into account. Therefore additional assumptions have been made for the emission of DEHP from landfill of PVC.

In the earlier mentioned MFA studies, no direct emission of DEHP from waste incineration or landfill to air or surface water is reported. For incineration it is assumed that DEHP is decomposed into CO_2 and H_2O. For landfill it is assumed that DEHP is degraded into CO_2 and CH_4 [26] or enters the waste water, which subsequently is treated in the WWTP [27].

The above described landfill refers to a highly controlled landfill site with emission precaution measures. For less-controlled landfill sites, DEHP emissions will probably occur and should be estimated accordingly. The evaporation factors used for estimating emissions in the use phase are used for landfill sites as well, as a crude first estimate [1].

Since no data on recycling processes are available, estimates had to be made in addition as well, described by Åström et al. [5].

The conclusion from this exercise is that although data are missing to a large extent, it is possible based on the literature and some educated assumptions to come up with reasonable estimates. In the absence of real data, such an approach is preferable to ignoring additives altogether, since they can contribute to impacts significantly.

4.1.2 Paper

In the case study on sheet-fed offset printed matter described by Larsen [2], emission data related to chemicals including additives are only to a limited degree taken from LCA databases. This is due to the fact that LCI data on printing production is almost generally missing in available databases. Most of the non-energy-related emissions are therefore based on measured and estimated emissions from 10 to 71 Scandinavian printing houses including litterature values and estimates based on mass balances taking physical/chemical substance properties into account to some degree. Both recycling, incineration and landfill (in a sensitivity analysis) of printed matter are included in this case study but potential impact of additives/impurites in the recycled paper is not included due to lack of relevant data. As mentioned above ongoing research on additives/impurities in food packaging based on recycled paper [20, 21] might make it possible to include these potential impacts in future case studies on printed matter/recycled paper.

As part of the case study described by Larsen, a generic sheet-fed offset printing ink composition (about 12 components) is created based on input from former active managers of ink production, a search in the Danish Product Register, a literature search and information from several suppliers/producers/knowledge centers within the printing industry. Based on former investigations at printing houses and a literature search it is assumed that 1% is emitted via wastewater, 20% ends up as chemical waste (hazardous waste) and about 80% stays on the paper. Looking at pigments, being one of the essential components in printing ink, the potential impact from their production has been estimated. For the azo-pigment Pigment Yellow 14 (diarylamide) and the phthalocyanine pigment Pigment Blue 15, both types highly used in printing inks, the emitted amount is based on estimates by Andersen and Nikolajsen [28].The estimations by Andersen and Nikolajsen are done using lowest values on emitted amounts from the EU Technical Guidance Document on risk assessment assuming wastewater treatment at the production facilities. For Pigment Yellow14 the main contributing emissions are water emissions of 3,3-dichlorobenzidine and 2-chloroaniline during the synthesis of the pigment. For Pigment Blue 15 the main contributor is water emisssions of cuprous chloride also during synthesis. Unfortunately, it has not been possible to include potential impacts of pigments in the recycling process and as impurities in recycled paper, due to lack of data.

In the ongoing printed matter case study related to the EU FP7 project LC-Impact the EcoInvent v. 2.2 unit processes on graphic paper, which seems to be the most comprehensive avaliable database, are going to be included. Even though these unit proceses include recycling and deinking of paper, very few of the chemical emissions related to the problematic on additives in paper are included and emissions of additives/impurities in recycled paper are not included at all. For the production of printing inks the plan is to use the EcoInvent v. 2.2 unit process on "printing colour, offset, 47.5% solvent at plant" but only as a starting point. In this database process organic pigments are substituted by polyethylene terephthalate and the only other components included are carbon black, binders (alkyd resin, bitumen, soya oil, palm oil), solvents (substituted by light fuel oil) and filler (limestone). So, typical components of offset printing inks are highly substituted or non-occuring like siccatives, antioxidants and litho additives (e.g. EDTA). Chemical emissions are therefore missing to a high degree in this unit process, but even though it is probably the best existing one. However, one should be aware that while it might be used as a proxy for the energy and infrastructure of printing ink production, it is no good for the emissions (of precursors, metabolites, etc.) directly related to the production of many printing ink components like the dominating azo-pigments and phthalocyanine pigments. Here an approach like the one by Andersen and Nikolajsen [28] might be used.

4.2 LCIA Data

Missing LCIA data have been supplemented by impact factors calculated with USEtox™.

As mentioned above, there are characterization factors for a number of different impact categories, e.g. acidification, eutrophication, climate change, human toxicity and ecotoxicity. However, characterization factors are missing for many additives, especially for human toxicity and ecotoxicity, which makes it difficult to assess the potential impact that a product will cause during its entire life cycle. A major reason that characterization factors are often missing is the lack of data regarding substance properties, such as physical chemical properties and toxicity.

One method of deriving characterization factors for additives with regard to human toxicity and ecotoxicity is by using the LCIA model USEtox™ [29]. Based on the physical chemical properties and toxicity of the substance, USEtox™ calculates characterization factors for both human toxicity and aquatic ecotoxicity. According to the USEtox™ manual [29], preference should be given to experimental values when deriving characterization factors with USEtox. However, the lack of experimental data is often the reason that characterization factors are missing. Experimental tests are often both expensive and time consuming to perform. Thus there is a need to be able to generate these data by the use of other methods.

In a study by Andersson et al. [30], the possibilities to use quantitative structure-activity relationship (QSAR) models to predict physical chemical and ecotoxicological properties of approximately 200 different plastic additives have been assessed. Physical chemical properties were predicted with the U.S. Environmental Protection Agency Estimation Program Interface (EPI) Suite, Version 3.20. Aquatic ecotoxicity data were calculated by QSAR models in the Toxicity Estimation Software Tool (T.E.S.T.), version 3.3, from U.S. Environmental Protection Agency, as described by Rahmberg et al. [31]. To evaluate the applicability of the QSAR-based characterization factors, they were compared to experiment-based characterization factors for the same substances taken from the USEtox™ organics database [32]. This was done for 39 plastic additives for which experiment-based characterization factors were already available.

In a first attempt to derive characterization factors with QSARs, the entire dataset of plastics additives was included, and aquatic ecotoxicity was predicted for two different trophic levels. This generated characterization factors that did not correspond well with the ones derived from experimental data [30]. Hardly surprising, but a clear indication that two trophic levels are unsufficient. A second attempt to derive characterization factors with QSARs are currently being performed [31]. In this second attempt, substances that are difficult to model in QSAR models have been removed from the dataset and the ecotoxicity has been predicted for three different trophic levels instead of two. However, results have not yet been obtained from this second attempt. If the results show that it is possible to derive reliable characterization factors by the use of QSARs, the current data gap regarding characterization factors for human toxicity and ecotoxicity could be reduced, even though, with present knowledge, QSAR-based characterization factors are to be considered as interim.

5 Approaches to Improve LCA Studies with Respect to Additives

There are both data issues, and methodological issues to deal with when assessing additives in LCA.

5.1 Method Issues

Additives are part of materials, and materials are used in products. That means that for LCA case studies three life cycles have to be kept in mind:

- The life cycle of the product, which is the usual entrance in an LCA.
- The life cycle of the material, which can be different from that of the product. Materials are produced and have a functional use in a product, after the products life span the materials may be recycled to enter another life cycle, possibly in another product.
- The life cycle of the additive, which in turn can be different from that of the material additives are produced and then have a functional use in a material. They follow the life cycle of the material but may disappear from it during the use phase or in landfill, and when incinerated or recycled may end up in different streams. Methodologically speaking this may be the biggest challenge: besides the challenge of mapping its fate, when to consider a material/additive as a resource and not as a waste?

As the collective LCA studies on plastics show, these three life cycles have in many cases not been respected. The LCA framework does not force the user to do so. In order to do that, additional tools may have to be used, especially Material Flow Analysis.

Another methodological issue, although of a different nature, is allocation. Especially in waste management processes, allocation is problematic, while at the same time it can influence the LCA outcomes significantly. In case of landfill, things are straightforward: the end of all three life cycles. In case of incineration it can be an issue when energy is generated from the incineration process. Then the process delivers two services, waste treatment and energy generation, over which the emissions must be divided. This is not specific for additives, though. In case of recycling, the process delivers a waste treatment service while at the same time producing secondary materials. Here, it is interesting to regard additives: do they disappear in the process, do they end up in a waste stream, are they recovered somehow, or are they also present in the secondary material? This makes a difference, also in how to allocate.

5.2 LCI of Additive Production

As was pointed out in the case study on plastics above, little attention has been given to additives in products in LCAs and therefore the available information on production of additives is very limited. Thus, there is a need to include production of additives in the LCI-databases to make LCAs more complete. To obtain these data, cooperation with relevant industry is needed.

5.2.1 Emissions from Compounding and Product Manufacturing Processes

Information regarding emissions of additives during compounding and product manufacturing can often be found in the Organisation for Economic Co-operation and Developments (OECDs) Emission Scenario Documents (ESDs) [33]. These documents describe emission processes and exposure scenrios for different industrial sectors. In the ESDs, emissions are described on a general level, for example emission factors are given for an entire group of substances and a certain industrial process. These emission factors are often conservative in order to safeguard the health of humans and other organisms that are exposed. Other possible sources of information are risk assessments and MFAs/SFAs. One example where SFAs have been used to track emissions is the Control of hazardous substances in the Baltic Sea region (COHIBA) project, where SFAs were conducted for 11 hazardous substances in the Baltic Sea area [34].

5.2.2 Emissions During Use

The ESDs developed by the OECD also include estimates of emissions of additives during use. As for the emissions during compounding and product manufacturing, these emissions are often conservative estimates based on rough models that give an overview of the emissions from the products produced by an entire industry sector.

Emissions during use has also been quantified in the research programme ChEmiTecs – organic chemical emitted from technosphere articles. Within the research programme, emissions during use have been quantified by both measurements in emission chamber and by the use of modelling [35]. The modelling approach focussed on two different levels, one model describing emissions on a molecular level [35] and one model that describes emissions of organic substances on a national level [36].

This type of emission estimates can be included in LCAs to make them more complete.

5.2.3 Emissions from Waste Management Processes

As stated earlier, in general data on emissions of additives from waste processes are scarce.

Landfill

Worldwide, most waste is landfilled. Emissions from landfill occur via evaporation and leaching. Landfill sites can be managed to reduce those emissions, but in many cases they are not. Data on leaching and evaporation of additives from landfill sites are scarce.

Incineration

Organic compounds are degraded during incineration and converted to compounds such as CO_2 and H_2O. Sometimes, pollutants such as dioxins are formed during incineration processes, leading to toxic emissions to the atmosphere. Inorganic compounds, in the case of additives usually metals, are not degraded. In well-managed incineration plants, they end up in waste streams such as slag and bottom ash. Re-use of such waste streams may lead to leaching of metals, depending on the use and on the state of immobilization of the metals.

Recycling

Additives often form a problem in recycling processes. Material recycling is often not possible or only with a considerable loss of quality. Plastics recycling is notoriously difficult due to the mixed composition of the plastics waste stream. The recycled material can only be used in certain applications that do not demand a pure material. Recycling of the additives themselves is theoretically possible only for metals, but in practice this type of recycling is not feasible. The metals occur only in low concentrations. Recovery from fly ash and bottom ash is possible, but expensive: in view of growing scarcity problems it may become a viable options for at least some metals.

5.3 Towards a Harmonized Approach for LCAs of Additives

5.3.1 Conclusions

Additives are badly represented in LCA case studies. This is not because they do not contribute to impacts, but because they are not included in the assessment. The most likely reason for that is that specific LCI data for additives are missing to a large extent, and additive data are not included in the compound materials. Moreover, this fact is not obvious. Possibly, LCA practicioners are not aware of this gap. Additive data for the use phase and waste treatment phase are lacking as well. LCIA data for additives are also lacking. Approaches exist, however, to estimate interim characterization factors based on substance characteristics.

Additives can have a significant impact in a products life cycle as shown by the case studies on plastics and printed matter/paper. Omitting them can therefore be crucial for the outcome of an LCA study. Not only for LCIA factors, but also for LCI data, approaches can be developed to use in case of lacking data. Such an approach is outlined below.

5.3.2 A Harmonized Approach

The approached outlined refers to the LCI, since they are the largest and most prohibitive gaps.

- Data on additive production: if such data are missing, they must be collected, there is no way around that. In some cases, however, proxy energy consumption and proxy emission data may be estimated if the synthesis way and the default emission factors for the technology used are known.
- Data on material production: the composition of materials is relatively easy to obtain information. Hence it follows how much additive is needed. In the process of producing the material, emissions of additives take place. MFA studies exist that provide estimates of such emissions, based on inputs and outputs of processes. These studies refer to a specific situation in a country. An attempt can be made to modify them for different situations. If this is not possible, it is always better to use the existing data as a first rough estimate than not to do so.
- Data on the production of products from the materials: these cannot be missing from the LCA study. What may be missing is an estimate of emissions of additives during that process. Emissions can be expected to be typically a lot lower than for the material production, however.
- Data on the use phase: during use of the product, additives may leach out. Here, too, emission factors may be derived from MFA studies or from the literature in general.
- Data on the waste management phase: those are really difficult to obtain. Measurements of additive emissions are scarce. Material specific emissions data are always modelled. Estimates can only be based on rough assumptions. Especially in cases of unprotected landfills, the leaching from landfill sites may be important: here, too, it is better to use crude estimates than nothing at all. Assumptions on emission rates together with an assumed time horizon should be made.

5.3.3 Recommendations

A first recommendation is to take additives seriously as a part of the life cycle, at least for plastics and printed matter/paper.

A second recommendation is to complete LCI databases with data on additives. Both production data of additives and emission data of additives from compound materials in the use and waste phase are missing and should be supplemented. An important role in this data remediation process should be played by industry.

A third recommendation is to expand LCI databases with data on various waste treatment process in a material specific way. This is especially applicable to recycling processes.

A fourth recommendation is to expand LCIA databases with characterization factors on additives. Ideally this should be done on the basis of measured physical/ chemical and effect data but even interim characterization factors based on sound QSAR estimations are better than none.

Finally, it is generally recommended to use estimation approaches, combined with sensitivity analysis, for additives when data are missing, when performing an LCA case study on additive containing products, such as outlined above. Only when they are included it is possible to draw conclusions on the importance of additives over the life cycle of a product.

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Characterization of Environmental Exposure: Measuring Versus Modeling

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Abstract Knowledge of pollutants' occurrence in the environment is essential in order to undertake accurate risk assessment studies. Determining the concentration of chemicals is a crucial step to quantify the levels to which both ecosystems and human population can be exposed. Traditionally, analysis has been the main way for determining concentrations in the environment but in recent years innovative occurrence models enabling their prediction either in real or fictitious scenarios have been developed. These models allow obtaining reliable estimations by reducing the need of resource-intensive monitoring programs that are needed for laboratory analysis.

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Prediction of chemical occurrence is a difficult task that depends on multitude of factors (i.e., physical–chemical properties, climate conditions, amount of product, mode of application, and exchange processes), but these models in combination with laboratory analysis can be a powerful tool for evaluating the chemical occurrence in the environment.

In this chapter the new trends in analytical chemistry for determining classical and emerging pollutants, as well as the use of predictive exposure models have been reviewed and their respective benefits and shortcomings have been briefly discussed.

Keywords Analytical chemistry, Environmental concentration, Measuring, Modelling, Risk assessment

Contents

Abbreviations

CNT	Carbon nanotubes
DBPs	Disinfection by-products
EINECS	The European inventory of existing commercial chemical substances
GC	Gas chromatography
GCxGC	Two-dimensional gas chromatography
GIS	Geographic information system
IDA	Information-dependent acquisition
KOC	Organic carbon partition coefficient
KOW	Octanol-water partition coefficient
LC	Liquid chromatography
LOD	Limit of detection
MAE	Microwave-assisted extraction
MEC	Measured environmental concentration
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
PAHs	Polyaromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PEC	Predicted environmental concentration
PFCs	Perfluorinated compounds
POCIS	Oolar organic chemical integrative samplers

QqLIT	Hybrid quadrupole linear ion trap
QqTOF	Hybrid quadrupole time-of-flight
QSAR	Quantitative structure–activity relationship
REACH	Registration, evaluation, and authorization of chemicals
SFE	Supercritical fluid extraction
SPME	Solid phase micro extraction
SRM	Selected reaction monitoring
ToF	Time-of-flight
TWA	Time-weighted average
UPLC	Ultra high performance liquid chromatography
UV	Ultraviolet

1 Introduction

One may reasonably estimate that about 100,000 synthetic chemicals are currently utilized by our technological society, of which 30,000–70,000 are of common daily use (EINECS inventory) [1]. Furthermore, worldwide chemical production is expected to extensively grow in the next decades. As a consequence of the human activity many of these organic and inorganic compounds together with their degradation products may ultimately enter the environment as a consequence of human activity. Once they reach the environment, depending on their physical–chemical properties, partitioning between the different environmental compartments (air, soil, water, sediments, etc.) can also take place. In addition, many compounds may undergo transformation processes giving rise to the corresponding metabolites or degradation products. The result is a potential exposure to a cocktail of contaminants whose environmental and health effects in short and long term are unpredictable.

This intensive growth has led to the need to enhance the international assessment of chemical risks and strengthen the national and international regulatory efforts for the proper management of chemicals. In this context, the existing European regulation REACH (Registration, Evaluation, Authorisation of Chemicals) (EC 1907/2006) [2] promotes the regulation of the chemicals used in commerce and consumer products and the evaluation of the risk of human or environmental exposure to these chemical compounds as well.

Risk assessment constitutes a cornerstone for the control of chemicals for both scientific and management purposes. Environmental risk management deals with regulatory measures based on risk assessment [3]. Strategies such as the prioritization of chemicals represent a useful tool to optimize efforts for both regulatory and monitoring purposes [4, 5].

The analysis of chemical risk is a process comprising the following elements: hazard identification, exposure assessment, dose–response assessment, and risk characterization [6]. Figure 1 shows the main elements that constitute the risk characterization process together the methodologies used for their determination. The essence of risk characterization is to relate the exposure (the concentration of a

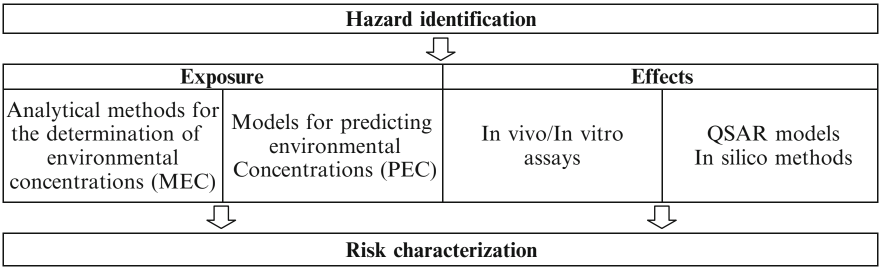


Fig. 1 Risk characterization of chemicals: main methodological steps for determining their exposure and effects. Adapted from [7]

chemical substance or mixture) with effects (the relationship between dose and the associated impairment caused on organisms) to provide a scientific basis for evaluating risks to both the environment and the human health.

The exposure assessment stage is crucial and consists of quantifying the level of chemicals to which populations, population subgroups, and individuals are exposed, in terms of magnitude, duration, and frequency [8]. In this chapter both modelling and measuring procedures that are currently used for determining environmental concentrations are briefly discussed.

Measuring is certainly the preferred method for quantifying concentrations of chemicals (organic and inorganic) in environmental matrices. However laboratory measurements are costly and time-consuming processes requiring intensive efforts: field sampling campaigns, development and validation of analytical methodology, thorough treatment of data, etc.

On the other hand, indirect methods should be considered as an alternative when analytical measurements are not feasible. Predicting methods involve extrapolating exposure estimates from existing data, e.g., previous environmental monitoring, data about emissions and chemicals production, and questionnaires. Distribution of chemicals among the different environment compartments is also a key aspect for predicting environmental concentrations. Therefore psysicochemical properties (see Sect. 4) are required inputs in these tools.

2 Exposure Assessment: Experimental Measuring or Modeling

As mentioned before, environmental exposure is the first key aspect to develop risk characterization from a defined scenario (see Fig. 1). Experimental analysis is the most obvious and classical procedure for determining the chemical occurrence in the environment. Measuring environmental concentrations (MECs) is more accurate and reflects the reality better than any other method, but the main drawback is the large amount of resources required for these laboratory measurements. Field environmental monitoring programs have become increasingly expensive as a consequence of constantly rising environmental quality criteria, the elevated number of environmental matrices (surface waters, ground waters, soils, sediments, biota, air, etc.) and the necessity to determine concentrations of pollutants at extremely low concentrations (ng/L). It means that monitoring programs may become highly time consuming and thus very costly; hence monitoring campaigns are not always a feasible procedure since it is not possible to have a full coverage of time and space. Nonetheless environmental studies based on experimental determinations are highly time consuming and require great laboratory facilities and human resources (qualified personnel and expensive equipments).

An interesting alternative to experimental measurements is modeling, which allows estimating environmental concentrations through appropriate calculations derived from some input data and reliable and well-established physical–chemical principles (usually referred as PEC or Predicted Environmental Concentrations). Modeling is fast and relatively affordable and has very good time and space coverage possibilities, being, on the other hand, its main weakness the strong dependence on the model chosen and its inherent uncertainty because of the lack of reliable data (production volume, mode of application, emission sources, degradation rates, etc.). Concentrations can be underestimated or overestimated by models due to the complexity of the environments. Many processes are involved in the dynamics of pollutants in the different environmental scenarios, which affects directly to leaching and degradation processes. Thus, it appears that the exposure models do not come up to the whole complexity of the real environment. Therefore, although predicted concentrations cannot replace measurements, they suppose a useful tool to choose target compounds which are important to be monitored or to point out which compound form (metabolite or parent compound) and compartments (liquid versus solid fraction) should be measured.

Ideally, measuring and modeling should be seen as complementary rather than excluding approaches; the wisest recommendation would be making use of both alternatives in order to benefit from their respective advantages. Unfortunately, such desirable complementary approach is rarely seen together (see as instances [9, 10]). In Table 1 are summarized the main strengths and weaknesses of both procedures. The main drawback of measuring is that it is usually focused on certain target analytes and there is thus low chance of finding new targets. Other aspects of concern are their limited possibilities regarding time and space coverage (it is impossible being everywhere at every time). As mentioned before, sampling campaigns may be a limiting factor because of their prohibitive economic cost. On other hand, the main advantage of experimental measurement is that it provides reliable results that are quite independent of the laboratories (at least, it is true for those that have an adequate Quality Assurance/Quality Control System). In turn, modeling is fast and relatively affordable and has very good time and space coverage possibilities, being, on the other hand, its main weakness the strong dependence on the model chosen and its inherent uncertainty because of the lack of reliable inputs.

Table 1 Comparative overview of strengths and weaknesses of analytical measurement vs. modeling in environmental studies (Adapted from [7, 11])

Analytical measurement	Pros	– Results obtained reflect well reality – Repeatability and reproducibility of results (at least between good qualified labs) – Measurements are independent of information/data sources – Multipurpose analytical methods can cover many compounds on a single run – Even the best model will ultimately need to be experimentally checked – Discovery of new emerging contaminants is possible
	Cons	– Determination of compounds at very low quantities may be difficult – Time and space coverage require expensive monitoring campaigns – Sampling campaigns may miss crucial episodes – Analytical measurements give a snapshot, rather than a continuous picture – Expensive analytical equipment and method development – Target monitoring may miss pollutants: “you only find what you are looking for”
Predicting (modeling)	Pros	– Very good coverage capabilities of time and space – Computation equipment is affordable – Possibility of application to hypothetical scenarios: “What if?” – Useful for extrapolations to future (predictions on space and time, even for products not yet in the market) – Simultaneous modeling of many compounds – Once the model is set up are fast and cheap to use
	Cons	– Different models may render very different results – Models are strongly dependent on parameter and data input – Diffuse sources of pollution may be very difficult to model

3 New Trends in Analytical Chemistry for Measuring Environmental Concentrations

As discussed in previous sections, measurements in the laboratory suppose the most accurate solution for determining environmental concentrations. In this section the main advantages of analytical measurements as well as the new trends in analytical instrumentation and experimental methodologies are discussed.

Last decades, the trends of environmental analysis were focused on determining organic “priority pollutants.” These priority pollutants are characterized by their high toxicity, high environmental persistence, and/or high hydrophobicity. Some of them cause endocrine disruption effects on aquatic organisms and consequently, they could represent a risk to environment and human health. On reviewing the literature, thousands of methodologies are presented for the determination of these priority compounds including polychlorinated biphenyls (PCBs) [12, 13], polyaromatic hydrocarbons (PAHs) [14], chlorinated pesticides [14], organotin compounds [15], alkylphenolic compounds [16], polybrominated compounds [17, 18], etc. Although there is a multitude of methods for their determination, still today new analytical methodologies appear oriented towards improvements on their determination by reducing the analysis time, the detection limits, sample manipulation, etc. The development of multiresidue methods is also a current practice in environmental monitoring, since it allows determining simultaneously a large number of chemicals in a single analysis run.

In recent years the interest of environmental analytical chemistry was turned to the so-called “emerging contaminants” or “new” unregulated contaminants including pharmaceuticals, endocrine disruptors, detergents, personal care products, plasticizers, flame retardants, gasoline additives, etc. These compounds are released continuously to the environment and can be found in water, sediments, soils, etc. In most of the cases they are found at trace level concentration (ng/L); therefore, powerful analytical capabilities are required for their determination.

For this purpose, the gas (GC) and liquid chromatography (LC), coupled to mass spectrometry (MS), are identified as the techniques par excellence. Whereas GC is more addressed to the analysis of nonpolar and volatile compounds, LC is the technique of choice for the separation of polar organic pollutants. MS has increasingly become the preferred detector for the identification and quantification of organic contaminants in environmental samples. MS offers some unique advantages in terms of sensitivity and specificity. In the case of very complex matrices, such as wastewater, sludge or biota, tandem mass spectrometry (MS/MS) offers a better detection limit because of the reduction of “chemical noise” and thus an improvement in the overall signal-to-noise ratio. In Table 2 are summarized some of the most representative multiresidue analytical methods for monitoring classical and emerging pollutants in environmental matrices are summarized.

With recent instrumental development, such as fast LC, fast GC and two-dimensional gas chromatography (GCxGC) and advanced tandem hybrid MS detection systems (i.e., QqTOF, QqLIT, Orbitrap) the analysis of complex mixtures

Table 2 Summary of some representative current analytical methods for quantitative determination of selected priority and emerging organic contaminants in environmental samples. Adapted from [7]

Analytes	Matrix	Extraction method	Detection	Range of concentrations detected in the environment	REF
Pharmaceuticals *Multi-residue of 74 compounds*	River waters, effluent wastewater and drinking water	Online SPE	LC-MS/MS (QqLIT)	River waters: < LOD-307 ng/L Effluent wastewaters: <LOD-1,120 ng/L Drinking water: <LOD-201 ng/L	[19]
Pharmaceuticals *Multi-residue of 43 compounds*	River sediment Particulate matter River waters	*Water*: off-line SPE (Oasis HLB) *Solids*: PLE (MeOH/H_2O 1:2, v/v) and SPE (Oasis HLB)	LC-MS/MS (QqLIT)	River sediment: <LOD-222 ng/g Particulate matter: <LOD-657 ng/g River water: <LOD-1,162 ng/L	[20]
Drugs of abuse *27 compounds*	Drinking water	Off-line SPE (Oasis HLB)	UPLC-MS/MS (QqQ)	*Spanish tap water* Mean conc: <LOQ-50 ng/L Median conc: <LOQ-24 ng/L *Tap water from other countries* Mean conc: <LOD-40 ng/L Median conc: <LOD-37 ng/L	[21]
Drugs of abuse *17 compounds and metabolites*	Influent and effluent wastewater and river water	On-line SPE	LC-MS/MS (QqLIT)	Influent wastewater: <LOD-3,790 ng/L Effluent wastewater: <LOD-510 ng/L River water: <LOD-346 ng/L	[22]
PFCs *13 perfluorinated acids, 4 perfluorosulfonates and PFOSA*	Sewage sludge	PLE (MeOH) and SPE (Oasis WAX)	LC-MS/MS (QqLIT)	Sewage sludge: <LOD-101 μg/Kg	[23]

14 PFCs	Surface, sea and sewage water	SPE (Oasis HLB)	LC-TOF-MS	Sea water: <LOD-4.2 ng/L Harbor water: <LOD-12.8 ng/L Surface water: <LOQ-38.9 ng/L	[24]
16 Pesticides *Triazines, phenylureas, OPs, chloroacetanilides, thiocarbamates*	River water	Online SPE	LC-MS/MS (QqQ)	River water: <LOD-818 ng/L	[25]
28 priority pesticides *OCs, OPs, triazines, anilides*	River sediment	UE (Hexane/Acetone, 1:1, v/v)	GC-EI-MS	River sediment: <LOD-450 μg/Kg	[26]
OPs pesticides and metabolites	Sewage sludge	UE (AcN 1% HAc) and DSPE (PSA)	LC-MS/MS (QqQ)	Sewage sludge: <LOD-344 ng/g	[27]
Nanomaterials *C_{60} and C_{70} fullerenes*	Suspended material of wastewater effluents	UE (toluene)	LC-MS/MS (QqLIT)	Wastewater effluent: <LOD-65,900 ng/L	[28]
9 UV-filters	River, lake and treated wastewater	SBSE	TD-GC-MS	Lake water: <LOD-250 ng/L River water: <LOD-30 ng/L Treated wastewater: <LOD-54 ng/L	[29]
8 UV filters	Sewage sludge	PLE (MeOH)	UPLC-MS/MS (QqQ)	Sewage sludge: <LOD-9.17 μg/g	[30]
11 PPCPs *4 preservatives, 2 antimicrobials and 5 UV filters*	Surface and wastewaters	SPE (Oasis HLB and Bond Elute Plexa)	UPLC-MS/MS (QqQ)	Influent wastewater: <LOD-5,613 ng/L Effluent wastewater: <LOD-100 ng/L	[31]
Surfactants *LAS, CDEAs, NPEOs and DPs*	Wastewater and receiving coastal waters and sediments	*Water*: SPE (C_{18}) *Sediments*: PLE (Acetone-MeOH, 1:1)	LC-MS	Influent wastewater: <LOD-1,920 μg/L Effluent wastewater: <LOD-872 μg/L Sea water: <LOD-26 μg/L	[32]

(continued)

Table 2 (continued)

Analytes	Matrix	Extraction method	Detection	Range of concentrations detected in the environment	REF
				Marine sediments: <LOD-86,940 µg/kg	
Surfactants *LAS and major metabolites (SPC)*	Soil amended with sewage sludge	PLE (MeOH/H_2O 90:10, v/v) and SPE (RP-C_{18})	LC-MS/MS (QqQ)	Soil amended with sludge: <LOD-1,049 µg/kg	[33]
PBDEs, PCDDs, PCDFs and PCBs	Coastal sediments	Soxhlet (toluene) and clean-up with silica gel +alumina+PX-21 active carbon column	GC-EI-MS	Coastal sediments: <LOD-28,769 pg/g	[34]
19 Phytoestrogens, progestogens and estrogens	River water, one channel and a lagoon	SPE (RP-18)	LC-MS/MS	Range of concentrations of positive samples: 0.34–366 ng/L	[35]
Estrogens and conjugates	River sediment	MAE (MeOH/H_2O 25:75, v/v) and SPE (Oasis WAX)	LC-MS/MS (IT)	River sediment: <LOD-2.37 ng/g	[36]

PLE pressurized liquid extraction, *SPE* solid phase extraction, *UE* ultrasonic extraction, *DSPE* dispersive solid phase extraction, *SBSE* stir bar sorptive extraction, *TD-GC-MS* thermal desorption-gas chromatography-mass spectrometry, *LAS* linear alkylbenzene sulfonates, *CDEAs* coconut diethanol amides, *NPEOs* nonylphenol ethoxylates, *DP* degradation products, *SPC* sulphenyl carboxylates, *PCDD* dibenzo-p-dioxins (PCDD), *PCDF* dibenzofurans, *PCBs* biphenyls in environmental matrices has been considerably improved. Ultra high performance liquid chromatography (UPLC) has recently arisen as a technique that uses short columns, with narrow bore columns, high mobile phase flow-rates and ultra-high pressures. Although UPLC relies on the same selectivity and retention principles than HPLC, their smaller stationary-phase particle diameter (sub-2 μm) allows shortening analysis time up to nine times comparing to the conventional HPLC. Therefore, UPLC allows working with high mobile phase flow rates and ultrahigh pressures which allows developing faster methods with improved chromatographic separations. Shortening the analysis time is important for attaining the high sample throughput often required in laboratories conducting monitoring studies.

The recently developed technique known as "two-dimensional gas chromatography (GCxGC)" is gaining significant popularity for complex sample analysis. GCxGC separation is attained by coupling two GC columns with different selectivity (usually the first is a nonpolar column and the second a polar stationary phase) allowing to separate compounds first by their volatility and then for their polarity. The advantages of this recent technology are increased sensitivity and greater utilization of separation space, which helps reduce the problem of co-elution in complex samples. GCxGC is often coupled with a time-of-flight (ToF) detector because of its rapid acquisition capability [37].

Regarding sampling and sample preparation, solid phase extraction (SPE) still remains as the most widely used mean of extraction and concentration of organic contaminants in aqueous matrices. A new SPE device called "Bag" extraction consisting of a polystyrenedivinylbenzene enclosed in a woven polyester fabric, which can be immersed in water samples, has been reported during the last 2 years. For instance, measured concentrations of pharmaceuticals using this approach have been shown to be comparable to those obtained with Oasis HLB cartridges, which is one of the most widely used polymers in SPE extraction [37]. The benefits of using this Bag SPE technique are the use of handling, unattended water extraction, and that no further filtration is needed.

Other recent approaches for the analysis of organic contaminants in water samples involve: (1) automation through coupling of sample preparation units and detection systems (i.e., online solid phase extraction (SPE)-LC, online solid phase micro extraction (SPME)-LC or (SPME)-GC), (2) application of tailored sorbents (i.e., molecular imprinted polymers, immunosorbents, nanomaterials), and (3) integration of several sample preparation steps into one (i.e., application of passive samplers for simultaneous sampling, extraction and enrichment of pollutants from liquid and gaseous samples, such as the "polar organic chemical integrative samplers" (POCIS)). POCIS devices have the capacity to handle large volumes of water over long periods, thereby giving time-weighted average (TWA) concentrations and allowing monitoring episodic changes in environmental contaminant concentrations, which are often misinterpreted with conventional discrete samples [38].

For solid samples PLE, microwave-assisted extraction (MAE) and supercritical fluid extraction (SFE) [39, 40] are the preferred extraction methods.

Current analytical methods only focus their attention on parent target compounds and rarely include metabolites and transformation products, which sometimes can be more toxic and persistent than original compounds. Moreover, identification of reaction pathways and identification of transformation products are of crucial importance in understanding the fate or organic contaminants in the environment. On the other hand, high complexity of environmental samples sometimes requires application of high-resolving power techniques in order to provide additional structure information needed for unequivocal identification of contaminants and confirmation of positive findings. The introduction of Orbitrap, TOF, QqTOF and QqLIT instruments, which allow the simultaneous determination of both parent and transformation products, within a single analytical run, overcomes this drawbacks and provides a higher degree of certainty in compound identification. In comparison with triple quadrupole mass spectrometers, which operate at unit resolution and generally in the selected reaction monitoring (SRM) or multiple reaction monitoring mode (MRM) modes for specific target analytes, TOF, QqTOF, and orbitrap mass spectrometers are capable of acquiring full-scan mass spectra at high resolution for all analytes without loss in sensitivity. Since these instruments have high resolution (at least 10,000 and higher) at full-width-half-maximum (fwhm) peak height, isotopic patterns are evident and chemical structures can be proposed for unknowns or confirmed for target analytes [37, 41]. Concerning Orbitrap instruments, they still do not have such a widespread use due to higher costs. Nevertheless, the Orbitrap technology introduced by Thermo Fischer Scientific (San Jose, CA, USA) seems to be one of the future mass spectrometry trends due to high-resolving power of the Orbitrap [41]. Regarding QqLIT, it allows performing sensitive quantitative analysis combined with unequivocal identification due to the application of the Information Dependent Acquisition (IDA) function, where a targeted screening is performed in combination with an Enhanced Product Ion Scan, achieving MS/MS spectra that are matched with MS/MS spectra present in a library [41].

Due to scientific and public concern about environmental pollution, new developments in environmental analysis are focused on the implementation of environmental-friendly practices in the laboratories. Main strategies are addressed to saving energy and to reduce solvent consumption with the minimum sample manipulation by using on-site, online, and direct analysis (e.g., biosensors) [42].

4 Predicting Environmental Concentrations Through Modeling

Owing to the complexity and dynamic character of real environmental scenarios, it is not always possible to predict concentrations with desirable level of precision. Nevertheless, even though experimental measurements are not replaceable by PECs, this approach can still serve as a useful tool for supporting hazard assessment programs. Making predictions also can help identifying compounds or compounds families that should be monitored, as well as what the most exposed compartments are. In order to carry out a realistic prediction of concentrations, several questions must be first answered: What is the purpose of the predictions? What decisions will be made after the approach? What precision is required? Which are the weaknesses of the approach? The prediction will be successful only if it satisfies the initial requirements. Otherwise experimental measurements will be necessary.

For environmental purposes, different approaches for predicting environmental concentrations have been used. Table 3 gives some representative examples of these studies. The input data required are usually the production or consumption of chemicals in the studied area that allow estimating their emission rates to the environment. Depending on the complexity of the scenario, different number of variables can be used to achieve the prediction.

Mueler et al. and Gottschalk et al. [43, 44] presented a model for predicting concentrations of nanoparticles including nano-Ag, nano-TiO_2, nano-ZnO, fullerenes, and carbon nanotubes (CNT) in different environmental compartments. The results of this study demonstrated that modeling is a meaningful utility to carry out quantitative risk assessment of nanoparticles.

Stuer et al. [46] evaluated the presence of the 25 most used pharmaceuticals in the primary health sector in Denmark (e.g., paracetamol, acetyl salicylic acid, diazepam, and ibuprofen). They compared PECs with experimental determinations and they conclude that measured concentrations were in general within a factor of 2–5 of PECs. Carballa et al. [45] also determined PECs for pharmaceuticals (17), musk fragrances (2) and hormones (2) in sewage sludge matrix. For that purpose they used three different approaches: (1) extrapolation of the per capita use in Europe to the number of Spanish inhabitants for musk fragrances; (2) annual prescription items multiplied by the average daily dose for pharmaceuticals and; (3) excretion rates of different groups of population for hormones. They indicated that these PECs fitted with the measured values for half of them (carbamazepine, diazepam, ibuprofen, naproxen, diclofenac, sulfamethoxazole, roxithromycin, erythromycin, and 17α-ethinylestradiol).

PECs also were calculated by Domènech et al. [47] for determining the presence of cocaine and its main metabolite (benzoilecgonine) in different environmental compartments (air, water, soil, etc.).

Additionally, the integration of geographic information system (GIS) with analytical data is an effective procedure in addressing the problem of spatial and temporal variability of the different parameters involved in the environmental fate of chemicals. Based on accurate local estimations, GIS-based models would then also allow deriving realistic and representative spatially averaged regional PECs. Table 4 shows some studies that have used GIS-based methodologies to perform a site-specific risk assessment of PECs in different exposed ecosystems.

Verro et al. [53] evaluated the risk associated with the presence of alachlor herbicide in surface waters (released by drift and runoff) from Lombardia region (Northern Italy). They applied a GIS-based model for representing the obtained PECs in risk maps showing a static image of a worst-case simulation in each river subbasin.

Table 3 Review of some relevant studies addressed to the estimation of PECs. Main inputs used for determining PECs are also indicated

Compounds	Matrix	Studied location	Model inputs	Ref.
Nano silver (nano-Ag), nano TiO2 (nano-TiO2) and carbon nanotubes (CNT)	Air, soil and water	Switzerland	– Estimated worldwide production volume – Allocation of the production volume to product categories – Particle release from products – Flow coefficients within the environmental compartments	[43]
Nano-TiO2, nano-ZnO, nano-Ag, carbon nanotubes (CNT) and fullerenes	Air, surface water, STP effluent, and sewage sludge, soil, sludge-treated soil and sediment	U.S., Europe and Switzerland	– Annual production, manufacturing, and consumption – Waste treatment processes (sewage treatment, waste incineration, landfill and recycling) – Deposition and elimination/degradation of engineered nanomaterials	[44]
17 PhACs, 2 musk fragrances and two hormones	Raw sewage	Galicia and Cataluña (Spain)	– Per capita annual consumption – Number of inhabitants served by each STP – Average flow treated	[45]
25 PhACs	Water	Denmark	– Amount of PhACs used by year (kg/year) – The removal in percent – Number of habitants in Denmark – Volume of waste water per day per capita – Dilution factor in the environment	[46]
Cocaine and its metabolite benzoilecgonine (BE)	Air, water, soil, sediments and suspended matter	Regional environmental system	– Initial cocaine intake – Partial degradation of the parent compound to BE – Treatment of wastewater – Environmental fate	[47]

CNT carbon nanotubes, *PhACs* pharmaceuticals, *BE* benzoilecgonine

Table 4 Some representative studies which determine chemical concentrations in the environment using models based on GIS methodology

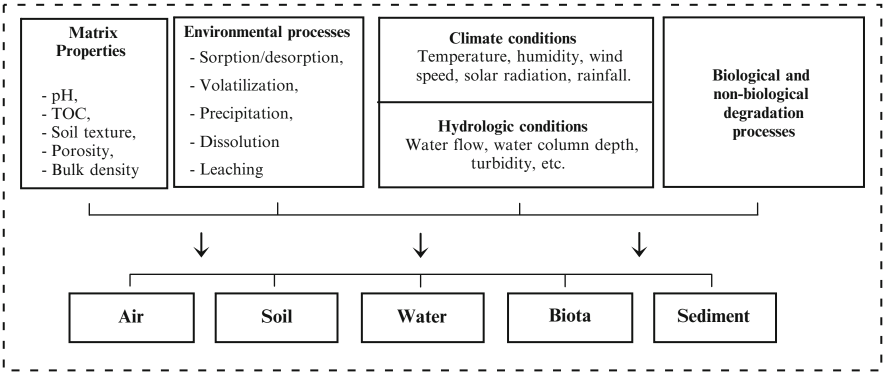
Chemicals	Application area	Environmental matrix	Model inputs	REF
(Heavy metal) Zinc	Lebano	Soil	– Soil pH – Organic matter content – Lithology – Surroundings of waste areas – Proximity to roads – Distance to drainage line – Slope length	[48]
(Consumer-product ingredients) Boron, LAS, EDTA, NTA and triclosan	River Itter (Germany)	Surface water	– Consumption figures in consumer products – WWTP-elimination – Sewer removal – In-stream-removal – Background concentration	[49]
(Pharmaceuticals) Ethinyl oestradiol, paracetamol, aspirin, dextropropoxyphene, clofibrate and oxytetracycline	Aire river (UK), Lambro river (Italy) and Rur river (Germany)	Surface water	– Product consumption – Worst-case influent – Excreted post-metabolism – WWTP removal – River water die-away	[50]
(Pesticide) Triclosan	Aire River (UK)	Surface water	– Physical, chemical, and biochemical parameters – Geographical production and consumption patterns	[51]
(Pesticide) Pyrethroids	European continent	Soil and water	– Total pesticide use – Spatial distribution of crops – Crop types (cereal, maize, oilseeds, citrus, etc.) – Runoff and soil moisture – Fate and transport parameters	[52]

(continued)

Table 4 (continued)

Chemicals	Application area	Environmental matrix	Model inputs	REF
(Pesticide) Alachlor	Lombardia Region (Northern Italy)	Surface water	– Meteorological data – Application rate – Active ingredient lost by drift – Percentage of active ingredient lost by runoff	[53]
(Cyclic volatile methyl siloxane) D5	Nene and Great Ouse Rivers (England)	Surface water	– Influent dry weather flow – WWTP influent concentration – Effluent discharges flow	[54]

LAS linear alkylbenzolsulfonate, *EDTA* ethylenediamine-tetraacetic-acid, *NTA* nitrilotriacetate, *D5* decamethylcyclopentasiloxane



TOC: Total organic carbon

Fig. 2 Main processes and factors affecting the fate and transport of chemicals in the environment

Regardless the complexity of the models used for predicting environmental concentrations, they share some common requirements regarding to the influencing factors that govern the occurrence and fate of chemicals in the environment:

(1) anthropogenic factors (emission rates, types of emissions and sources, waste management, etc.); (2) intrinsic physical–chemical properties of the chemical compounds and (3) environmental (external) conditions. In Fig. 2 are represented some of the key factors that influence the fate and behavior of chemicals.

The first step for the determination of PECs is the recognition of the anthropogenic activities that constitute the main sources of chemicals into the environment. Exposure models are based on estimations through exposure-related databases, manufacturing and trade inventories, sales reports, previous experimental studies and surveys. Chemicals present in products can be released into the environment in any stage of their life cycle (during their production, the finished product or waste). Therefore estimating emissions from finished products sometimes may be even more difficult because the composition and amount of chemicals present in these products is often lacking. The mode of use (closed cycle, spreading or used as chemical additives) and emission characteristics (point or diffuse) are also some of the factors to be considered.

Once chemicals are released into the environment, their behavior and fate are highly dependent on their physicochemical properties. These intrinsic properties of chemicals are decisive for their mobility throughout the different environmental compartments. Some of the most representative properties involved in mobility and behavior of chemicals are: partition constants (K_{OW} and K_{OC}), Henry's law constant, vapor pressure, solubility, evaporation temperature, as well as processes related to degradations (biological and nonbiological) such as hydrolysis, adsorption/desorption, and photolysis. Sorption/desorption processes play a major role in the availability of chemicals reaching target living organisms and the amounts that can be volatilized, leached, and/or degraded [55]. There are evidences that the mobility of chemicals in soils depends on several factors including the soil geologic characteristics (presence of gravel, clay, sand, etc.), particle size, porosity, pH, conductivity, the total organic carbon and the dissolved organic carbon fraction in water [56].

Finally, the third major input information required is external (i.e., extrinsic to the compound itself): the environmental physical conditions (see Fig. 2). Temperature and water regimes are often the most determinant factors which affect the mobility of chemicals in the environment by accelerating volatilization or sorption processes. Solar radiation is also crucial in the chemicals fate since it is strongly related to photodegradation and volatilization processes as well.

Therefore any attempt to model the spatial occurrence and fate of chemicals in the environment will require an appropriate choice of all the factors discussed above, which have a definite influence on the behavior of the chemicals considered. Figure 2 summarizes some of the most relevant. It is worth mentioning that the availability of spatial data sets has been greatly enhanced by the current progress achieved on remote sensing technologies [57, 58].

5 Future Challenges

Though it is impossible to anticipate all the directions in which environmental risk assessment will expand during the forthcoming years, below are presented some hot issues that nowadays are already attracting considerable scientific research.

Sometimes for some very potent pollutants analytical methodologies provide limits of detection (LODs) higher than the concentrations that cause effects, as derived from ecotoxicological studies. Therefore efforts in the field of analytical chemistry (see Sect. 2) are focused on making available the necessary analytical capabilities to detect pollutants at the required low levels found in the environment. This was the case of pharmaceuticals, illicit drugs, perfluorinated compounds (PFCs), sunscreens/UV filters, etc. few years ago. However, this list is likely to increase with new family candidates.

During recent years several groups of organic contaminants have emerged, including sucralose (and other artificial sweeteners), nanomaterials, disinfection by-products (DBPs), siloxanes, and algal toxins among others. Moreover, there is a further emerging group of contaminants of concern, the ionic liquids, whose occurrence and analysis in the environment points are the hottest topic within environmental analytical chemistry. Ionic liquids are salts with a low melting point ($<100^{\circ}$C) that are being promoted as "green chemistry" replacements to traditional solvents used in industry because they have low volatility and flammability. In fact, their use is highlighted in many papers as an innovative approach to sustainable chemistry. However, there is still limited information about their toxicity and environmental fate [37, 59].

The occurrence, behavior, and toxicity of all these emerging contaminants continue to be an intensive area of research, especially investigations about their removal from environmental waters (e.g., through advanced oxidation, photolysis, microbial degradation, etc.). Therefore, the identification of intermediates and degradation products originated as a result of these removal mechanisms is of crucial importance, as well as the evaluation of their toxicity, or the biological activity for the transformation products. Although many researchers are combining analytical chemistry with the study of biological effects, the identification and structural elucidation of transformation products of organic contaminants still require further analytical efforts.

6 Conclusions

As it has been shown in this chapter knowing the concentrations of chemicals in the environment is a key aspect in order to carry out meaningful hazard and risk assessment studies. Predicting concentrations of chemicals can serve as a quick and robust way to produce an acceptable screening level assessment; however if further precision is desired, the complexity of real environmental scenarios can make it a cumbersome and unaffordable task. Models improvement requires not only refining their computation algorithms but also and more important, implementing new inputs and processes in order to better describe real scenarios.

Laboratory measurements are still the most reliable way for determining environmental concentrations of chemicals (organic and inorganic) but this procedure supposes a great investment of time and money on both analytical equipment and monitoring efforts. Even so, monitoring has some obvious and unavoidable limits in terms of space and time coverage. The use of sensors and remote sensing techniques working on line at real time can only partially overcome such difficulties, but still the great majority of micropollutants of concern cannot be surveyed using these techniques.

In the Environmental Chemistry domain there is a growing need to develop reliable analytical methods, which enable a rapid, sensitive, and selective determination of pollutants in samples, at trace levels concentrations. Multi-residue analytical methodologies are becoming more utilized for routine analysis since they enable obtaining on a single run a wider and reliable knowledge about the occurrence of groups of compounds with similar properties (e.g., pharmaceuticals, illicit drugs, pesticides, and semivolatile compounds).

To conclude, a combination of both modeling and measuring procedures should be the most appropriate and wise recommendation for assessing chemical exposure in environmental scenarios.

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Environmental Fate Models

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Abstract The environmental fate of chemicals describes the processes by which chemicals move and are transformed into the environment. Environmental fate processes that should be addressed include: persistence in air, water and soil; reactivity and degradation; migration in groundwater; removal from effluents by standard wastewater treatment methods and bioaccumulation in aquatic or terrestrial organisms. Environmental fate models are by no means compulsory for managing priority substances. Efficient source control can be done without them, i.e. by reducing emissions gradually and monitoring the environment to track changes. However the environmental fate models are proposed for use for two main reasons: (a) because the quantitative models can improve the understanding of the managed system and (b) because the models can be used to predict long-term impacts of planned actions. Furthermore the residence times of some of the priority substances may be very long (e.g. 50 years for mercury in water column); therefore, only monitoring could be not enough to detect if the taken measures are enough to reach the good ecological status. The use of environmental fate models in decision making is not a new concept. They are routinely used in the framework of

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environmental risk assessment. The output of environmental fate models can be expressed as time series of predicted concentrations in different medium of both indoor and outdoor environments.

Keywords Chemicals, Fate, Modelling, Risk assessment

Contents

1 Introduction

The environmental fate of chemicals describes the processes by which chemicals move and are transformed into the environment. Environmental fate processes that should be addressed include: persistence in air, water and soil; reactivity and degradation; migration in groundwater; removal from effluents by standard wastewater treatment methods and bioaccumulation in aquatic or terrestrial organisms.

To address media-specific problems, *single-media models* for air, surface water, groundwater and soil pollution have been developed and used by different disciplines. Although these models generally provide detailed description of the pollutant distribution in space and time and incorporate mass transfer from other media as boundary conditions, they are not capable of characterizing the total environmental impact of a pollutant release. *Multimedia models* have been, therefore, developed to predict the concentration of chemicals in multiple environmental media simultaneously with consideration of chemical transport and transformation within and among media [1].

In this chapter, a brief description of the concepts and tools available for multimedia modelling to support the environmental risk assessment is given. The environmental fate assessment is the base of a more complex study, the

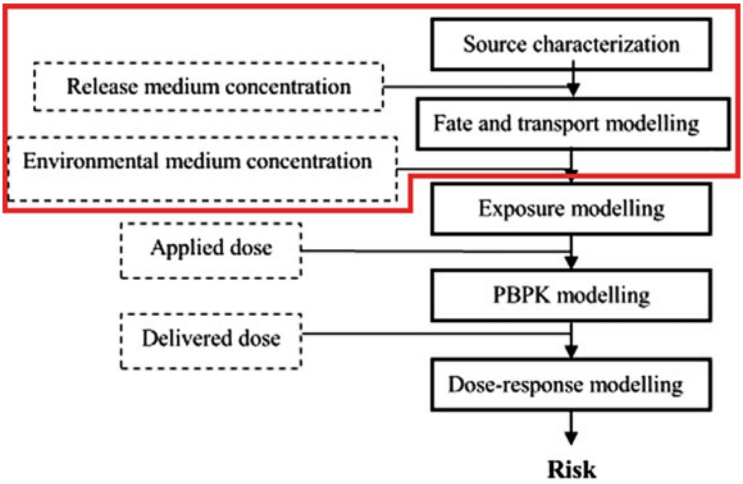

Fig. 1 Integrated environmental health risk assessment scheme (based on [2]); the *boxes within the red line* are the issues discussed in this chapter

environmental health and risk assessment (Fig. 1). Each of the tools is summarized and evaluated by a fixed number of principal characteristics:

- *Impact categories* (*model outputs*): eco-toxicity impacts and/or human toxicity impact
- *Exposure routes*: ingestion, inhalation, dermal
- *Fate, exposure and effect*: if fate, exposure and effect analyses are included or not
- *Chemicals considered*: organic pollutants and/or metals
- *Media considered*: air, water (fresh, ground, sea, etc.), soil, sediment, vegetation, food chain, etc.
- *Spatial variation*: regional scale, continental scale, global scale, country and seas boundaries
- Source code availability
- *Model availability*: pay model or free model
- Availability for sensitivity and uncertainty analyses
- *Population category*: if the differences in man/woman and adult/child are considered or not

This chapter considers the recently developed tools and the latest versions of the old tools. Some of the tools comprise not only the environmental compartments used on environmental risk assessment but also the human compartment necessary for human health risk assessment. For this reason, when summarizing the models, as described in the second part of this chapter, several characteristics of human compartment are discussed as well. However, a detailed description of human compartment together with a wide range of tools developed for exposure and human risk assessment is presented in the next chapter.

2 Multimedia Models

Based on the descriptions of spatial variation in each environmental compartment, multimedia models can be categorized into multimedia compartmental models (MCMs) [3–20], spatial multimedia models (SMs) [21–24] and spatial multimedia compartmental models (SMCMs) [25–27]. MCMs assume homogeneous landscape properties in each medium and assume all environmental compartments are well mixed. SMs are collections of single-media models in which the output of one model serves as the input to the others. Each individual model in the SMs is a spatial model describing the variation of environmental properties in one or more directions. SMCMs are similar to MCMs, but consider one or more environmental compartments as nonuniform regions.

In order to achieve that an environmental fate model is successfully applied in a screening level risk assessment and ultimately incorporated into the decision-making tools, the model should have computational efficiency and modest data input. Moreover, the model should incorporate all relevant compartments and all sources of contamination and should consider the most important mechanisms of fate and transport. Although spatial models describe the environment more accurately, such models are difficult to apply because they require a large amount of input data (e.g., detailed terrain parameters, meteorological data, turbulence characteristics and other related parameters). Therefore, MCMs are more practical, especially for long-term environmental impact evaluation, because of their modest data requirements and relatively simple yet comprehensive model structure. In addition, MCMs are also widely used for the comparative risk assessment of new and existing chemicals [28–33].

Among MCMs reported in environmental science literature, the following models are most widely used: CalTOX [7, 8], ChemCAN [12], HAZCHEM [10], SimpleBox [9], Qwasi [34], and 2-FUN TOOL [20]. Most of these models consider the lower atmosphere (troposphere), surface water, soil and sediment as the main compartments, with some sub-compartments or add-on indirect exposure models (e.g., vegetation) included. CalTOX has the capability to estimate chemical concentration in groundwater based on the leachate from the vadose-zone soil, and ChemCAN considers the chemical transfer from the air compartment to higher altitude. However, all of these models do not treat some important compartments, such as the stratosphere and groundwater, as separate compartments. The inclusion of the stratosphere compartment in a model enables an individual to estimate the ozone depletion potential for existing or new chemicals.

Although some of the other existing models treat the vegetation as a separate compartment [14, 35, 36] and some include the groundwater as a main compartment [4, 11], none of the models incorporates all important compartments at the same time. However, ignoring some important compartments may result in large difference of concentration in the media of interest. For example, the inclusion of a canopy compartment decreases the average air concentrations during the growing season by a factor of 5 for some semi-volatile organic compounds [37]. Therefore, the CHEMGL multimedia model has been developed by Zhang et al. [38], which includes all the relevant aforementioned compartments. This may represent an improvement over the existing models developed before.

2.1 Fugacity and Markov Chain Principles

Most of the above-mentioned models are based on the fugacity principle. The term "fugacity" was introduced in 1901 by G.N. Lewis to describe the "escaping" tendency of a chemical species from a particular environmental compartment (e.g., air, water, soil, etc.). Where chemical potential within a particular compartment is related logarithmically to concentration, the equilibrium criterion of fugacity is linearly related to concentration. Fugacity (f) has units of pressure and environmental compartments, in equilibrium with each other, have equal fugacity values (i.e., the tendency to leave one compartment and enter a second is equal to the tendency of the chemical to leave the second and enter the first). Each environmental medium has a certain fugacity capacity (Z) that describes the relationship between chemical concentration and fugacity in the same way that heat capacity describes the change in temperature of a given material for a particular input of heat. Thus, environmental media with high Z values can retain greater amounts of a given chemical while maintaining low fugacity values.

The earliest or Level I fugacity models simulate the simple situation in which a chemical achieves equilibrium between a number of phases of different composition and volume. The prevailing fugacity is simply $f = M/\sum V_i \times Z_i$, where M is the total quantity of chemical (mol), V_i is volume (m^3), and Z_i is the corresponding phase Z value ($\mathrm{mol\ Pa^{-1}\ m^{-3}}$). Although very elementary and naive, this simulation is useful as a first indication of where a chemical is likely to partition. It is widely used as a first step in chemical fate assessments.

More realistic Level II fugacity models introduce the rate of chemical reaction or degradation and advection, but interphase equilibrium is still assumed. Level III fugacity models introduce inter compartmental transfer rates, thus equilibrium no longer applies. For Level III fugacity models it is then necessary to specify the chemical's mode-of-entry to the environment, that is, to air, water, or soil, or some combination of these media. Valuable insights obtained from these models include those of overall chemical persistence or residence time and potential for long-range transport (LRT) in air or water. Level IV fugacity models, which involve the solution of differential mass balance equations, can be used to describe the time dependent or dynamic behavior of chemicals.

Besides the fugacity models, the environmental science literature reports the use of models based on Markov chain principle to evaluate the environmental fate of chemicals in multimedia environment. Markov chain is a random process, and its theory lies in using transition matrix to describe the transition of a substance among different states [39, 40]. If the substance has all together n different kinds of states, which are expressed as $i = 1, 2, \ldots, n$, the transition matrix would be described as the following matrix:

$$P = \begin{pmatrix} p_{11} & p_{12} & \cdots & p_{1n} \\ p_{21} & p_{22} & \cdots & p_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ p_{n1} & p_{n2} & \cdots & p_{nn} \end{pmatrix},$$

where the element p_{ij} in the matrix is the transition probability for the substance transiting from state i to j in each unit time. Supposing the initial state vector of the substance is $T(0) = (y_{10}, y_{20}, \ldots, y_{n0})$, at k time, the state vector will be

$$T(k) = T(0) \times Pk.$$

This approach has been extensively applied to fields as agriculture [41, 42], forestry [43], biology [44, 45], medicine [46, 47], business [48, 49] and chemical engineering [50, 51], whereas in environmental protection, it was used to evaluate the operation of environmental facilities [52], and the transportation of pollutants along the food chain in ecological system [53]. However, Markov chain approach used for evaluation of environmental fate of chemicals in environment multimedia was recently adopted as reported by Zhang and Dai [54] and Dazhi and Xuqian [55]. The studies were developed at regional scale and mainly for PAHs organic pollutants.

3 Models Description

As already mentioned before, a list of nine models, comprising six models describing the fate and transport of chemicals in the environmental compartments (Qwasi, ChemCAN, CHEMGL, GREAT-ER, SimpleBox, BETR) and three models able to assess the fate and transport of chemicals in the environmental and human compartments (CalTOX, ExtraFod, 2-FUN Tool) are described in this section. The next chapter gives detailed descriptions of the human compartment and the processes necessary for exposure and human health risk assessment.

3.1 Qwasi

The quantitative water air sediment interaction (Qwasi) model was developed in 1983 in order to perform a mathematical model which describes the behavior of the contaminants in the water. Since there are many situations in which chemical substances (such as PCBs, pesticides, mercury, etc.) are discharged into a river or a lake resulting in contamination of water, sediment and biota, it is interesting to implement a model to assess the fate of these substances in the aquatic compartment [34].

The Qwasi model estimate the fate of a chemical in a water system (lake, river, etc.) consisting of water, bottom and suspended sediments, and air. The model is

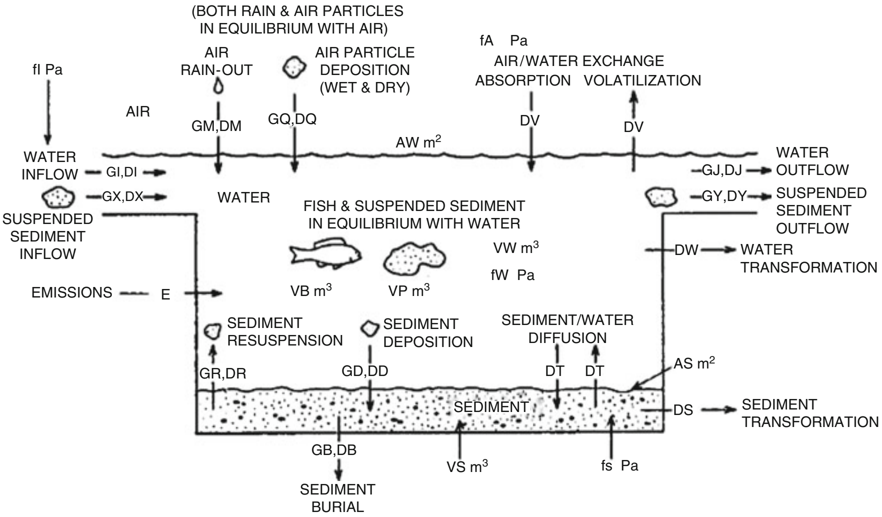

Fig. 2 Qwasi processes considered [34]

Table 1 Principal characteristics of Qwasi model (based on [34])

Principal characteristics	Mathematic for fate calculations of water systems
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Only fate of chemicals in water systems considered
Chemical considered	Organic and inorganic chemicals
Media considered	Not considered
Spatial variation	Local scale
Source code availability	Yes, equations available
Model availability	Yes
Dynamic or steady-state	Both steady an unsteady state considered
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

based on the fugacity concept which provides an overview of the contaminants in the aforementioned compartments.

The model is composed by different equations which in all cases can be used in unsubscribed format in a basic language program. An important point to highlight is that Qwasi takes into account both steady and unsteady state solutions for the equations for systems involving contamination of lakes (or rivers). The equations considered by Qwasi involve more than 15 physicochemical processes (such as partitioning, sediment transport, deposition, etc.) to estimate the fate of the studied system. These processes and the main involved variables and parameters are summarized in Fig. 2.

As summary, the principal characteristics of the Qwasi model are listed in Table 1.

3.2 ChemCAN Model

The ChemCAN model describes the *fate of a chemical in a region*, assuming *steady state conditions* in the environment. The model estimates average concentrations in four primary environmental media consisting of air, surface water, soil, and bottom sediment, and three secondary media consisting of groundwater, coastal water and terrestrial plants. Chemical fate is determined through the solution of the set of mass balance equations for the primary media as described by Mackay [56]. The model is intended to assist in human exposure assessment where a specific target population may be identified.

This model was originally designed for use in Canada. Therefore, a database of 24 regions of Canada is available. However, other regions can be defined by the user. In the model, the appropriate dimension of surface areas is set between 100 km × 100 km and 1,000 km × 1,000 km. The regional divisions of Canada were based on the eco-zones identified by Environment Canada and with consideration of the distribution of population and industrial activity, political boundaries, drainage basins, and climate to give areas of sufficiently homogeneous ecological conditions such that meaningful assessments of chemical fate can be conducted.

The transparency of this model was achieved by making it possible for the user to view the equations within the model. By viewing a section of the program code, the user can know how this steady-state model mimics the physical reality. The model is intended to provide regionally specific estimates of chemical concentrations in the primary media. These estimates can be compared to monitoring data and be used for exposure estimation.

A current application of this model was presented in Webster et al. [57] and its main characteristics are presented in Table 2.

Table 2 Principal characteristics of the ChemCAN model

Principal characteristics	Multimedia model with steady-state condition
Impact categories	Human toxicity
Exposure routes	Not specified
Fate, exposure and effect	Fate
Chemical considered	Organic compounds and non-volatile compounds
Media considered	Air, surface water, soil, bottom sediment, groundwater, coastal water, and terrestrial plants
Spatial variation	Regional
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state
Availability for sensitivity and uncertainty analyses	No
Population category	No

3.3 CHEMGL

Increasing concern about environmental problems as ozone depletion, groundwater pollution and human health risks via exposure from the food web suggests it would be valuable to construct a model that includes the compartments of the upper atmosphere (stratosphere), groundwater and vegetation. The CHEMGL model was developed with this scope. Furthermore, the model is capable of providing the information about whether a chemical will accumulate in the lower atmosphere or upper atmosphere. If a chemical accumulates in the air boundary layer (ABL), it will cause problems locally. However, if it accumulates in the stratosphere, it presents a great possibility to lead to global problems.

Moreover, most environmental multimedia models are used for exposure assessment, but few are linked with decision-making tools for screening level manufacturing process design. CHEMGL has the advantage of a possible incorporation into an economic and environmental decision analysis tools. This tool allows an individual to make decisions for manufacturing processes based on environmental, safety and economic criteria. In such tools, CHEMGL is used to estimate the concentration of a chemical and is linked with a risk index calculator for the evaluation of several environmental impacts resulting from chemical manufacturing [58].

As shown in Fig. 3, CHEMGL considers 10 major well-mixed compartments: air boundary layer, free troposphere, stratosphere, surface water, surface soil, vadose soil, sediment, ground water zone, plant foliage and plant route. In each compartment, several phases are included, for example, air, water and solids (organic matter, mineral matter). A volume fraction is used to express the ratio of the phase volume to the bulk compartment volume. Furthermore, each compartment is assumed to be a completely mixed box, which means all environmental properties and the chemical concentrations are uniform in a compartment. In addition, the environmental properties are assumed to not change with time. Other assumptions made in the model include: continuous emissions to the compartments, equilibrium between different phases within each compartment and first-order irreversible loss rate within each compartment [38].

The main characteristics of the CHEMGL model are summarised in Table 3.

3.4 GREAT-ER Model

The GREAT-ER model was developed as an aquatic chemical exposure prediction tool for use within environmental risk assessment (ERA) schemes and river basin management. The GREAT-ER software calculates the distribution of predicted environmental concentrations (PECs) of consumer chemicals in surface waters. Compared with other regional generic models, realism is increased within GREAT-ER by incorporating spatial and temporal characteristics of the receiving environment in the models and underlying databases (Fig. 4). The design of the GREAT-ER system has been approached in a modular way containing: the data

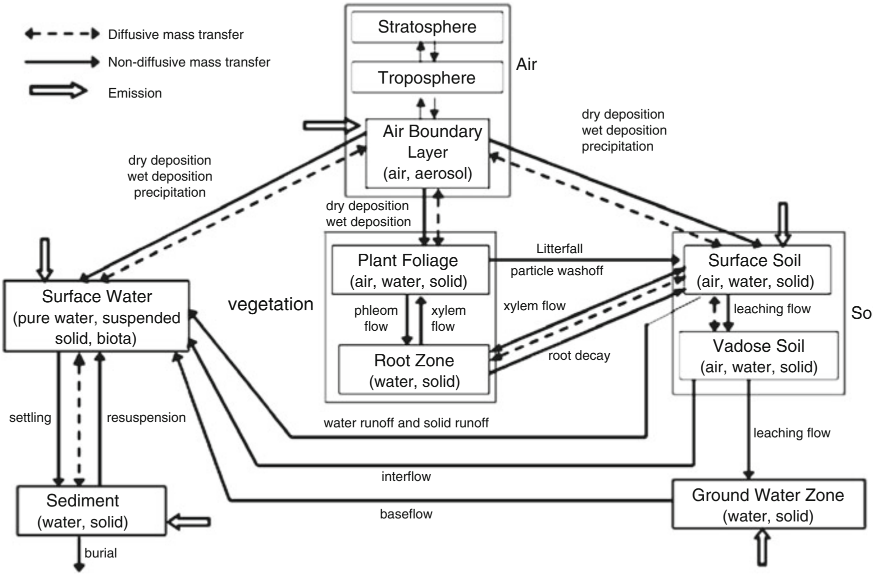

Fig. 3 The MCM domains and fate mechanisms incorporated into CHEMGL [38]

Table 3 Principal characteristics of CHEMGL model (based on [38])

Principal characteristics	Multimedia model for fate and exposure analyses of chemicals
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Fate and exposure of chemicals considered
Chemical considered	Organic chemicals
Media considered	Air (free troposphere, stratosphere), water (surface and ground water), soil (two layers), sediment, vegetation (plant foliage and plant route)
Spatial variation	Local scale
Source code availability	Yes, equations available
Model availability	Yes
Dynamic or steady-state	Both steady an unsteady state considered
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

manipulation module, hydrology module, the waste pathway and river modelling module and the end-user desktop GIS module [60].

In the data manipulation module, input data sourced from several databases and from the hydrology module are transformed into appropriate geographical information system (GIS) formats [61]. Before that, the hydrology module combines several hydrological databases with a hydrological model, providing to the

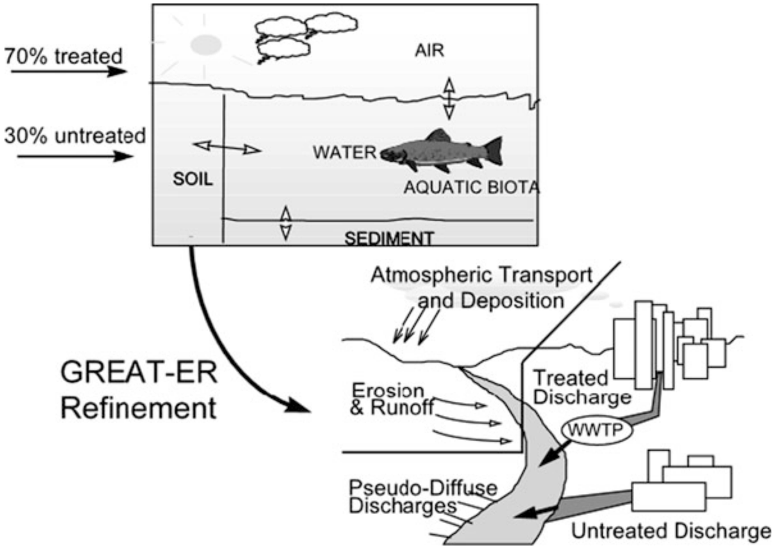

Fig. 4 GREAT-ER – refinement of generic regional exposure models, by taking into consideration actual discharge pathway, river flow and waste water treatment plant (WWTP) (as described by Schowanek and Webb [59])

GREAT-ER system the required river flow distributions, flow velocities and river characteristics.

The waste pathway and river modelling module is used for the prediction of chemical emission, of chemical removal/transformation during conveyance and treatment, and of chemical fate in rivers [62]. Chemical fate in wastewater treatment plants (WWTP) and in rivers is described deterministically, with several levels of complexity being available to reflect the available information concerning both the chemical and the environment.

In the last module, the end-user desktop GIS, access to and visualization of the databanks and model results is achieved, as well as the linking of the models with the data banks. The GIS databanks, the waste pathway models and the river models are integrated into one coherent simulation system. Such integration process results in an operational end-user system, which runs on a PC platform. The hydrological models and the ARC/INFO spatial data processing steps are not integrated into the end-user software system. The user interface is the front-end between the user and the software system. It allows the selection of catchments, chemicals as well as the input of model and scenario parameters. The user interface also handles filtering and visualization of model results by the GIS. Avenue (ESRI®) has been used for the development of this interface in an ARCVIEW (ESRI®) environment. ARCVIEW® 3.0a or 3.1 software is required to run GREAT-ER. Furthermore, a variety of river catchments in the EU are available to the user or under development (www.great-er.org).

In Table 4 an overview of the principal characteristics of GREAT-ER model is presented.

Table 4 Principal characteristics of GREAT-ER model (based on [60])

Principal characteristics	Aquatic chemical exposure prediction tool
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Fate and exposure of chemicals in surface water
Chemical considered	Organic and inorganic chemicals
Media considered	Not considered
Spatial variation	Regional scale
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state
Availability for sensitivity and uncertainty analyses	Yes
Population category	Not considered

3.5 SimpleBox Model

SimpleBox is a nested multimedia environmental fate model in which the environmental compartments are represented by homogeneous boxes. It consists of five spatial scales; a regional scale, a continental scale and a global scale consisting of three parts, reflecting arctic, moderate and tropic geographic zones (Fig. 5)

SimpleBox is a generic model, it can be customized to represent specific environmental situations. In its default setting, the SimpleBox computation represents the behavior of micropollutants in a regional and continental scale, representing a densely populated Western European region, and the whole European Union, respectively. SimpleBox follows the Mackay concept of sequentially carrying out the modelling procedure at different stages of complexity of "levels" [56]. The model allows to perform the non-equilibrium, steady-state computation, as well as the quasi-dynamic non-equilibrium, non-steady-state computation.

Whereas the fugacity approach was used by Mackay for the computation of mass flows and the concentration levels, the SimpleBox adopt the concentration-based "piston velocity" type mass transfer coefficients (ms^{-1}). This is, mainly, because most scientific papers express the mass transfer in these terms, rather than in terms of the fugacity-based "conductivity" type coefficients ($\mathrm{mol\ h}^{-1}\ \mathrm{Pa}^{-1}$). Furthermore, the transfer and transformation phenomena are treated as simple pseudo first-order processes, similar to Mackay models.

The environmental compartments are represented by boxes and the concentration of a chemical in these boxes is affected by processes that cause mass flows of the chemical to and from the boxes. The chemical can be *input* into a box from outside the system, *output* from a box to outside the system, or transported by means of *advective* or *diffusive* processes to and from other boxes. A mass balance equation can be written for each of the boxes representing the mass flow of the chemical. Generally, the magnitude of these mass flows depends on the concentration of the chemical in the boxes. If mathematical expressions which relate the mass flows to the concentrations are available, the set of mass balance equations (one for

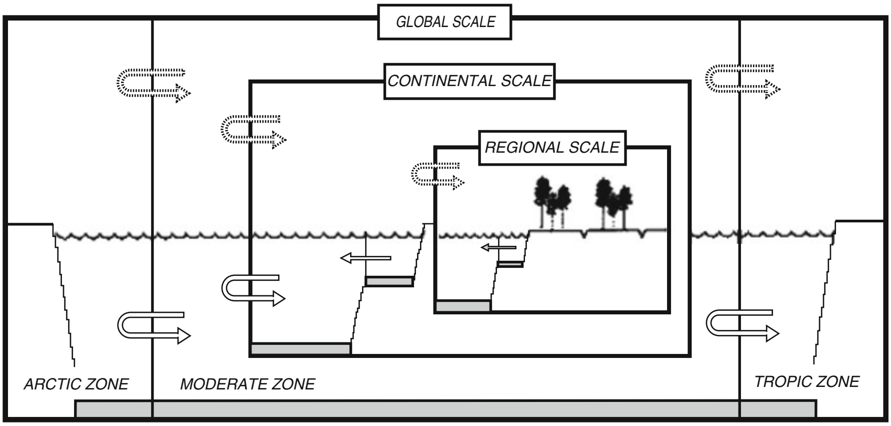

Fig. 5 SimpleBox 2.0 model

Table 5 Principal characteristics of SimpleBox model (based on [63])

Principal characteristics	Nested multimedia environmental fate model
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Just the fate of chemicals is considered
Chemical considered	Organic chemicals
Media considered	Air, water, soil, sediments and vegetation
Spatial variation	Regional, continental and global scale
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state and quasi-dynamic
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

each box) can be solved. Therefore, the concentrations in each of the boxes can be computed.

An overview of the principal characteristics of the SimpleBox model is given in Table 5.

3.6 BETR Model

The BERT model is based on the fugacity concept and exploits existing contaminant fate modelling techniques. The BERT model is built on a general framework that links individual regional contaminant fate models to create a model that encompasses a larger, spatially heterogeneous area. It can thus address issues of long-range transport of chemicals between regions within the continent [64].

Background concentrations can be specified to include advective inflow of chemical in air or water from outside the model area, or the regional environments can be linked into a closed system. Thus the framework is capable of describing contaminant fate on specific national, continental, or even global scale. Appropriate boundary conditions must, of course, be selected for each system. Models of larger geographic areas are built up from box models of chemical fate in smaller regions, with regional boundaries selected to account for considerations such as geographic features, political boundaries and chemical use patterns. The BERT model, for example for North America, is composed of 24 linked regional environments with boundaries based on geographic features, principally watersheds and soil types.

In the BERT model, the environment in each region is described as a connected system of seven discrete, homogeneous compartments. Describing the environment in this fashion is a characteristic of multimedia environmental models, and all models of this type use a similar approach, as already specified in the previous described models. Furthermore, the number of compartments considered in existing, and partially described in this chapter, models varies from two, for simple aquatic fate or air–soil interaction models, to about 10 for models of regional environments that include different soil and water types in individual regions. Figure 6 illustrates the seven compartment regional environment of the BETR model framework whereas in Table 6 are given its main characteristics.

3.7 CalTOX

The CalTOX model was originally developed as a set of spreadsheet models and spreadsheet data sets for assessing *human exposures* from continuous releases to air, soil, and water [7]. Hertwich [65–67] applied the CalTOX model for the assessment of human toxicity in Life Cycle Assessment (LCA). *Ecotoxicicity is not evaluated* in the model.

The current version of CalTOX (CalTOX4) is an eight-compartment regional and *dynamic multimedia fugacity model*. CalTOX comprises a multimedia transport and transformation model, multi-pathway exposure scenario models, and add-ins to quantify and *evaluate variability and uncertainty*. To conduct the sensitivity and uncertainty analyses, all *input parameter values are given as distributions*, described in terms of mean values and a coefficient of variation, instead of point estimates or plausible upper values.

Sub-systems included in CalTOX refer to the prediction of *the fate, the exposure and the effect*. Next, a brief description of these sub-systems is given:

- *Fate and exposure analyses*. The multimedia transport and transformation model is a *dynamic model* that can be used to assess time-varying concentrations of contaminants that are placed in soil layers at a time-zero concentration or contaminants released continuously to air, soil, or water. This model is used for determining the distribution of a chemical in the environmental compartments. An overview of the partitioning among the liquid, solid and/or gas phases of individual compartments is presented in Fig. 7. The exposure model encompasses

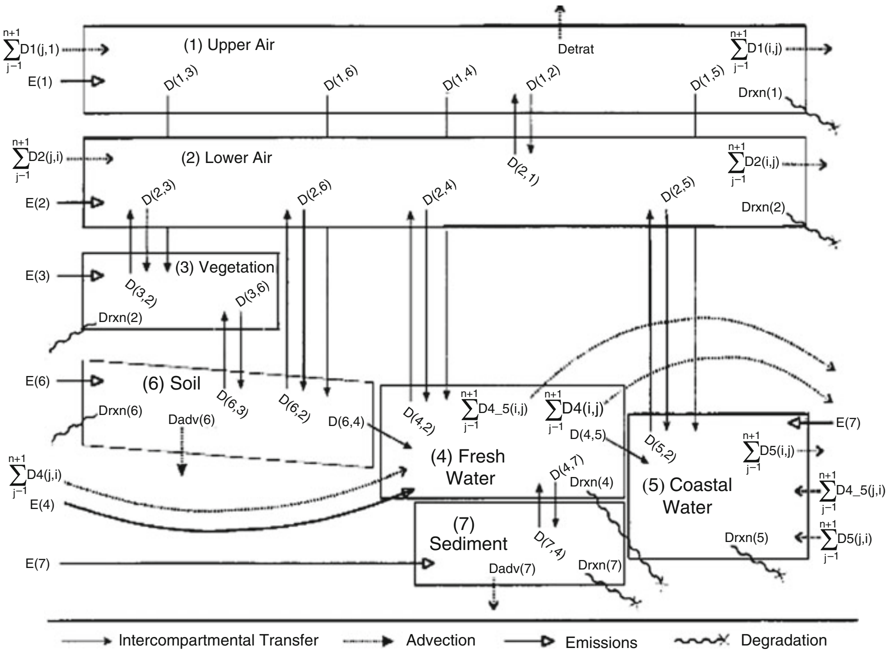

Fig. 6 Environmental compartments and contaminant fate processes in region "*i*" of the BETR linked regional model framework as described by MacLeod et al. [64]

Table 6 Principal characteristics of BETR model (based on [64])

Principal characteristics	Multimedia environmental fate model
Impact categories	Ecotoxicological effects
Exposure routes	Not considered
Fate, exposure and effect	Just the fate of chemicals is considered
Chemical considered	Organic chemicals
Media considered	Air, water, soil, sediments and vegetation
Spatial variation	Regional, continental and global scale
Source code availability	Yes
Model availability	Yes
Dynamic or steady-state	Steady-state and dynamic
Availability for sensitivity and uncertainty analyses	Not considered
Population category	Not considered

23 exposure pathways through *inhalation*, *ingestion* of foods and *dermal contact*. They are used to estimate average daily doses within human population linked geographically to a release region. More information characterizing this type of models are given in the next chapter.

- *Effect analysis*. The CalTOX scheme can calculate cancer and non-cancer human toxicity potential (HTP) values for air and surface water emissions of 330 compounds. However, more information concerning the HTP and toxicity of a compound are available in the next chapter.

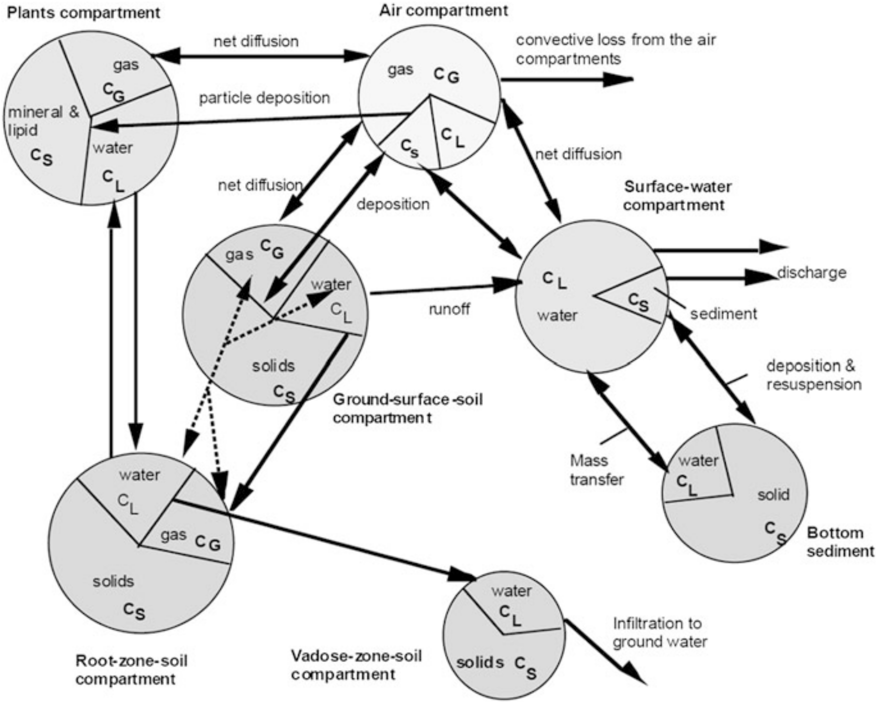

Fig. 7 Overview of the partitioning among the liquid, solid and/or gas phases of individual compartments [8]. *Note*: In the current version of CalTOX (CalTOX4), the plant compartment comprises two sub-compartments [plant surfaces (cuticle) and plant leaf biomass (leaves)]

The main characteristics of the CalTOX model are presented in Table 7.

3.8 XtraFOD Model

The XtraFOOD model was developed within the framework of a research project initiated by the Flemish Institute for Technological Research (VITO) [69]. The model calculates transfer of contaminants in the primary food chain (Fig. 8). In the project, the transfer model was coupled with historical food consumption data to *estimate human exposure to contaminated food products*. The model focuses on the *terrestrial food chain*. The XtraFOOD model consists of three modules, which are inter-linked:

- *A mass balance model at the farm level*: Calculation of inputs and outputs.
- *Bio-transfer module*: Calculation of the transfer of contaminants to vegetable products (vegetables, cereals, animal feed) and animal products (meat, milk dairy products, poultry, eggs).
- *Exposure and impact module*: Calculation of the exposure from food (and other exposure routes) and comparison with reference values.

Table 7 Principal characteristics of the CalTOX (based on [68])

Principal characteristics	Multimedia model for fate analysis and extensive analysis of exposure pathways
Impact categories	Human toxicity
Exposure routes	Inhalation, ingestion and dermal contact
Fate, exposure and effect	Fate, exposure and effect are considered
Chemicals considered	Organic and inorganic compounds
Media considered	Air, water, sediments, three soil layers, vegetation (two sub-compartments)
Spatial variation	Not considered
Source code availability	Yes, as Excel spreadsheet
Model availability	Yes
Dynamic or steady-state	Dynamic
Availability for sensitivity and uncertainty analyses	Yes
Population category	Not considered

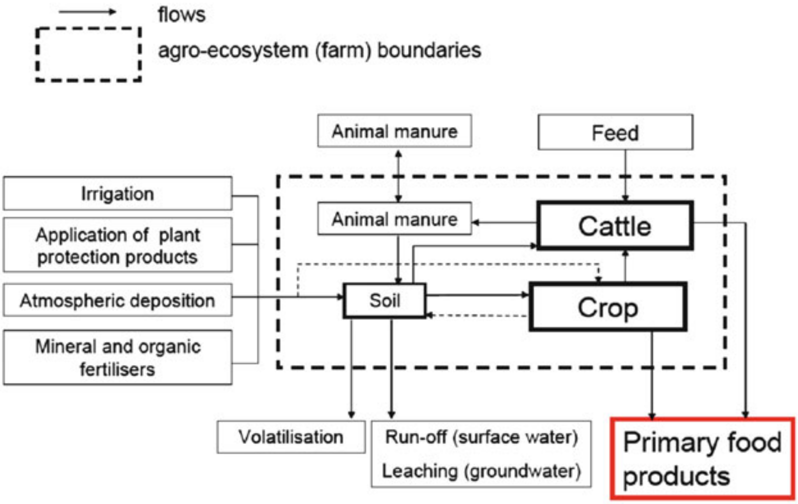

Fig. 8 Overview of contaminant flows in a model agro-ecosystem to the food chain [69]

The XtraFOOD model calculates as *output the food intake and resulting contaminant intake, independently for age and gender categories*. Exposure can be calculated as being representative for a population or separately for local and background intake. All these intakes are linked to the model output. Additional intakes are provided to add concentration data in non-farm-related foods (e.g. fruit juice, fish, etc.).

An overview of the principal characteristics of the XtraFOOD model is given in Table 8.

Table 8 Principal characteristics of the XtraFOOD model

Principal characteristics	Multimedia model focused on the primary food chain
Impact categories	Human toxicity
Exposure routes	Ingestion
Fate, exposure and effect	Fate and exposure are considered
Chemicals considered	Organic compounds and heavy metals
Media considered	Air, soil, farm-related crops, animal
Spatial variation	Not considered
Source code availability	Not considered
Model availability	Not specified
Dynamic or steady-state	Steady-state
Availability for sensitivity and uncertainty analyses	Yes
Population category	Age and gender are considered

3.9 2-FUN Tool

2-FUN tool is a new *integrated software* based on a *multimedia model*, *physiologically based pharmacokinetic* (*PBPK*) *models and associated databases*. The tool is a dynamic integrated model and is capable of *assessing the human exposure to chemical* substances via *multiple exposure pathways and the potential health risks* (Fig. 9) [70]. 2-FUN tool has been developed in the framework of the European project called 2-FUN (Full-chain and UNcertainty Approaches for Assessing Health Risks in FUture ENvironmental Scenarios: www.2-fun.org).

The multimedia model present in the 2 FUN tool was developed based on an extensive comparison and evaluation of some of the previously discussed multimedia models, such as CalTOX, Simplebox, XtraFOOD, etc. The multimedia model comprises several environmental modules, i.e. air, fresh water, soil/ground water, several crops and animal (cow and milk). It is used to simulate chemical distribution in the environmental modules, taking into account the manifold links between them. The PBPK models were developed to simulate the body burden of toxic chemicals throughout the entire human lifespan, integrating the evolution of the physiology and anatomy from childhood to advanced age. That model is based on a detailed description of the body anatomy and includes a substantial number of tissue compartments to enable detailed analysis of toxicokinetics for diverse chemicals that induce multiple effects in different target tissues. The key *input parameters* used in both models were given *in the form of probability density function* (*PDF*) to allow for the exhaustive probabilistic analysis and sensitivity analysis in terms of simulation outcomes [71].

The environmental multimedia and PBPK models were built and linked together on the common platform software called Ecolego® (www.facilia.se). One of the main characteristics of Ecolego system is the use of Interaction Matrices to build and visualize models (Fig. 10). The effective graphical simulation interface presented in

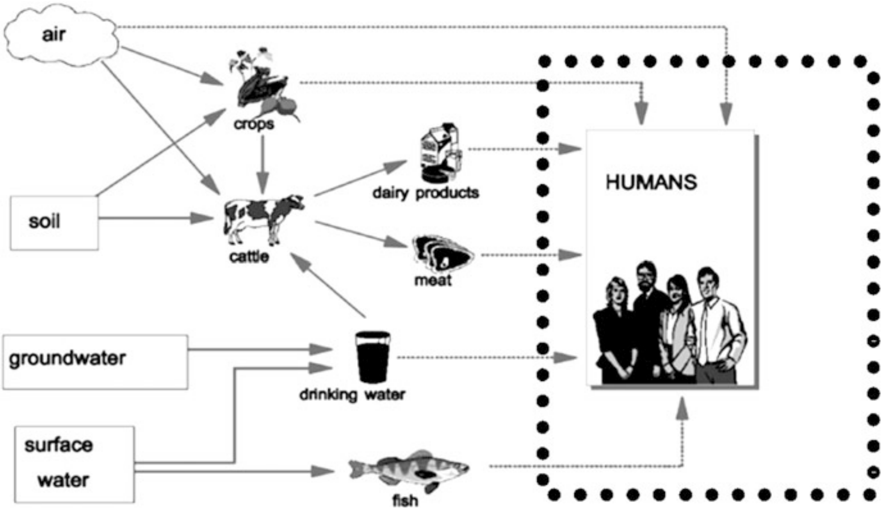

Fig. 9 Multi-pathways that substances can take to reach humans (the area enclosed by a *dashed line* emphasizes the indirect pathways to humans via food chains) [70]

the *Ecolego system* can facilitate a comprehensive identification and visualization of the exposure pathways and allow classification of the role of different environmental modules (subsystem) in terms of transfer relationship. In the Ecolego system, advanced methods concerning *probabilistic and sensitivity analyses* can be selected: (a) Monte Carlo methods for the propagation of parametric uncertainties; (b) an optimization function to correlate input parameters with simulated outputs in the Monte Carlo process and then to optimize the values of input parameters and (c) several regression and Fourier tests for conducting sensitivity analysis [20].

The complete 2-FUN tool allows for realistic and detailed lifetime risk assessments for *different population groups* (general population, children at different ages, pregnant women), considering human *exposure via multiple pathways* such as drinking water, inhaled air, ingested vegetables, meat, fish, milk, etc.

The main characteristics of the 2-FUN tool are described in Table 9. 2-FUN tool has the following prominent features which differentiate it from other models.

- Its capability to conduct *full-chain risk assessment* on a common system, which allows for linking the simulation of chemical fate in the environmental media, multiple pathways of exposure and the detailed analysis for multiple effects in different target tissues in human body (by PBPK models).
- Its capability to assess the *health risk of specific human groups* vulnerable to toxicants, i.e. for woman, infant.
- It contains a wide range of *methods for sensitivity and uncertainty* analyses.
- It contains an exhaustive *database of PDF for input parameters*.
- It can be *user-friendly* because of its effective graphical simulation interface and its flexibility, which facilitates users to design scenarios for target regions and

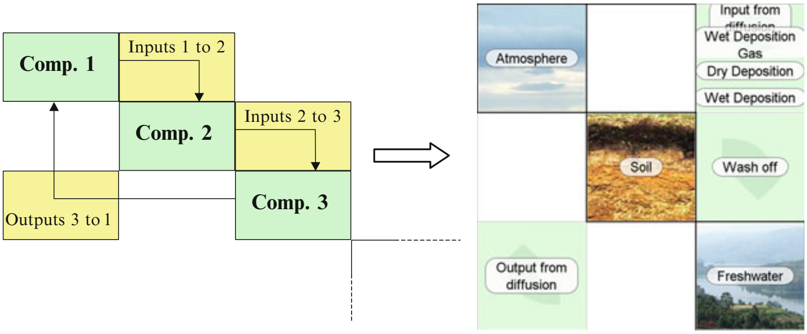

Fig. 10 The schematic of interaction matrix (*left*) and representation of the interaction matrix in the Ecolego system (*right*)

Table 9 Principal characteristics of 2-FUN tool [70]

Principal characteristics	Integrated tool coupling an environmental multimedia model and PBPK models
Impact categories	Human toxicity
Exposure routes	Ingestion, inhalation and dermal intake
Fate, exposure and effect	Fate, exposure and potential effect are considered
Chemicals considered	Organic and inorganic chemicals
Media considered	Air, fresh water, soil/ground water, farm-related crops, and animal (cow and milk)
Spatial variation	Not considered (mainly used for regional scale)
Source code availability	Yes
Model availability	Yes in the near future
Dynamic or steady-state	Dynamic
Availability for sensitivity and uncertainty analyses	Yes
Population category	Age and gender are considered

arrange the tool on their ways, i.e., users can select only the environmental modules necessary for their regional scenarios.

4 Conclusions

A large and growing volume of literature exists on multimedia models. They serve an essential role as tools for bringing together information on chemical and environmental properties with a view to estimating chemical fate. They can be configured in various ways and can range greatly in complexity, but in principle it is preferable to use the simplest model that can generate the desired result.

Mainly, the available models have been developed based on the fugacity approach, which use the fugacity as surrogate of concentration, for the compilation and solution of mass-balance equations involved in the description of chemicals fate. However, a new approach based on Markov chain principle it starts being investigated for the development of models able to estimate the environmental fate of chemicals.

Furthermore, there can be identified two opposing trends in model development. One is a trend toward more detailed models with higher fidelity to the real system, driven by the availability of highly resolved environmental data, increases in computer power, and progress in atmospheric and earth sciences. The other trend is toward models that are tailor-made to specific scientific questions or decision-making problems, driven by the philosophy of parsimony and the increase in the need for scientific results as a basis for decision-making in modern society.

However, in the future, as in the past, models will be required to address a range of interdisciplinary scientific questions about chemicals in the environment. Certainly, mass-balance models at different spatial and temporal scales and with different levels of detail, including multimedia models based on the unit world approach, will continue to be essential tools in research, education and decision support in the future. In the last 30 years, models based on these principles have accrued significant credibility by providing insights into many key problems in environmental chemistry. These tools are now well established and mature, and available to study the new generation of environmental pollutants. The principles that have been developed for mass-balance models of chemical substances also stand ready to be adapted to address emerging challenges including supporting the development of green chemistry, addressing engineered nanomaterials, which are of increasing economic importance and behave differently from the common chemicals.

Therefore, 30 years after the establishment of the field, we believe multimedia environmental contaminant fate modelling remains a vibrant scientific discipline that has a central role in science and decision-making in environmental chemistry.

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Toxicological and Ecotoxicological Studies for Additives

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Abstract As the world has become ever more industrialized, an alarmingly large number of chemicals have entered as contaminant mixtures in waste, air, water, and soil.

The need to decrease costs and reduce animal suffering for chemical risk assessment has ever more encouraged the use of methods alternative to the use of animals to predict toxicity. These alternative methods can be generally divided into two subgroups: study of toxicity in laboratory tubes on small organisms (in vitro) and computational techniques (in silico).

These techniques have recently become more important due to mandates such as the categorization of the Canadian Domestic Substance List [Canadian Domestic Substance List; Canadian Environmental Protection Act, 1999 (Section 74, CEPA 1999)], the European Union's REACH [REACH; REGULATION (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives [91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC], and Cosmetics Regulations [European Union's Cosmetics Regulations; REGULATION (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products], the Japanese Chemical Substance Control [Japanese Chemical Substance Control

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Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. (Act No. 117 of October 16, 1973 amended in 2009)], as well as their continued use by the U.S. Environmental Protection Agency (EPA) [Kavlock R, Dix D. J Toxicol Environ Health B Crit Rev 13(2–4):197–217, 2010] and U.S. Food and Drug Administration (FDA) [U.S. Environmental Protection Agency (EPA) and U.S. Food and Drug Administration (FDA); TSCA (1976) Toxic Substances Control Act. United States Publ. Law 94–469, 90 Stat 2003, USA].

Day by day, the number of scientific works and techniques based on in vitro tools has increased their relevancy, supporting the hypothesis of the use of in vitro models as refinement technique due to their ability to provide information on central events involved in toxicant mode of action.

In vitro tools could be used alone or in test batteries with increased potency of the description of cellular events and changes. The chapter provides a brief introduction on the components of an in vitro system, the main differences between models for research and models for testing and a list of validated alternative methods according to the European Centre for the Validation of Alternative Methods (ECVAM) (http://ecvam.jrc.it/, http://ecvam.jrc.ec.europa.eu/) evaluation.

Furthermore, in recent years more and more studies have been carried out in which computational programs have been used to predict the toxicity of chemical compounds. The main driving force behind this trend has been the emergence of new chemical descriptors, algorithms, and statistical perspectives, in addition to the higher expectations as to how such programs can have specific applications, such as for regulatory purposes or drug discovery (Benfenati E. Chem Cent J 1:32, 2007). The performance of the computational models discussed in this chapter relates to the chemical information available and nature of mathematical algorithms. Obtaining a good quality QSAR model depends on many factors, such as the quality of biological data and the choice of descriptors and statistical methods. As a consequence, the uncertainty of the QSAR-predictions is a combination of experimental uncertainties and model uncertainties (Computational chemistry: risk assessment for pharmaceutical and environmental chemicals, edited by Ekins S, WILEY Series on Technologies for the Pharmaceutical Industry, 2007). In this chapter we will consider the applications of QSAR models, and see how interactions are possible between different computational techniques, as well as in vivo and in vitro methods.

Keywords Alternatives to animal testing, Computational toxicology, In silico, In vitro, Predictive models, QSAR models, Regulation

Contents

1 Introduction

The requirements arising from the regulation and the need to better characterize the toxicological, eco-toxicological and environmental properties of an increasing number of chemicals have the consequence of an increased number of animal experiments, to provide answer to these data needs [1].

However, this request of more animal testing faces several issues. There is an ethical concern on the millions of animals used every year for experiments. These tests are also highly expensive. Thus, this poses questions about the costs for these experiments and the resources available to cover them. Many of these tests, especially those chronic, require a long time, years in some cases. The number of available laboratories in Europe to cover this potential request is insufficient.

For all these reasons, some European regulations foresee the use of methods alternative to animal testing, such as the REACH legislation [2], and actually the cosmetics directive [3] foresees the complete ban of animal tests for cosmetics by 2013.

Alternative tests can be divided into two categories: in vitro and in silico. In vitro methods refer to the fact that experiments are done in a tube, generally. In silico methods refer to the use of the computer to model a certain property of interest. Below, we will analyze these two categories, and which criteria can be used to choose a suitable methodology.

The term alternative includes "all procedures which can completely replace the need for animal experiments, reduce the number of animals required, or diminish the amount of distress or pain suffered by animals in meeting the essential needs of man and other animals." Its purpose is to promote the development and implementation of new methods to Replace, Reduce, Refine (the "3 Rs") animal testing with modern alternative approaches. Russell and Burch [4] proposed the framework of the 3 Rs more than 40 year ago. The authors proposed that all research using animals should be evaluated to see if the 3 Rs could be applied. Since that landmark publication, significant progress has been made, especially in the arena of regulatory testing [5].

An important point made by the ECVAM is that these three aspects should not be considered as alternatives that could replace each other, but as parts of an integrated system which should lead to progress in the development of non-animal tests and testing strategies.

Non-animal tests therefore comprise:

1. Maximizing the use of existing information, including the reasons for producing a chemical and its uses, as well as knowledge of its toxic hazard potential.
2. The use of data concerning the physicochemical properties of chemicals (e.g., stability, solubility, pH, octanol-water partition coefficient, and protein binding).
3. Predictions based on structure–activity relationships (SARs), including qualitative and quantitative mathematical models, and the use of read-across data from related chemicals.

4. The biokinetic modeling of physiological, pharmacological, and toxicological processes.
5. Experiments on lower organisms not classed as "protected animals" (bacteria, fungi, plants, invertebrate animals).
6. Studies on vertebrates at early stages of development (before they become protected animals).
7. Studies on in vitro systems of various kinds (including whole perfused organs, tissue slices, cell, tissue and organotypic cultures, and sub cellular fractions).
8. Human studies (including estimations of occupational and environmental exposure, epidemiological investigations, post-marketing surveillance for medicines, cosmetics and household and agricultural products, and the ethical and properly controlled use of human volunteers) [6].

1.1 In Vitro Tests

In the last 30 years, the use of in vitro tools for toxicological studies and evaluation has become relevant and the number of scientific works and techniques has increased day by day. One of the most important advantages of in vitro systems is their ability to serve as model for the central events in the in vivo toxicological process, and a depth evaluation of the intrinsic cellular toxicity can provide useful information for toxicological safety evaluation.

An in vitro toxicity system is made by three components:

- The biological models
- The endpoint and the method to measure it
- The protocol

The biological model consists of the biological systems which will be used and its specific culture conditions. Organ cultures, tissue slices, primary cells, cell lines, sub cellular organelles, macromolecular system and prokaryotic, fungi or plant culture are the most used biological components. The ability of the biological model to produce accurate, valid, and usable data for a possible in vivo extrapolation depends on the similarity of the same system with the cellular phenotype to model: for example, primary alveolar cells or lines derived from lung tumors are more relevant and suitable for inhalation toxicity studies comparing to intestinal cells.

Specific culture conditions are essential to ensure that the biological model maintains unchanged, as long as possible, its intrinsic characteristics in terms of biological response and cell function.

The endpoint is the final effect to be measured within the biological system after the exposure to chemicals. Referring to in vitro systems, it is generally a type of biological response such as the release of an enzyme, the activation of a pathway, changes in the cell cycle or death. The measurement of the endpoint allows defining the concentration–response relationship in the used system. The specificity of the endpoint is a fundamental key point to make a biological system more useful in obtaining relevant information on mechanistic basis of the chemical–cell interactions.

Also, the test procedure (protocol) is fundamental because it allows comparing results from different laboratories and from different experimental sets. Moreover, selected test protocol could affect the interpretation of the results, the information content and its application in the safety evaluation process, as stated by Frazer "if the biological system is exposed to a test chemical for 24 h and the endpoint assay is immediately conducted, the data produced would be most relevant to the acute toxicity of the test material. If, on the other hand, the system is exposed to material for 24 h and the system is cultured in the absence of the test material for additional 48 h before the endpoint assay is conducted, the data would be more relevant to recovery from toxicity rather than acute toxicity" [7].

Analyzing the use of models, it is possible to underline that in vitro systems are mainly used for research and for testing/screening of compounds. In the first case, these tools are employed to test hypothesis and the experimental model is chosen taking into account the nature of the hypothesis to be tested.

The final goal of models used for "testing" or "screening" is to verify whether a special condition or feature is present or not. In this case the model system should be selected a priori based on scientific consensus and the testing protocols must be standardized in order to obtain comparable values when the same test is performed by two different laboratories or operators. Moreover, the existence of standardized methodologies could be very useful for regulators which need a certain degree of reliability to make appropriated decisions.

This is the main difference between models for research and for testing but in some cases, especially in the environmental sector and in the screening of chemicals, it is very difficult to establish the dividing line between these two realities. According to Frazier, what is important is to verify the adequacy and the specificity of the model system to answer the posed question.

Focusing on testing purpose, it is possible to classify the models into three categories:

- Screens: used to obtain preliminary information sufficient to make limited management decisions.
- Adjuncts: are often integrated part of regulatory evaluation strategies, but usually the derived information is not sufficient to support a final safety decision.
- Replacements: are in vitro tests able to completely replace the use of in vivo toxicity test in a specific area of toxicity testing.

In vitro tools could be used alone or in test batteries. Multiple endpoint batteries increase the power of the evaluation because they provide information of different cellular functions. This information can be useful to investigate the mode of action of toxicity and to provide data regarding the mechanistic nature of the toxicological effects of the chemical [8].

In spite of the great effort and advances made on in vitro testing, we are still far to have alternative methods robust enough to cover developmental, neurotoxic, reproductive, or carcinogenic potential for the substances evaluated. However the use of some distinct approaches may cover a great part of the potential toxic effects of some environmental pollutants.

Focusing on validation process of in vitro methods, it is possible to underline some differences between tools for research and ones for toxicological testing. A research model is validated when there are some specific evidences confirming that the information from the model is able to correctly describe the process in the intact animal. Tools for toxicity testing are often used to evaluate safety hypothesis so they can be used without requiring in vivo confirmation. They are validated using a subset of well-known materials and, once validated, systems will be applied to new unknown materials or mixtures in order to evaluate their toxicity and compare their potential with other chemicals.

In both cases, the validation process could be divided into two components: reliability and relevance. Reliability (precision) is the ability of the method to obtain reproducible results between laboratories while relevance (accuracy) is defined by the comparison of the output from the applied method with the ones obtained using a "gold standard" test which works as a reference at international levels.

ECVAM as part of the JRC fulfills the task to validate alternative methods. Its advisory group ESAC advises ECVAM scientifically and gives expert judgment on the different proposed non-animal tests.

1.1.1 Advantages and Disadvantages of Using In Vitro Methods

The advantages of these methods are that they are generally short-term tests giving results in few hours or days, they require only small amount of chemical and space and they are generally cheap to run compared to in vivo experiments.

On the other hand, it is often very difficult to relate a response to a specific concentration because it is difficult to keep the concentration constant in such systems, for example in the presence of plastic materials and media with high content of other organic compounds. Moreover toxico-kinetics aspects such as distribution in different compartments are also lacking information in these models.

The disadvantages of these methods are that they only reflect part of what is going on inside the specific tissue or enzymatic process and thus do not take degradation in the whole organism into consideration or other processes that may influence the same process in an intact organism [9].

A survey of the regulatory status is given in Table 1, indicating those in vitro procedures that are accepted by EU, OECD [10], and/or the USA (based on http://www.ccac.ca; http://ecvam.jrc.ec.europa.eu/). However, there are methods that are scientifically validated reported by ECVAM, but still not properly accepted for regulatory purposes. This is the case of carcinogenicity (non-genotoxic, e.g., Three Cell Transformation Assays (CTA) using Syrian hamster embryo cells (SHE) and the BALB/c 3T3 mouse fibroblast cell line for in vitro carcinogenicity testing), monoclonal antibodies production, haematotoxicity and reproductive toxicity.

Table 1 In vitro procedures that are accepted by EU, OECD and/or the USA

Endpoint	Non-animal testing method	Validation/regulation
Acute aquatic toxicity	Fish acute toxicity – UTC-step-down approach	EU
	Fish embryo toxicity (FET) test	OECD – Assessing evaluation
Acute oral toxicity	Up-and-down procedure for acute oral toxicity testing	EU
	Acute toxic class method for acute oral toxicity testing	EU
	Fixed dose procedure for acute oral toxicity testing Fixed dose procedure for acute oral toxicity testing	EU
	Neutral red uptake (NRU) test with human cells	US
	Neutral red uptake (NRU) test with rodent cells	US
Eye irritation	Isolated chicken eye test	EU US
	The bovine corneal opacity and permeability (BCOP) and the isolated chicken eye (ICE) test methods for eye irritation	EU US
	Hen's egg test – chorioallantoic membrane (HET-CAM) test method	EU/US: not sufficiently validated
	Isolated rabbit eye (IRE) test method	EU/US: not sufficiently validated
	Slug mucosal irritation (SMI) assay	EU: is being evaluated
Chromosomal aberration	Micronucleus test as an alternative to the in vitro chromosome aberration assay for genotoxicity testing	EU; OECD
Genotoxicity	Bacterial reverse mutation test (Ames test)	OECD, US: Approved
	Saccharomyces cerevisiae gene mutation assay	OECD
	Saccharomyces cerevisiae mitotic recombination assay	OECD
	In vitro mammalian chromosome aberration test	OECD, US
	In vitro mammalian cell gene mutation test	OECD, US
	In vitro sister chromatid exchange (SCE) test	OECD
	In vitro unscheduled DNA synthesis (UDS) in mammalian cells test	OECD
Monoclonal antibody production	In vitro production of monoclonal antibodies	EU
Haematotoxicity	The colony forming unit-granulocyte/macrophage (CFU-GM) assay for predicting acute neutropenia in humans	EU

(continued)

Table 1 (continued)

Endpoint	Non-animal testing method	Validation/regulation
Phototoxicity	3T3 neutral red uptake (NRU) phototoxicity	EU, OECD
Pryrogenicity	Five in vitro pyrogen tests	EU, US
Reproductive and developmental toxicity	Embryonic stem cell test (EST) for embryotoxicity	EU
	Micromass (MM) embryotoxicity assay	
	Whole rat embryo embryotoxicity assay	
	Extended one-generation reproduction toxicity study	OECD: new test guideline
	Combined repeated dose toxicity study with the reproduction/developmental toxicity screening test	OECD
	Micromass embryotoxicity assay	EU
	Whole rat embryo embryotoxicity assay	EU
	Frog embryo teratogenesis assay – *Xenopus* (FETAX)	Not sufficiently validated
	EST-1000 method for skin corrosivity testing	EU
	SkinEthic™ human skin model for skin corrosivity testing	EU
	CORROSITEX assay for skin corrosivity	EU, US
Skin corrosion	EpiDerm™ skin corrosivity test	
	EPISKIN™ skin corrosivity test	EU, US
	Rat transcutaneous electrical resistance (TER) skin corrosivity test	EU, US
	Two in vitro skin irritation tests: EpiDerm SIT and SkinEthicTM RHE assay	EU
	Artificial skin models (EpiSkin®, EpiDerm®) for skin irritation testing	EU
	Reduced local lymph node assay (rLLNA) for skin sensitization	EU, US
Skin irritation	Local lymph node assay for skin sensitization (LLNA)	EU, US
	The relevance of the target-animal safety test for batch safety testing of vaccines for veterinary use	EU
Skin sensitization	ELISA test for batch potency testing of erysipelas vaccines	EU
	ELISA test for batch potency testing of tetanus vaccines for human use	EU
Vaccines	ELISA test for batch potency testing of tetanus vaccines for human use	EU

1.2 In Silico

The use of computational techniques to predict toxicity, or in silico approaches, aims to decrease costs and reduce animal suffering for chemical risk assessment.

These techniques may be coarsely classified into techniques that mimic human reasoning about toxicological phenomena (Expert Systems) and methods that derive predictions from a training set of experimentally determined data (Data Driven Systems).

Expert Systems attempt to formalize the knowledge of human experts, who assess the toxicity of a new compound, in a computer program [11].

This approach is intuitively appealing to most users, because it promises easy access to toxicological knowledge, and some of the most used predictive toxicology software tools are in fact Expert Systems [e.g., Derek Nexus (https://www.lhasalimited.org/) and Toxtree (http://toxtree.sourceforge.net/)].

Data Driven Systems are formalized methods for the extraction of prediction models directly from experimental data. These systems vary in sophistication from the relatively simplistic approach of forming chemical groupings (read-across and grouping) to the more complex development of SARs [Qualitative identification of chemical substructures with the potential of being reactive or toxic; the SAR model investigates the existence of a relationship between a certain chemical property, such as a fragment, and the effect, such as carcinogenic effect, without assigning a numerical continuous value to the toxicity (http://ecvam.jrc.it/; http://ecvam.jrc.ec.europa.eu/)] and QSARs (quantitative prediction of relative reactivity or toxicity) [12].

The non-testing method called read-across implies the use of endpoint information for one chemical, called a "source chemical," to make a prediction of the same endpoint for another chemical, called a "target chemical." The source and target chemicals are considered to be similar in some way, usually on the basis of structural similarity. It is assumed that, in general, similar compounds will exhibit similar biological activity. In principle, read-across can be applied to characterize physicochemical properties, fate, human health effects and ecotoxicity, and it may be performed in a qualitative or quantitative manner, depending on whether the data being used is categorical or numerical in nature [13, 14]. To estimate the properties of a given substance, read-across can be performed in a one-to-one manner (one analogue used to make the estimate) or in a many-to-one manner (two or more analogues used) (http://toxtree.sourceforge.net/).

The reliability of read-across depends on the selection of appropriate analogues associated with the availability of reliable experimental data. In some cases, it is only possible to identify a limited number of suitable analogues, whereas in other cases, it is possible to build up a larger and more robust chemical group, called a chemical category. A chemical category is a group of chemicals whose physicochemical and human health and/or environmental toxicological and/or environmental fate properties are likely to be similar or follow a regular pattern as a result of structural similarity (or other similarity characteristic). The presence of common behavior or coherent trends in the chemical category is generally associated with a common underlying mechanism of action. In general, the application of read-across between analogues in a chemical category is considered to be more reliable than the application of read-across in a smaller group of analogues (in which trends are not apparent) [15].

There are software that use more approaches for the prediction of toxicity; expert systems, QSAR, and read-across (http://www.insilico.eu/use-qsar.html).

Here we will address in particular QSAR, being more used. However, the idea is to extract the common criteria for all in silico methods.

1.2.1 QSAR, and SAR Models

QSAR means quantitative SAR. It is a model that relates the chemical structure to an activity. In the so-called SAR the quantitative aspect of the phenomenon is not addressed, and the study refers to categories, such as “toxic” and “non toxic.” In a certain way, this is a simplified version of the QSAR model. The expression QSAR sometimes covers both cases. If the modeled feature is a property, the expression QSPR is also used.

1.2.2 The Components of the QSAR Models

The basic hypothesis of a QSAR model is that the activity (or effect or property) can be put in relationship with the chemical, using some parameters to describe the chemical. Thus, the three main components of the QSAR model are: the activity to be modeled, the chemical information, and the way to establish a link between these two components. For this, we need some suitable ways to describe the chemical and a good mathematical algorithm.

Below we will analyze more in detail these three components of the QSAR model.

1.2.3 The Chemical Information

There are two main ways to describe a chemical compound: using global descriptors, or using specific fragments. Indeed, there are many QSAR models using global descriptors, but there are also a certain number of them using fragments. Furthermore, several models use both fragments and general descriptors.

Some simple global descriptors are: molecular weight, number of atoms present in a molecule (e.g., number of chlorine atoms), number of double bonds, etc. Other descriptors represent the ramification of the molecule. Certain descriptors take into consideration the electronic charge on a certain atom, or its polarity.

Another kind of descriptors is the so-called physicochemical ones. They include log P, lipophylicity, etc. Log P is the logarithm of the partition coefficient between octanol water. This descriptor has been used since the first QSAR models, and originally it was measured. Nowadays it is much more common to calculate it.

Nowadays there are thousands of molecular descriptors which have been proposed.

1.2.4 The Modeling Algorithms: Classifiers and Regression Models

In the last decades not only thousands of chemical descriptors but also many advanced, powerful modeling algorithms have been made available, The older QSAR models were linear equations with one or a few parameters. Then, other tools have been introduced, such as artificial neural network, fuzzy logic, and data mining algorithms, making possible non linear models and automatic generation of mathematical solutions.

We can distinguish the algorithms in two kinds: for the regressions and the classification. Regression methods get a continuous value. Classifiers find the category, for instance the toxicity class, of elements of a population.

Typically a QSAR model is built up starting with a set of chemicals with known property values.

In some cases, especially in case of genotoxicity models, the human expert identified fragments which can be related to the genotoxic effect. For instance, it is known that nitrosoamines are genotoxic. The visual examination of a series of chemicals sharing the same fragment may be used for this purpose. In this case the effect is simply the toxic effect (genotoxic or not, for instance), and the chemical information is simply the fragment. The algorithm is, in this case, the rule. Expert systems have been built up in this way. Examples of this kind of models are HazardExpert, Derek, and Toxtree.

More typically the process of building up the QSAR models requires more complex chemical information. For a set of compounds, with known property value, the descriptors are calculated. The process of model building proceeds through a reduction of the molecular descriptors, in order to indentify the most important ones. Then, using these selected chemical descriptors and a suitable algorithm, the model is developed. Finally, the model so obtained has to be validated.

On the basis of the QSAR models there are three components: the toxicity (or environmental) property of the chemicals, the chemical information associated with these chemicals, and the mathematical function which links these two components: the property and the chemical information.

Model development involves the use of chemical compounds with known toxicity levels, which are then used as the training set. This is a very important point since models can only be developed based on knowledge – and the bigger the database the better the model. The model is subsequently developed using chemical parameters and a suitable algorithm.

QSAR are rapidly evolving, for a series of advancements in the scientific field and expectations as alternative methods. Indeed, new information technology techniques have been introduced, and new ways to describe the chemical information, offering new perspective, on the one hand, and on the other regulations, such as REACH, call for the availability of robust models.

A few decades ago the range of chemical descriptors used was very limited. Let us take the example of Corwin Hansch's studies, in which he described the relationship between ecotoxicity and a series of parameters, including log P

(P = partition coefficient between octanol and water). On the basis of this model, toxicity could then be understood by quantifying uptake of the compound into the fish's body.

Over time other descriptors have been investigated in an attempt to better explain certain factors, such as chemical reactivity and molecular size. Nowadays thousands of chemical descriptors can be calculated and thousands of fragments can be obtained using other programs.

The growth in the number of chemical descriptors and fragments is also the result of the availability of more powerful modeling algorithms. The older QSAR models used linear equations with a very limited number of parameters, in general one or two. Multilinear regressions have now been developed, which offer the possibility of screening a high number of parameters. Non-linear models and the automatic generation of mathematical solutions have now been made possible by the emergence of other tools such as artificial neural network, fuzzy logic, and data mining algorithms.

1.2.5 Purposes in Predicting Models and Related Criteria

Regulatory models require not only powerful methods, but also certain characteristics related to the intended use, such as use of suitable values as input of the model, great consideration of the output of the model, which should fit into the format identified by the law, with given thresholds and uncertainty, depending on the use, and other features, such as transparency and reproducibility of the model.

The requirements for regulation may be different from those for other purposes. Academic applications of QSAR models are the most typical. Here no strict restrictions and needs exist, beyond the interests of the scientific community.

Models used within industry are also different. In this case, in most situations, confidential data are used, and the interest is to avoid false positive, i.e. the industry wants to avoid to make studies (and spend money) for chemicals which then result to be non active (false positives).

Regulatory QSAR models are more demanding because of their relationship with the law, which introduces requirements, some internal to the QSAR model process, others external. Internally the model needs a high level of quality control. Externally, the model has to comply with, and be suited for, the regulatory use.

1.2.6 Criteria for Evaluation of QSAR Models for Regulatory Purposes

Criteria which are suitable for regulatory purposes, to cope with a reduction of the risk complying with the EU regulations, the REACH legislation provides a good guidance on the requirements, since QSAR models are explicitly mentioned within the law, in Annex XI.

According to REACH, a (Q)SAR is valid if:

- The model is recognized scientifically valid.
- The substance is included in the applicability domain of the model.
- Results are adequate for classification and labeling and for risk assessment.
- Adequate documentation of the methods provided.

Let's discuss the first requirement, a criterion for us. We notice that it is not requested that the model is validated. Validation is a formal process, which takes many years. The formal validation process of a QSAR model would end after REACH probably.

Thus, according to REACH the validity has to be assessed through scientific criteria, considering the performance of the model in its results in prediction. Of particular interest is the check for the predictive performance of the model.

For regulatory purposes greater attention should be given to models which avoid false negatives. Thus, in the evaluation, preference should be given when the model has lower false negatives.

The fact that the model works, that is predictive, should be quite obvious. It is our opinion that this criterion should be applied to all in silico methods, not only QSAR, and actually to all alternative methods. The same applies to all criteria listed by REACH.

The second criterion is quite interesting. It requires demonstrating if the model, which fulfills the requirements for the model, is appropriate for the chemical it has been applied to. Thus, it is not enough to demonstrate that the model works. It is assumed that it does not work in all cases. Thus, a specific evaluation has to be done.

There are some chemometric (chemometrics is a statistical area which combines statistics and chemistry) tools which use the chemical descriptors and/or fragments of the chemicals used to build up the model, and compare if the chemical descriptors and/or fragments of the target chemical are similar. An example of this approach is given by the freely available software AMBIT. A major disadvantage of this approach is that it is based only on the chemical information.

Another recent tool has been developed within the ORCHESTRA project. The tool keeps into account both the chemometric information and the toxicity predictions done by the model, and in particular what kind of errors have been done by the model. It applies to the CAESAR QSAR models. Furthermore, this tool is based not only on the a priori data and information, as the other approaches, but also on the a posteriori result of the model. The user knows if the model can or cannot be used for a certain compound. In some cases a warning is given, recommending expert opinion. In all cases the reasons for the reliability is given, and it can be evaluated in a transparent way.

The third criterion is that the model should target an endpoint relevant for REACH. Only models that address the endpoints of interest for REACH are appropriate within this purpose. We notice that REACH mentions different purposes for the QSAR models: classification and labeling, is one possible target of the model, and risk assessment in another. In the first case models are classifiers; in the second case a regression more is more suitable. Indeed, in the first case the output of the model is a class, while in the second one it is a continuous value. A continuous value is necessary to get the ratio between the effect dose and the exposure level.

The fourth criterion asks to transparency. This is reasonable, since all documentation on the basis of the assessment of the properties of a chemical should be clearly available and checkable. One of the driving forces of REACH was to have the correct knowledge on the properties of the chemical substances on the market. If some of the information is hidden, this clearly goes against the spirit of REACH.

Besides the criteria, we may identify other criteria, which are related to the presence of desirable characteristics of the QSAR model.

QSAR models with a regulatory purpose should mimic the in vivo (and occasionally, in vitro) data, which are typically used in the context identified by the law. As a consequence it should be very much preferable that also the data on the basis of the QSAR models are experimental data suitable for the regulation. In any case, their quality should be very high, and a check should be done on it.

Furthermore, knowledge on the variability and uncertainty associated with each component of the model should be addressed, and described. For any risk assessment process, the uncertainty of the component is fundamental.

Another criterion is the model reproducibility. This refers in a certain extent to the uncertainty, which was mentioned before, relatively to the knowledge on the input parameters. Here we address the reproducibility of the final result.

Related to this is the easiness of the model. If we imagine a model which is complicated, and has several parameters to be chosen, we may easily get different results. Thus, ideally this is further criterion.

The clarity of the result should be another criterion. It may happen that the output of the model is of difficult interpretation.

The access to the model is another criterion. Some models are free, others very expensive.

The time necessary to get the results (speed of the model) is another desirable criterion.

Another useful feature is the possibility to run predictions in batch, in order to save time.

Other principles for the validation of QSAR models for regulatory purposes were edited by OECD in 2007 [8]. A good model must have:

- A defined endpoint
- An unambiguous algorithm
- A defined domain of applicability
- Appropriate measures of goodness-of-fit, robustness and predictivity
- A mechanistic interpretation

The definition of the endpoint is essential to understand what kind of experimental systems is being modeled by the in silico method.

The second principle is to ensure the transparency of the model, describing the algorithms used to generate predictions. This information is critical to evaluate the performance of the model. In the case of commercial models, the used algorithms are not always made publicly available but the model's reproducibility must be explained in the guidance material.

The description of the applicability domain is needed to express the limitations in terms of the types of chemicals; properties of mechanism can be generated by the model with an acceptable reliability.

The information about internal and external validation for the model is used to evaluate the performance of the in silico tool.

Regarding the last but not the least principle, it is recognized that it is not always possible to provide a mechanistic interpretation of a given QSAR model but the absence of this information does not preclude the use of the given model in the regulatory context.

OECD also provides a check list for the application of its principles in the context of QSAR validation. This checklist can be useful to help scientists and regulators during the selection of a QSAR model and to evaluate its robustness/validity [9].

2 Considerations on the Applicability of the Alternative Methods

Some important general considerations should be done, to clarify the context of the use of these alternative tools.

As it will be discussed later in this chapter, a number of regulatory initiatives exist, dedicated to the validation of the alternative methods. However, the REACH legislation clearly refers to "valid" QSAR methods, and not to "validated" methods. Explaining this argument, Annex XI of REACH states the "scientific validity" should be considered. Thus, for QSAR methods, which represent a major group of the in silico methods (other in silico methods are the docking methods, which are important for pharmaceutical industry and drug discovery, and will not be addressed here), it is important to underline that, according to legislation, the scientific validity is the key factor, and not a formal process of validation. According to REACH by now QSAR methods are applicable to the following tasks: to fulfill information requirements (use of predictions instead of test data), as part of the weight of evidence approach, to support category justification (use to justify structural and metabolic similarities) and for integrated testing strategies. Thus, we will adhere to this position. However several publications show the effective capacity of QSARs in the prediction of different endpoints, such as carcinogenicity [16].

The recent position of the USA is to take into consideration the scientific validity of the tool, and not necessarily the validation process. This is the philosophy adopted within the Tox21 (http://epa.gov/ncct/Tox21/) and ToxCast (http://www.epa.gov/ncct/toxcast/) initiatives. The reason for this is that the validation process takes 10 years or more before a method is officially approved, and this period would seriously limit the possibility to rapidly produce the necessary data needed within few years. Furthermore, the techniques are rapidly changing.

What we describe here is not necessarily the result of a formal validation process, but conversely we preferred to provide a list which is scientifically updated and may offer advanced, modern tools useful for stakeholders. However, for in vitro methods, the formal validation process should be followed.

A second important consideration refers to the applicability of these two different categories of approaches. QSAR methods have to be applied to individual chemicals. The QSAR approach can be profitably used coupled to a chemical analysis, exploiting the information on the contaminant occurrence. However, if the user wants to address a mixture of chemicals, the components of the mixture have to be addressed separately and individually. In case of unknown compounds, QSAR cannot be used.

3 Conclusions

It is expected that the alternative methods are going to be more and more used. The overall prospective is that these methods will offer possibilities addressing toxicity on a different angle compared to classical methods. Thus, they can also be integrated within a weight of evidence approach.

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A Revision of Current Models for Environmental and Human Health Impact and Risk Assessment for Application to Emerging Chemicals

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Abstract Nowadays, we are living in the global circular economy, where products are produced, used, and finally disposed in different parts of the world. These products have a huge amount of additives, that in many cases can be hazardous if they are not treated properly. The risk assessment of human health and the environment due to exposure to chemical additives is necessary.

In this chapter the risk assessment is briefly introduced. Risk assessment is divided into four steps: hazard identification, hazard characterization, exposure assessment, and risk characterization. This chapter also highlights five risk and life cycle impact assessment models (EUSES, USEtox, GLOBOX, SADA, and MAFRAM) that allows for assessment of risks to human health and the environment. In addition other 12 models were appointed. Finally, in the last section of this chapter, there is a compilation of useful data sources for risk assessment. The data source selection is essential to obtain high quality data. This source selection is divided into two parts. First, six frequently used databases for physicochemical

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and/or toxicological properties (TOXNET, eChemPortal, ATSDR, CPDB, IUCLID, and ECOTOX) are presented. Second, six estimation data tools are pointed. The estimation tools are useful when it is not possible to find data parameters to assess the risk, for example, in the case of emerging pollutants or new substances.

In conclusion, there is no risk assessment model better than another. All models have their strengths and weaknesses. Many of them are focused on one particular aspect such as a single environmental compartment or in a kind of pollutant. It is important to remark that the selection of the data source is essential to obtain quality results.

Keywords Environmental and risk assessment models, Life-cycle Impact assessment models, Physicochemical and toxicological database

Contents

1 Introduction

Currently, in the global economy, products are manufactured in one part of the world, used in another part and there is little knowledge about where these products will be disposed of. Most consumer products contain a large variety of chemical additives, in many cases, new substances, since they are poorly studied. This together with the lack of knowledge about the additives used, cause concern about the impact of these additives on human health and the environment.

These additives may come into contact with humans and the environment not only during the use of the product but also through their life cycle: during the

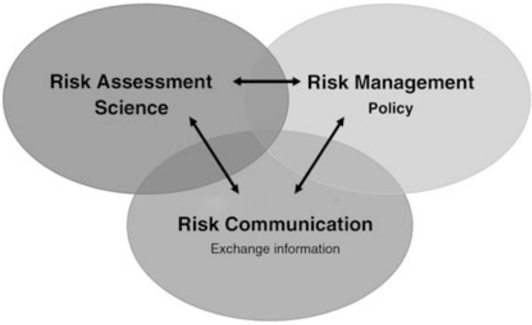

Fig. 1 Risk analysis structure (adapted from FAO [2])

production of the additive, during the manufacture of consumer product where the additives are used, and during the product's end of life treatment. As discussed in the previous chapter (see [4]), the emissions of the additives in a given environmental compartment are distributed to others. Therefore, the human population is not only exposed directly to these additives by the use of products but also indirectly through the environment. Moreover, these substances can also enter into the food chain and accumulate in fish, animals, crops, fruits, and vegetables where they could later be ingested by humans.

Due to this, it is necessary to assess the risk to human health and the environment due to the exposure to these chemical additives. In this chapter the impacts that a substance can cause to a certain receptor (humans and the environment) and the harms to the receptor at different exposure levels are identified in hazard identification and hazard characterization steps, respectively. Exposure assessment takes into account the amount, frequency, and duration of the exposure to the substance. Finally, risk characterization evaluates the increased risk caused by such exposure to the exposed population.

This chapter also highlights a selected number of models that allow for assessment of risks to human health and the environment. Finally, in the last section of this chapter, there is a compilation of useful data sources for risk assessment.

2 Risk Assessment

Risk analysis is defined as a process for controlling situations where a target could be exposed to a hazard [1]. It consists of three parts: risk assessment, risk management, and risk communication (Fig. 1). Risk communication is the exchange of information about risks between risk assessors, public managers, policy makers, interested groups, and the general population. Risk management is related to decision-making processes involving considerations of political, social, economic, and technical factors with relevant risk assessment information.

The organization for economic co-operation and development (OECD) defines risk assessment as the process intended to calculate or estimate the probability, including the identification of attendant uncertainties, of an adverse effect in an organism, system, or (sub) population caused under specified circumstances by exposure to an agent, taking into account the inherent characteristics of the agent of concern as well as the characteristics of the specific target system [1]. According to this definition the risk assessment process consists of four steps:

1. Hazard identification consists in identifying the type and nature of adverse effects caused by the agent in the receptor (target organism, system, or (sub) population).
2. Hazard characterization (or dose–response assessment) is the qualitative and, as far as possible, quantitative description of the inherent properties of an agent or situation having the potential to cause adverse effects. This step should include a dose–response assessment that describes the severity of adverse effects (the responses) related to the amount and condition of exposure to an agent (the dose).
3. Exposure assessment is the process of predicting or estimating the concentration or amount of an agent, the frequency, and the duration that reaches the receptor.
4. Risk characterization is the determination, qualitative and as far as possible quantitative, of the probability of occurrence of adverse effects in a given target, under the predicted or estimated exposure conditions.

In the following two sections, a deeper explanation of human health and environmental risk assessment is given.

3 Human Health Risk Assessment

3.1 Hazard Identification

The goal of the hazard identification is to identify the effects of substance to environment or human health.

A substance can cause one or more effects. Common effects are acute and long-term toxicity, skin irritation, corrosiveness, sensitization, mutagenicity, carcinogenicity, reproductive effects, and developmental toxicity.

3.2 Hazard Characterization

Hazard characterization is the estimation of the relationship between the dose of a substance and the effects observed. To evaluate this relationship, the following studies can be performed (in order of reliability):

- Human studies including case reports, epidemiological studies, and, in some cases, direct human studies (with volunteers). The advantages of these studies are that toxic effects are evaluated in humans and no interspecies extrapolation is needed. However, the subjects of these studies are exposed to an uncontrolled environment that may interfere with the results.

- Animal toxicological and in vitro studies. In animal or in vitro studies the system is more controlled than in human studies, the external influences are minimized (more in in vitro than in animal tests). However, in both cases, an extrapolation is required: interspecies in the case of animal studies and at least from system to organism extrapolation in the case of in vitro test.
- Qualitative structure–activity relationship (QSAR) methods (see Sect. 5.2).

For the two aforementioned steps, hazard identification and hazard characterization, data adequacy is of high importance. The data adequacy is defined by the reliability and the relevance of the data for human risk assessment [3].

3.3 *Exposure Assessment*

Exposure assessment is one of the most important steps in risk assessment. It is the process that predicts or estimates the amount of the substance under study that reaches the human body. To assess the exposure, it is necessary to define in detail the exposure pathway, the route of exposure, the concentration of the pollutant in the particular media, the contact rate, the frequency of exposure, and the population exposed (age, gender, and vulnerable population, among others). A general equation (Eq. 1) to determine the exposure dose is as follows:

$$\text{Dose} \equiv \frac{\text{Concentration} \times \text{Contact\_Rate} \times \text{Frequency}}{\text{Body\_weight}} \tag{1}$$

3.3.1 Exposure Routes

Exposure pathway describes how the substances enter into the human body. All possible pathways are not considered for all substances and emission scenarios, only the ones that are relevant for a specific substance and emission scenario are included. For example in the case of substances that are not present in the air, the inhalation route is not taken into account.

The most common routes of exposure are:

- Inhalation, of air and particles.
- Ingestion, of soil, dust, food, and drinking water.
- Dermal contact: absorption through the skin.
- Other common routes of exposition could be percutaneous, in the case that the substance enters into the body through a wound in the skin, or intravenous in the case of direct injection into the bloodstream.

3.3.2 The Need of Realistic Scenarios for Exposure Evaluation

For human health risk assessment, it is necessary to elaborate realistic scenarios. Knowledge of real scenarios where the contaminant is emitted to the environment will help to obtain information about the fate and transport of the contaminant once emitted to the environment and the route of exposure for the human beings living in this scenario of concern. There are different types of exposure, i.e., direct, indirect (as is the case of food contaminated by the air, water, or soil contaminated by the emission), occupational exposure, and consumer goods coming from outside the scenario of concern. Depending on the objective of the study, it will be necessary to consider in the exposure assessment one or more types of exposure.

In each context, it is essential to define suitable parameters of the exposure scenario for a realistic risk assessment:

- Environmental exposure (direct). Exposure through air inhalation, soil and dust ingestion, and dermal contact of soil and dust are the principal exposure pathways. Other exposure pathways (e.g., water dermal contact) can be taken into account in some scenarios. Monitoring campaigns or multimedia fate models are used to assess the exposure (see [4]).
- Food and water ingestion (dietary exposition). To assess the dietary exposure, ingestion rates of the different food products and water are needed. Multimedia fate models or food sampling campaigns are the main ways to determine the concentration of substances in food products and water at the specific scenario. These models consider cattle, meat, milk, fish, crops, and drinking water, among others.
- Occupational exposure (work place exposure). Exposure may occur as a singular event, a repetition singular event, or as continuous exposure during the work time. Exposure can be through inhalation, ingestion, or dermal contact. Every workplace has its characteristics, therefore information have to be collected about the substances, duration of exposure, and frequencies of exposure, among others. One aspect to be considered in the exposure assessment at work is whether or not workers are using personal protective equipment. Exposure models and monitoring of contaminants in the workplace are the two most widely used tools for exposure assessment. Biological monitoring (e.g.. blood, hair, breast milk) of the workers can give additional information on the occupational exposure to a substance.
- Consumer goods (nondietary). The consumer is a member of the general population, who may be exposed to (a new or existing) substance by using consumer products. The examples are almost endless, exposure to solvents used in adhesives, paints, and furniture, substances that can be released from a consumer product, the exposure to substances used for cleaning and decoration of houses, exposure to raw materials of cosmetics, etc. The wide range of cases makes it impossible to generalize a scenario. Substance data quality (amount in products, exposure pathway) and the consumer goods (frequency and duration of use, users of that product) are essential to build a realistic exposure scenario.

3.4 Risk Characterization

The last step in risk assessment is the risk characterization where the probability and the severity of adverse health effects in the exposed population are assessed.

3.4.1 Noncarcinogenic Risk

In the case of noncarcinogenic substances, there exists a threshold; this is an exposure with a dose below which there would not be adverse effect on the population that is exposed. This is the reference dose (RfD), and it is defined as the daily exposure of a human population without appreciable effects during a lifetime. The RfD value is calculated by dividing the no observed effect level (NOEL) by uncertainty factors. When NOEL is unknown, the lowest observed effect level (LOEL) is used. NOEL and LOEL are usually obtained in animal studies. The main uncertainty factor, usually tenfold, used to calculate the RfD are the following: the variations in interspecies (from animal test to human), presence of sensitive individuals (child and old people), extrapolation from subchronic to chronic, and the use of LOEL instead of NOEL. Noncancer risk is assessed through the comparison of the dose exposed calculated in the exposure assessment and the RfD. The quotient between both, called in some studies as hazard quotient, is commonly calculated (Eq. 2). According to this equation, population with quotient >1 will be at risk to develop some specific effect related to the contaminant of concern.

$$\mathrm{Risk}_{\mathrm{noncancer}} = \frac{\mathrm{Dose}}{\mathrm{RfD}}. \tag{2}$$

3.4.2 Carcinogenic Risk

There is some controversy regarding the carcinogenic effects [5]. There exist two main points of view that define the carcinogenic risk characterization. The first one considers that there is no threshold dose in the carcinogenic substances due to exposure at any level of the substance that may have a probability to cause adverse effects (tumoral cell) [5]. The second point of view suggests that the human body can detoxify a carcinogenic substance in low doses and in consequence, a threshold exists for that carcinogenic substance. To protect the human health, the no-threshold approach is commonly chosen. Different mathematical models are used (linear in low dose model, nonlinear models, and multiextrapolation models). In the low-dose region, the equation (Eq. 3) is used to assess the risk, where SF is the slope factor, a toxicity value for evaluating the probability of an individual developing cancer from exposure to contaminant levels over a lifetime:

$$\mathrm{Risk}_{\mathrm{cancer}} = \mathrm{Dose} \times \mathrm{SF}. \tag{3}$$

4 Environmental Risk Assessment

The hazard identification and hazard characterization steps that some methodologies define as a single step as “Effect assessment,” estimate the predicted no effect concentration (PNEC) in each environmental compartment. PNEC, that means the concentration below which an adverse effect will most likely not occur, is usually calculated on the basis of results of laboratory monospecies test. The PNEC is calculated by dividing the lowest value of toxicity test L(E)C50 (short term) or no observed effect concentration (NOEC) (long term) by an assessment factor. The assessment factor represents the uncertainty in: the variability in intra- and interspecies, the short to long toxicity extrapolation, and the extrapolation of the laboratory toxicity test for a limited number of species to a real environment. The assessment factor depends on the number of species tested and the trophic levels selected, the quality of data, and the duration of the test (short or long term). For example, in the European Commission Technical Guidance Document on Risk Assessment [3], an assessment factor of 1,000 is used to calculate aquatic PNEC if a minimum of one short term L(E)C50 for each of the three trophic levels is known. On the other hand, an assessment factor of 10 is used if long-term NOECs are known for at least three species representing the three trophic levels.

Exposure assessment using monitoring data or fate and transport models calculate the predicted environmental concentration (PEC) in each environmental compartment. More information can be obtained from Suciu et al. [4].

Finally, in the risk characterization step, the PEC/PNEC quotient that defines the risk of the substance in the environment is calculated. If the quotient (PEC/PNEC) is less than 1, the substance do not present risk to the environment. More information is available in the European Commission “Technical Guidance Document on Risk Assessment” [3] and in the United States Environmental Protection Agency’s “Guidelines for Ecological Risk Assessment” [6].

5 Models

There are many models for assessing risks to human health and/or the environment. Some of them are multimedia models, which assess the exposure and risks in different environmental matrices, such as soil, air, water, and food chains with different degrees of complexity within each medium. Conversely, others are more specific with regard to a medium or a system (e.g., river or food chain). Other models assess only human health risks or environmental risks, while some assess both risks. Based on the type of scenario that is studied, an appropriate model will be chosen.

Table 1 Differences in the principles of assessing the potential for ecotoxicological and toxicological effects in risk assessment vs. life cycle impact assessment (based on Olsen et al. [7])

Risk assessment (RA)	Life cycle impact assessment (LCIA)
Absolute assessment	Relative assessment due to the use of a functional unit
Chemical-oriented	Product-oriented
For specific circumstances of use or environmental recipients	For products during their entire life cycles
Typically carried out by or for the authorities	Its use is controlled primarily by the needs of the companies
The result expresses a verifiable risk of effect	The result is a relative environmental impact potential that cannot be verified
Tiered approach; a conservative assessment of, particularly, the exposure can be used in the preliminary steps	A conservative assessment is unwanted; a true measure of the environmental impact is aimed

Apart from the risk assessment models, there exist models for assessing impacts to human health and the environment in LCA. Both tools [risk assessment and life cycle impact assessment (LCIA)] have different purposes and aims that are summarized in Table 1 [7].

Despite the fact that there exist some differences between both methodologies, the cooperation between the aforementioned tools seems to be advantageous to use in environmental management [7]. Moreover, there are also steps in LCIA that also exist in the risk assessment (i.e., exposure assessment). Therefore, models used in LCIA can be used also to assess human or environmental exposure to chemicals. For that reason LCIA models are also included in the review of models of risk assessment.

Following, a brief summary of selected models currently used is showed.

5.1 European Union System for the Evaluation of Substances

The European Union System for the Evaluation of Substances (EUSES) [8] is the software provided by European Chemical Bureau (ECB) to implement the EU Technical Guidance Documents on Risk Assessment for new notified substances, existing substances, and biocides [3]. The development of EUSES 2.1 was commissioned by the European Commission to the National Institute of Public Health and the Environment (RIVM) of the Netherlands. The work was supervised by an EU working group comprised of representatives of the JRC-European Chemicals Bureau, EU Member States, and the European chemical industry.

The EUSES environment is represented as a set of nested scales. The local scale is nested into the regional scale which is nested in the continental scale. The continental scale is nested into the moderate climate zone, which has two adjacent zones, an arctic and a tropic zone, respectively. All the scales are divided into boxes (environmental compartments). The boxes of all scales include at least air, soil, water, and sediment compartments.

The human and environmental protection goals in EUSES are: human populations (workers, consumers, and man exposed via the environment) and ecological systems (micro-organisms in sewage treatment systems, aquatic ecosystems, terrestrial ecosystems, sediment ecosystems, and predators). Repeated dose toxicity, fertility toxicity, maternal toxicity, developmental toxicity, carcinogenic risk, and lifetime cancer risk can be calculated for the cases that literature data is available.

The risk characterization procedure will result in a quantitative comparison per substance of the outcome of the exposure assessment and of the effects assessment. This comparison is made through the ratio PEC/PNEC. The generic name for PEC/PNEC in EUSES is risk characterization ratio (RCR). Other ratios are used in EUSES for the risk characterization such as the margin of safety (MOS) or the ratio of the estimated no-effect or effect level parameter to the estimated exposure level for human subpopulations and the acceptable operator exposure level (AOEL).

The exposure assessment in EUSES aims at “reasonable worst-case,” i.e., the exposure scenario was the worst scenario without being unrealistic and as much as possible using mean, median, or typical parameter values. If the outcome of the “reasonable worst-case” risk characterization indicates that the substance is “not of concern,” the risk assessment for that substance can be stopped with regard to the scenario considered.

5.2 USEtox™

In 2005, a comprehensive comparison of LCIA toxicity characterization models was initiated by the United Nations Environment Program (UNEP) and the Society for Environmental Toxicology and Chemistry (SETAC) in their life cycle initiative. The main objectives of this effort were to [9] (1) identify specific sources of differences between the models’ results and structure; (2) detect the indispensable model components; and (3) build a scientific consensus model from them, representing recommended practice.

An extensive comparison of the most obvious positive and negative aspects from seven evaluation models (ECOSENSE, EDIP, USES-LCA, CalTOX, BETR, IMPACT 2002+, and WATSON) led to the development of USEtox, a scientific consensus environmental model for characterization of human and ecotoxicological impacts in LCIA that contains only the most influential model elements. USEtox was developed following a set of principles, including [9]:

- Parsimony: as simple as possible, as complex as necessary.
- Mimetic: not differing more from the original models than these differ among themselves.
- Evaluated: providing a repository of knowledge through evaluation against a broad set of existing models.
- Transparent: being well-documented, including the reasoning for model choices.

USEtox calculates characterization factors for human toxicity and freshwater ecotoxicity. Assessing the toxicological effects of a chemical emitted into the environment implies a cause–effect chain that links emissions to impacts through three steps: environmental fate, exposure, and effects. Linking these steps, a systematic framework for toxic impacts modeling based on matrix algebra was developed to some extent within the OMNIITOX project [10]. USEtox covers two spatial scales, the continental and the global scales.

According to the creators, USEtox provides a parsimonious and transparent tool for human health and ecosystem characterization factor (CF) estimates. It has been carefully constructed as well as evaluated via comparison with other models and falls within the range of their results while being less complex.

5.3 GLOBOX

GLOBOX [11] is a spatially differentiated multimedia fate, exposure, and effect model. It is used for the calculation of spatially differentiated LCA characterization factors on a global scale. It can also be used for human and environmental risk assessment. The GLOBOX is based on the EUSES 2.0 model. It has primarily been constructed for the calculation of spatially differentiated LCA characterization factors on a global scale. In comparison with the EUSES model, the GLOBOX has a higher level of spatial differentiation, in such a way that the GLOBOX is spatially differentiated with respect to fate and human intake on the level of separated but interconnected countries and oceans/seas. The main goal of the GLOBOX is to construct location-specific characterization factors for any emissions at any locations over the world, considering summed impacts of such emissions in different countries and seas/oceans. The GLOBOX model consists of the following three main modules: an impact-category independent fate module, a human-intake module, and an effect module.

Twelve distribution compartments are distinguished: air, rivers, freshwater lakes, freshwater lake sediments, salt lakes, salt lake sediments, natural, agricultural and urban soil, groundwater, sea water, and sea water sediments. In contrast to the EUSES model, where different nested scales (one inside the other) are considered, the GLOBOX is a system of interconnected regions at the same level in the model.

5.4 Spatial Analysis and Decision Assistance

Spatial Analysis and Decision Assistance (SADA) [12] is a free software, developed at the Institute for Environmental Modelling at the University of Tennessee. SADA incorporates tools from environmental assessment fields into an effective problem-solving software. These tools include integrated modules for human health risk assessment and ecological risk assessment and also geographical information system (GIS), visualization, geospatial analysis, statistical analysis, cost/benefit analysis, sampling design, and decision analysis.

SADA provides a full human health risk assessment module and associated databases. The risk models follow the USEPA's Risk Assessment Guidance for Superfund (RAGS) and can be customized to fit site-specific exposure conditions. It calculates risks based on the following exposure pathways: ingestion, inhalation, dermal contact, food consumption, and also a combined exposure.

The ecological risk module allows users to perform benchmark screenings for surface water, sediment, soil, and biota. Accompanying the ecological risk module is a database of benchmarks and other information that are supported and updated on the SADA web site. Benchmarks are adjusted for site-specific physical parameters as appropriate.

5.5 Multimedia Agricultural Fate and Risk Assessment Model

Multimedia Agricultural Fate and Risk Assessment Model (MAFRAM) [13] is a comparing and ranking method for new and existing nonvolatile organic compounds (NVOCs) used in agricultural activities. MAFRAM was intended to compare and establish the general features of NVOCs behavior and assess the ecotoxicological risk to the ecosystem.

MAFRAM divides the agricultural environment into two main zones, which are the on- and off-farm zones. Six compartments (air, water, soil, sediment, aboveground plants, and roots) are included in on- and off-farm zones. The MAFRAM output includes the intercompartmental transport and transfer rates, the primary loss mechanisms, chemical concentration, amount, residence time, and the rank of risk in each compartment.

Table 2 Models used in human health and/or environmental risk assessment

Model	Description	Ref
BREEZE® Risk Analyst	Human health and ecological risk assessment modeling system designed to conduct multipathway human health risk assessments and food-web based ecological risk assessment modeling. BREEZE risk analyst combines databases, GIS functionality, fate, transport, and exposure modeling equations into one software application	[14]
IRAP-h View™	Interface for conducting a comprehensive multipathway human health risk assessment. It simultaneously calculates risk values for multiple chemicals, from multiple sources, at multiple exposure locations. IRAP-h view implements the US EPA – OSW Human Health Risk Assessment Protocol (HHRAP) US EPA [15]	[16]
Eco Risk View™	An advanced ecological risk assessment program for conducting a comprehensive multipathway ecological risk assessment by simultaneously calculating risk values for multiple chemicals, from multiple sources, at multiple exposure locations. EcoRisk view fully implements US EPA guidance for evaluating ecological risks [17]	[16]
EcoFate	EcoFate is a software package for conducting ecosystem based environmental and ecological risk assessments of chemical emissions by point and non-point sources in freshwater and marine aquatic ecosystems, including lakes, rivers and marine inlets	[18]
RISC5	RISC5 is a software package for performing fate and transport modeling, human health risk assessments and ecological risk assessments for contaminated sites. Fate and transport models are available in RISC5 to estimate receptor point concentrations in groundwater and indoor and outdoor air. It can be used to estimate the potential for adverse human health impacts (both carcinogenic and noncarcinogenic) from up to nine exposure pathways	[19]
Ecolego	Ecolego is a powerful and flexible software tool for creating dynamic models and performing deterministic or probabilistic simulations. Ecolego can be used for conducting risk assessments of complex dynamic systems evolving over time with any number of species. Ecolego has specialized databases and other add-ons designed for the field of radiological risk assessment	[20]
@RISK	@RISK performs risk analysis using Monte Carlo simulation to conduct sensitivity and uncertainty analyses	[21]
API-DSS	Exposure and Risk Assessment Decision Support System Software. Estimates human exposure and risk from sites contaminated with petroleum products	[22]
XtraFood	Xenobiotics transfer in the primary FOOD Chain model calculates transfer of contaminants in the primary food chain. This model describes the whole chain from immission of contaminants at the farm level over concentrations in food to human exposure. The model focuses on the terrestrial food chain	[23]
RISKAT	RISKAT assesses the risks to populations in the vicinity of plants processing and storing toxic and flammable materials	[24]
CHARM	CHARM is used to carry out environmental risk assessments of discharges of exploration and production of chemicals, from platforms into the marine environment	[25]
Impact 2002	This model provides close to 1,000 characterization factors for the midpoint categories human toxicity, aquatic ecotoxicity, and terrestrial ecotoxicity according to the LCIA methodology. The model is parameterized in a nonspatial and a spatial European model nested in a nonspatial world model, as well as a complete world model	[26]

5.6 Other Models

In addition to the models presented above, there are a number of other risk assessment models available. Table 2 briefly presents some of these models that can be used to assess the risk of human health and the environment.

6 Data Sources

In order to run these models, it is necessary to have input data, mainly physicochemical properties and toxicological data (for both human and ecosystems), which can be extracted from different information sources. The source selection is essential to obtain data of high quality. In some cases (e.g., emerging pollutants) there is a lack of physicochemical and toxicological data which makes it necessary to use tools such as QSARs.

6.1 Data Bases

Currently, there are many databases where the physicochemical, toxicological parameters required to perform a risk assessment can be obtained. It must be borne in mind that the existence of a quality control parameters included in the databases is of great importance. This quality control can be accomplished through periodic updating of the database, the inclusion of bibliographical references of the origin of each parameter, peer reviewed bibliography, etc.

In Table 3, a selection of physicochemical and toxicological databases is shown. These databases are selected according to the existence of quality controls and their free online availability.

6.2 Estimation Data Tools

Despite the existence of several databases for certain substances, it is not possible to find physicochemical and/or toxicological parameters to assess the risk for all substances. The lack of data is one of the main problems in risk assessment. This is especially true for emerging pollutants. One solution to solve this problem is the use of QSAR or estimation tools. QSAR models correlate the structure of the substance with their activities (physicochemical properties, environmental fate, and/or toxicological properties).

Table 3 Physicochemical and toxicological databases

Database	Description
TOXNET	The Toxicology Data Network is a cluster of databases covering toxicology, hazardous chemicals, environmental health, and related areas published by the United States Library of Medicine. The TOXNET includes, among others, toxicological databases such as Chemical Carcinogenesis Research Information System (CCRIS), Hazardous Substances Data Bank (HSDB), Integrated Risk Information System (IRIS), International Toxicity Estimates for Risk (ITER), and ChemIDplus
eChemPortal	eChemPortal is a global portal for information regarding chemical substances. It allows simultaneous searching of reports and datasets by chemical name, CAS number, or by chemical property. Direct links to collections of chemical hazard and risk information prepared for government chemical review programs at national, regional, and international levels are obtained. Classification results according to national/regional hazard classification schemes or to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) are provided when available
ATDSR	The Agency for Toxic Substances and Disease Registry produces the “toxic substances profile” for hazardous substances found in National Priority List (NPL) sites. These hazardous substances are ranked based on the frequency of occurrence at NPL sites, toxicity, and potential for human exposure
CPDB	The Carcinogenic Potency Database contains the results of 6,540 chronic, long-term animal cancer tests on 1,547 chemicals. The CPDB provides easy access to the bioassay literature, with qualitative and quantitative analyses of both positive and negative experiments that have been published over the past 50 years in the general literature through 2001 and by the National Cancer Institute/National Toxicology Program through 2004
IUCLID	The International Uniform Chemical Information Database is a software application to capture, store, maintain, and exchange data on intrinsic and hazard properties of chemical substances
ECOTOX	The ECOTOX is a database of single chemical toxicity data for aquatic life, terrestrial plants, and wildlife

A selection of the most relevant physicochemical and toxicological estimation tools, which are freely available, are presented below in Table 4.

7 Conclusions

In this chapter human health and environmental risk assessment steps were introduced. Five models (EUSES, USEtox, GLOBOX, SADA, and MAFRAM) risk and LCIA models were briefly described and also other 12 models were appointed. There is no risk assessment model better than another. All models have their strengths and weaknesses and many of them also are focused on one

Table 4 Most relevant QSAR tools to estimate physicochemical and toxicological properties

Tool	Description	Ref
EPI Suite v4.0	EPIsuite estimate among other K_{ow}, K_{oc}, K_{oa}, Henry's Law constant, melting and boiling points, aerobic and anaerobic biodegradability of organic chemicals, biodegradation of half-life of hydrocarbons, and bioconcentration factors	[27]
Danish (Q)SAR Database	The Danish (Q)SAR database is a repository of estimates from over 70 (Q)SAR models for 166,072 chemicals. The (Q)SAR models encompass endpoints for physicochemical properties, fate, ecotoxicity, absorption, metabolism, and toxicity	[28]
TEST	TEST allows for estimates of the value for several toxicity endpoints: 96 h *Fathead minnow* LC50, 48 h *Daphnia magna* LC50, 48 h *Tetrahymena pyriformis* IGC50, Oral rat LD50, bioaccumulation factor, developmental toxicity, and Ames mutagenicity. TEST also estimates several physical properties	[29]
CAESAR	Five endpoints with high relevance for REACH have been addressed within CAESAR: bioconcentration factor, skin sensitization, carcinogenicity, mutagenicity, and developmental toxicity	[30]
ECOSAR	Chemical's acute (short term) toxicity and chronic (long term or delayed) toxicity to aquatic organisms, aquatic invertebrates, and aquatic plants are estimated	[31]
OECD QSAR Toolbox	It is developed by OECD to make (Q)SAR technology readily accessible, transparent, and less demanding in terms of infrastructure costs. The toolbox has multiple functionalities allowing the user to perform a number of operations. The toolbox potentially covers all relevant regulatory endpoints	[32]

particular aspect such as a single environmental compartment or focused in a kind of pollutants. Finally, freely and on line available data sources (databases and estimation data tools) were reviewed. The selection of the data source and, in some cases the scarcity of data are an important issue to obtain quality results.

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Are Chemicals in Products Good or Bad for the Society? – An Economic Perspective

Stefan Åström, Maria Lindblad, Jenny Westerdahl, and Tomas Rydberg

Abstract Humans have introduced a large number of chemical substances into products over the past century. We use the chemicals since they provide utility for the product itself, and thereby for the society. However, since many chemicals are toxic and harmful for both the environment and human health, and as they are emitted from the products during its lifecycle, the social benefits of using them are reduced. According to standard economic theory, the value of the product is equal to its price. However, in most cases the full cost of a product is rarely shown in the price of the product. Even though the product is being purchased by an individual or a company, the impact of the product will affect other than the buyer of the product. There are also unknown impacts that can affect both the buyer and the producer of the product or a third party. These impacts are in economic terminology often summarized as "externalities" (external impacts). External impacts might be negative or positive. Also, they can come in many different shapes. They are external because the affected party does not receive any compensation and the polluter does not need to pay without being obliged. This chapter gives a fast version of environmental economics needed for understanding of the topic and discusses different socio-economic aspects related to chemicals in products with the aim to give an overview of the subject.

Keywords Environmental economics, Cost-benefit analysis, Chemical additives

Contents

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1 Introduction

Studies in environmental economics and economic valuation often produce results that can appear slightly difficult to accept for the layman (and experts).

As examples, economists have calculated the welfare loss induced by a premature death to some ~€1 million (central estimate) [1, 2]. The welfare loss caused by a mild cough is estimated to some €38 [2], and the loss of an IQ point is valuated to some €3,000–15,000 [3, 4]. The ecosystem services provided by a French forest provide welfare benefits corresponding to some €970 per hectare [5].

Some cost–benefit analysis (CBA) performed on climate change reach an optimal level of CO_2 concentration in the atmosphere of 650–700 parts per million (ppm) within a century or two (Weitzman 2009). Furthermore, the whole concept of assigning monetary values to the above mentioned is for many persons morally upsetting.

The aim of this chapter is to give the reader a setting (or back drop) to the moral and theoretical pre-conditions necessary to understand and accept before assigning monetary values to welfare impacts. After reading this chapter, the reader should at least understand *how*, from a philosophical, theoretical and practical point of view, monetary values of welfare effects can be produced by economists. Monetary values of welfare effects are crucial for economic planning and the allocation of economic resources, and the values are being used as decision support when planning for inter alia health services, infrastructure developments and environmental improvements.

However, in this chapter it is not specifically aimed for the reader to *accept* the concept of monetization of welfare effects. Acceptance or rejection is for the reader to decide.

2 Background Economic Theory Related to External Effects

Damages to human health and the environment are by economists most often considered as market failures since they are external costs not included in the price when a transaction is taking place on the market. If the damage were to be fully financially compensated in the transaction, the damage would not be an external cost and the market would function properly. A properly functioning market implies that there is no problem to be solved (from the point of view of an economist). “Externalities” is the term used by economists when exploring non-priced effects of transactions [6].

The text above is likely to be a bit unfamiliar to the reader, and to explain the economic way of thinking we will start from the very beginning.

The economy is in principle inhabited by *sellers* and *buyers*. These buy and sell on a *market*. They are all utilitarian, which basically means that a moral good is to maximize pleasure/happiness. A moral bad is to minimize pleasure/happiness [7, 8]. When related to economic and political decision making, pleasure/happiness is often translated into “utility” [9]. So what is the decision rationale for the *buyer* and *seller*? And how does *the market* function?

2.1 The Buyer: Homo Economicus

In the standard neoclassical economic theory, individuals are following a utilitarian ethical norm and are making decisions as if they are economically rational.

To be a utilitarian implies in the economic area that individual decisions are being made so as to provide as much utility for the individual as possible. The idea is then that the sum of utility-maximizing individuals leads to a maximum welfare for society. The overall idea is that the sum of the decisions taken will maximize society’s welfare.

Utilitarianism as the root for neoclassical economics has a common basis in Jeremy Bentham, Adam Smith, James Mill and John Stuart Mill (father and son) and others. They were influential philosophers and economists in the eighteenth and nineteenth century Britain [6, 7, 10].

The economic man (homo economicus) is an economically rational individual, meaning that actions are performed based on the following principles (preferences):

- Preferences are complete (I can compare and rank alternatives).
- Preferences are reflexive (stable).
- Preferences are transitive (I am consistent in my ranking).

Also:

- More is most often better than less (strongly monotonic), although diminishing.
- Utilities can be substituted to some extent (indifference).

The ambitions of the actions are to maximize individual utility (welfare) given a restricted budget [6, 11].

The economic man is one way of looking at decision making and preferences. But as should be evident to the reader there are many other ways and theories explaining human behaviour. Psychologists, anthropologists, sociologists, political scientists and even engineers all provide their version of human decision making and preferences. And the philosophers provide thoughts on how humans should behave. Still, the homo economicus is instrumental for the concept of economic valuation of environmental and health effects, which is what this chapter is all about. Why?

Because substitution of utilities allows the homo economicus to receive an economic transaction as a sufficient compensation for a species being diminished in numbers; because transitivity allows for comparison and ranking of distinct environmental end points and other goods/services; because stable preferences ensure that environmental policies will provide a social good.

The theories on individual decision making from other scientific disciplines tend to stress factors such as status, social peer pressure, time availability, mood, cultural aspects, self-affirmation, altruism, and self-perception. as explanatory variables to decision making [12, 13]. These latter factors are far less favourable for economic valuation since the value would be unpredictable and varying dependent on situation. They may, however, provide an equally or even better description of decision making.

However, economists do try to cope with and interpret some of these factors affecting human behaviour. Some of this work is done on the concept of donations.

Many theories attempt to explain why people are willing to voluntarily give money to a public good, and empirical research has been done on this issue. There are three main theories of individuals' motives to voluntarily give money to a public good: altruism, warm glow and conditional cooperation.

People are altruistic, which means that people care about others well-being as well as their own. An altruistic person likes to help them who help him/her, but also hurt them who are hurting him/her [14]. Furthermore, when people cooperate they contribute more to a public good than they would have done with only pure self-interest. People's enthusiasm for sacrificing for others diminish if they do not believe other people is doing their share. By providing public goods by charities, people feel relieved from guilt and get a warm-glow feeling when making a donation [15]. According to the theory of conditional cooperation, people are influenced from others' donations because of social pressure, social relations and social norms ([16]; Chap. 1. Kolm, Chap. 3 Schokkaert and Van Ootegem, Chap. 19 Antoci, Sacco and Zamagni). According to Hur [17] people give to charity both to demonstrate desirable quality and to satisfy their selfishness. Leading social forces and direction of public policies has an impact in the charity giving.

The discussion above serves to present a very important feature that is necessary when reading results from CBA performed on environmental impacts.

The ultimate feature of homo economicus, of relevance for this chapter, is basically that homo economicus can compare welfare with utility with money.

Money can be used as compensation for environmental degradation and environmental degradation can be translated into monetary losses (and vice versa).

Many objections have been raised against the notion of humans represented as a Homo economicus. Amongst the objections acknowledged in the economic text books one can find statements recognizing that it is impossible to measure utility completely, and that it is impossible to compare utilities of different people.

2.2 The Seller

The seller, or usually the corporation, company, business, or firm acts on similar principles as homo economicus. While the objective for the buyer is to maximize utility, the seller tries to maximize profits and/or minimize costs. While the buyers base their actions on a set of preferences, the sellers base the firms actions as consequences of mainly three decisions needed:

1. How much of a product to produce.
2. Which production technology to produce.
3. How much production input that is needed.

When the seller has some influence over prices, the price level will also be subject to a decision [6].

The firm is usually the party responsible for mitigation of environmental impacts and for taking the costs associated with mitigation. Whether or not these costs are transferred to the final customer is a topic for another book, but we will stick to explaining the abatement costs that the seller endures when reducing environmental impacts.

In general, abatement options are from a bottom-up perspective categorized into emission control technologies, substitution options or efficiency improvements.

All of these three usually consist of a number of partial costs. Investments, operation & management costs, fuel prices, labour costs, solvent costs, and in some cases waste disposal costs are all common costs that has to be taken into account.

There are other relevant options which can be of concern when reducing environmental impacts. Examples of those are technology substitution, shifts in production, and also adaptation costs.

From a top–down perspective, the seller can face other types of costs such as competitive disadvantages or profit losses. These are less direct and also more difficult to analyse but can nevertheless be important for a cost analysis of large-scale impacts.

2.3 The Market

The buyer and the seller interact in a place called the market. This is a place that needs apply to certain conditions in order for it to be a perfectly competitive market and thereby provide maximum welfare to society (in other words: *be effective*). These conditions can be summarized as follows:

1. The sellers produce identical products (homogenous).
2. There are no transaction costs.
3. Both the buyer and the seller have perfect knowledge.
4. Preferences are stable.
5. Only small (relative to the industry) actors that don't influence market prices participate (both buyer and seller are price-takers).
6. Market actors can enter or exit the market free of charge.
7. There are no economics of scale.
8. There are no external effects (externalities).

All deviations from these conditions can lead to an inefficient market that no longer provides maximum welfare to society.

Economic efficiency refers to the use of resources so as to maximize production of goods and services. One economic system is more efficient than another if it can provide more goods and services to society without using more resources. A situation can be called economically efficient if:

- No one can be made better without making someone worse off (Pareto efficient).
- No additional outcome can be obtained without increasing the amount of inputs.
- Production proceeds at the lowest possible per-unit cost.

All of the conditions for an efficient market are being studied in different sub-branches of economics. Environmental and health impacts are examples of the violation of the condition "no external effects" which is an area studied mainly by environmental economists. In other words, environmental problems are to an economist considered as a market failure, or more precisely a negative externality.

3 Externalities and External Costs

We will now look more deeply into the aspect of externalities and try to explain to the reader what the term refers to, as well as to present some of the more important theories relating to externalities.

3.1 Externalities

Externalities can in principle be either positive or negative. A positive externality may be the result of actions by an individual or a group benefiting others such as technological spillover, which for instance can be generated by foreign direct investments in a developing country. The positive externality may also lead to higher social benefit, being the profit of an activity to an entire society, including not only the benefit to those members of the society directly involved in the activity, but also the benefits to all other members.

Negative externalities arise when an action by an individual or a group implies harmful effects on others such as: unintended dispersion of chemicals to land, air and water; air pollution effects on health; forest growth; or fish reproduction. When negative externalities are generated they should be internalized into the market economy. By internalizing the externalities the economic value of environmental impacts are allocated to the pollution sources and included in the economics of the activities causing the problem. This would also allow for the market to function properly and thereby reach a socially optimal level of environmental impacts.

The problems with negative externalities arise because of market and government failures. Market failures occur because markets for environmental goods and services do not exist, or when the markets do exist, the market prices underestimate their social scarcity values. However, a market can only exist and function efficiently when property rights on goods and services exchanged are well defined, as well as when transaction costs of exchange are small. Basically, from an economists' perspective, a part of the problem with environmental degradation lies in the difficulty to assign property rights to a low-toxic environment, clean air and water, biodiversity, and a comfortable global atmospheric climate.

3.2 External Costs

External costs, damage costs, also often called just externalities, are a monetization of negative external effects being the consequences of, for example, some sort of environmental degradation. These effects and damages are external because the affected does not receive any compensation and the polluter does not need to pay for the damage. In order for physical measures of impacts to be commonly measurable, they must be valued in monetary units. The monetary valuation of different effects is not a straightforward procedure since many of the effects have no market value. The total value is often composed of both use values and non-use values.

External costs have to be considered and included in prices in order to give the product their real cost. One way to include external costs is to follow the Polluters Pay Principle (PPP). The PPP state that the polluter should bear the cost of policy measures and also ensure that the environment is in an acceptable state. According to PPP, polluters bear the full financial responsibility for pollution reduction.

3.2.1 Damage Costs = External Costs

Often in literature one comes across the term damage costs. Damage cost is in some cases expressed as something different than external costs. However, we want to stress that damage costs are either equal to, or a part of external costs. In principle, damage costs can be a subset of internal costs, but as such it serves little meaning to explicitly identify it as the impact of the cost is already properly allocated. Other meanings of damage costs are basically just misunderstandings of the concept. Another expression often used to describe an externality is the term *social costs*, as in contrast to *private costs*.

3.2.2 Private and Social Costs

In general, economic inefficiency in resource allocation would be the result of a divergence between private benefits or costs and social benefits or costs, i.e. the result of externalities. Private costs (or internal costs) are directly taken by the buyer. Private costs for a transport user would, for example, include expenses for: wear and tear, energy cost of vehicle use, transport fares, taxes and charges, as well as welfare effects such as own time costs.

Social costs reflect in this example all costs occurring from the provision and the use of transport infrastructure, such as wear and tear costs of infrastructure, capital costs, congestion costs, accident costs and environmental damage costs. Some of these costs are already indirectly included in the private costs through taxes and charges, while others are not. In the context of environmental economics, private and social aspects are of importance. Mainly since it is often the case that environmental degradation is a social cost caused by private activities. Hence, the distinction between private and social is as presented above another impact of costs not being properly internalized in prices.

3.3 Theories for Avoiding Welfare Losses

As a repetition, environmental degradation is usually a negative externality from, for example, the use of chemical additives, which cause a market failure, which in turn lead to welfare losses. If this is the case, and welfare loss is a bad thing, then something should be done about it. We have earlier presented the PPP as one way of correcting the market failure and we here present two other theoretical constructions to how market failures can be counteracted or avoided.

3.3.1 Pareto Efficiency

Pareto efficiency, also known as Pareto optimality, is named after an Italian economist, Vilfredo Pareto (1848–1923). The definition of a Pareto efficient economic system is that no re-allocation of given goods can be made without making at least one individual worse off (there is no way to make any person better off without hurting anybody else). Pareto improvement from a non-efficient system is achieved when a change to a different allocation makes at least one individual better off without making any other individual worse off [Varian 47].

3.3.2 The Kaldor–Hicks Compensation Principle

Two economists, Nicholas Kaldor (1939) and John Hicks (1940), authored the Kaldor–Hicks compensation principle (also known as Kaldor–Hicks criterion), which is a measure of economic efficiency.

According to the Kaldor–Hicks compensation principle, an outcome is more efficient if those that are made better off *could* (in theory) compensate those that are made worse off. However, the Kaldor–Hicks compensation principle does not require the compensation to actually be paid, just that the possibility exists [18].

3.3.3 The Coase Theorem

Another theory is the *Coase theorem*. The theorem specifies the need for property rights in order to achieve economic efficiency. Property rights, in the context of environmental degradation, relates to the right to have a certain level of environmental quality. The Coase theorem basically states that the original distribution of property rights doesn't matter if the following criteria apply:

1. Everyone has all information needed.
2. Consumers and producers are price-takers.
3. There is a costless court system for enforcing agreements.
4. Producers maximize profits and consumers maximize utility.
5. There are no income or wealth effects.
6. There are no transaction costs.

If these six criteria apply, the market for property rights (environmental endowments) is efficient [18].

4 Valuating Externalities

Having explored the term externalities and its implications, this chapter presents methods used to assert economic values to externalities related to environmental impacts.

4.1 Economic Values at Stake

In order for various environmental impacts to be measured on a single scale, they must be valued in monetary units. The monetary valuation of different effects is not a straightforward procedure since many of the effects have no direct market value. To set a "total" value on the environment, relevant values are divided into three groups: *use values*, *option values* and *non-use values*.

Use values are defined as the utility one person gains from using the good or service, for example walking in the forest or fishing. This use value includes direct and non-direct values. The direct use value is the value attributed to direct utilization of ecosystem services. Non-direct-use value or "functional" value relates to the ecological function performed, e.g. by forests, such as the protection of soils and the regulation of watersheds [19].

Non-use values, also referred to as passive use values, come from the utility an individual gain even if they never intend to use the resource by themselves. The non-use value includes: option value (the value of having the option to use the resource/service), existence value (the value of knowing something exists), altruistic value (the value of knowing that someone else gains utility) and bequest value (the value of passing environmental resources to future generation even though they never use it or intend to use it). The option value consists both of use and non-use values. The bequest value is similar to the altruistic value and contains both use and non-use values [18].

Figure 1 summarizes the welfare values presented above. It also lists the valuation methods suitable for the calculation of monetary values.

As is seen in the figure, the different economic values need different methods for economic valuation.

4.2 Methods to Valuing Externalities

There are two main scientific areas in which economic valuation takes place, environmental economics and ecological economics. The main difference between the two areas is whether or not the general description of how the economy functions is accepted or not. Environmental economists do basically accept the way the market functions and homo economicus (Sect. 2). Ecological economists

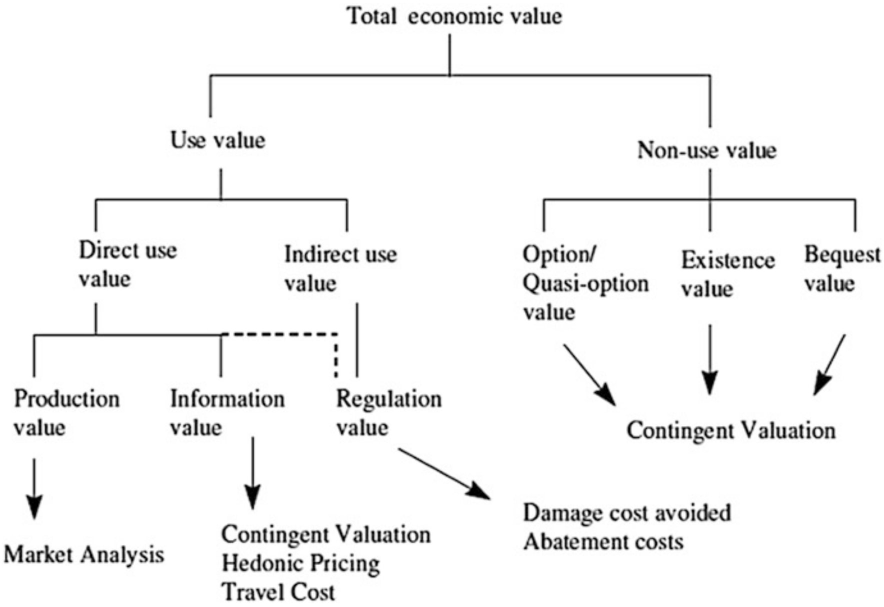

Fig. 1 Summary of economic welfare values related to environmental impacts and valuation methods applicable for the values [20]

have a different approach to the market function and express (inter alia) the need for alternative ways to express the usage costs and value of natural resources [21].

4.2.1 The Environmental Economics Approach

The main challenges of environmental economics are to develop methods for definition and valuation of externalities that are consistent with mitigation costs associated with the externality in question.

Consistency is achieved by deriving a demand function for the non-market good or service. The demand function is derived by researching the Willingness To Pay (WTP) money for obtaining an environmental good or service. Alternatively, studies derive the Willingness To Accept (WTA) monetary compensation for losing an environmental good or service. The purpose of measuring WTP is to estimate a change in welfare because a change in welfare is not directly observable [19]. The current preferences of the survey population state the current price (WTP/WTA), given their awareness of the subject and the information available. The derived value mirrors the current attribute and preferences, rather than the importance of the environmental impact. The result can be compared to the values of marketed commodities [22]. As a reminder, the value of a market commodity is seen in its price.

Basically, economic valuation is performed by two different main methods. You either observe indirect statements of economic value = Reveal preferences. Or you ask individuals for their economic value = State preferences. One important aspect to have in mind is that valuation is performed to identify demand for resources and services for which there is no functioning market [18].

The stated preference method is a direct approach and is used in order to value both use values and non-use values by using a hypothetical market. The choice experiment (CE) and the contingent valuation (CV) methods are the two most common examples of stated preference methods. In the CE method the respondents are asked to choose a level of environmental quality from a set of varying environmental qualities, called choice set. In the CV method the respondent is asked to imagine an environmental market situation and is then asked how she would act in that given situation. CE and CV attempts to find the WTP for a good or service by asking individuals direct questions about their preferences. Alternatively, researchers can ask the respondents for their WTA.

The main criticism towards the stated preference method is that the conclusions are drawn from a hypothetical survey, where the respondents who state they would pay a certain amount do not actually have to pay at all.

The revealed preference method is an indirect approach that is used in order to monetize *use values*. This method observes the real choice between money and the environmental goods. Methods often include observations of consumers' or producers' behaviour or actions, such as the hedonic price method and the production function method. The hedonic price method determines values from actual market transactions. These transactions are used to see how the price of a market commodity varies when a related environmental good changes, such as the effects of noise or air pollution on house prices. The production function method is used to estimate the value of the environmental effects on production. This method is suitable when consumption or production of a private good is affected by the environmental good. An example is the valuation of ground-level ozone levels by valuing the impact on the production of wheat or timber, which has market prices. The problem with the revealed preference method is that it does not contain all the individuals' values that affect the WTP.

One solution to the problem with hypothetical markets is to actually create a market with real payments where theories can be tested in a controlled setting. Experimental markets can take place either in a laboratory experimental market or in a realistic setting, such as a field experiment. In a field experiment the researcher construct a market where an environmental or public good is offered and real payment can take place in order to receive the public good [18]. However, natural field experiments are hard to construct because they generally require that the goods are excludable and rival, and that a similar market does not already exist.

Another method used at times is the Standard price method. This method presents environmental values as corresponding to the mitigation costs needed to avoid environmental degradation. The main disadvantage of this method is that the environmental value derived is poorly linked with the environmental impact.

Another approach often used is to transfer and adjust results from other related studies, a so-called Benefit Transfer. This procedure is often used since making new, locally adapted studies is expensive and time consuming.

4.2.2 Methods to Valuing Health Effects

In the case of health effects, other methods than stated or revealed preference methods are often used to estimate the impact of externalities and valuating the human health damages. Both productivity losses and costs for hospital admissions or other hospital-related activities are used to monetize health effects. Of special importance for the valuation of health effects are the metrics “Value of a Statistical Life”/“Value of Prevented Fatality” (VSL, VOSL or VPF) and “Value of a Life Year Lost” (VOLY).

VSL is derived based on the monetary sum people are willing to pay for reducing the risk of fatality. An example of a suitable monetary sum is the price premium for a safe car, which together with risk reduction estimates for the safe car is sufficient to calculate a VSL. The WTP for Δs (the change in the risk to die) leads to the value of statistical life such as:

$$\mathrm{VSL} = \sum_i \mathrm{WTP}_i / \Delta s N,$$

where i is the conditional probability to live to age i for a person of age a, N is the population at risk.

VOLY is most often linked directly with VSL. Within the ExternE project for instance, VSL is expressed as equal to the discounted value of VOLY [2]. Hence

$$\mathrm{VSL} = \mathrm{VOLY} \sum_{i=a}^{T} \left(aP_i / (1+r)^{i-a} \right),$$

where aPi is the conditional probability to live until year i for a person at age a, T is the maximum expected life length and r is the discount rate.

4.2.3 The Ecological Economics Approach

Environmental economists and ecological economists work in very similar fields but with some differences that it might be useful for the reader to know about. Ecological economics can be defined as “the field of study that addresses the relationship between ecosystem and economic systems in the broadest sense” [23]. While the ecological economist has a biophysical view of value, the environmental economist states that the value cannot be reduced to a simple physical metric [18].

As a simplification, environmental economists usually value *changes* in ecosystem services. An example of such a change is fresh water degradation of any kind. Ecological economists, on the other hand, rather value *the stock* of ecosystem services or goods. The corresponding example would be the value of water. Alternatively, one can say that environmental economists usually monetize marginal changes, while ecological economists value stock existence values.

For instance, Costanza et al. [24] estimated the value of 17 ecosystem services in 16 biomes to an average US$33 trillion (12 zeroes) globally. This value is almost twice the size of the compared global GDP (or Global Gross National Product to be precise). The ecological economists estimate these values so that ecosystems and biodiversity can be included in new calculations of economic efficiency and economic performance.

The background methods used for valuing ecosystem services are often similar for ecological and environmental economists. The valuation methods are presented earlier in this chapter.

5 Limitations with Economic Valuation

There are a number of concerns related to economic valuation of environmental impacts and health effects. These concerns are often valid and need to be stated explicitly so that a process of continuous improvements can be assured.

5.1 Valuation Methodology

The Stated preferences method is a controversial method and well debated between economists. The main criticism towards the Contingent Valuation (CV) method is that the elicited values and people's WTP is based on hypothetical answers and not real economic decisions and thereby meaningless because people are not facing real payments or a real budget constraint [18].

There are some biases concerning the stated response to WTP questions. Some responses might be from "yes-sayers" to please the interviewer. Others might give "protest zeros" responses, if the respondent disagree with the conducted scenario. While yet others desire a "warm-glow" since the respondent has a moral satisfaction from the act [25].

Another part of the debate concern a more philosophical approach, it discusses if passive use values or existence values should be included in economic analysis. The more traditional view emphasizes the necessity for a good to be physical or at least observable in order to get utility from buying it. In the non-use values, consumers get utility from a good without utilizing it physically. According to Diamond and Hausman [26], the CV method should not be used in CBA or damage assessment. They argue that WTP estimates from the CV method are not measurements of preferences for environment resources since it is difficult to compare the hypothetical responses with real economic choices.

Also, and this is a fairly economic discussion, one can be concerned with most valuation studies usually using income as the budget constraint. The income is a "flow" value while this flow is sometimes compared to "stock" values (i.e. natural resources). If the income were compared with the growth in stock, then this objection turns invalid.

A general critic against all the valuating methods, and the entire field of environmental economics, consists of whether it is possible and fair to put an economic value on the environment [27].

5.2 General Concerns Related to Economics

As we hinted in part 2 of this chapter, there are concerns with using the traditional neoclassical economics view of homo economicus as an expresser of welfare impacts. Not all persons can or wish to translate welfare into utility into money, and not all would be willing to accept monetary compensation out of moral reasons (these respondents are usually sorted out of WTP surveys as protest answers as we described earlier in this text).

There are also more fundamental problems. The problems of highest concern for the authors relate to: the existence of a utilitarian moral; preferences for decision making and the function of the market.

The utilitarian man is a basis for decision making in economics. And it is a description that is valid in most market situations in the western societies at least. But, the utilitarian ethics is something that few other social sciences can find as rational for human decision making outside the usual market setting, as described earlier.

That the preferences are complete is an important statement for rational decision making but a preference that can be difficult to replicate in environmental valuation studies. It is basically very difficult to compare cleaner air with otter preservation with the purchase of a car with avoidance of cancer with reduced fish populations. In other words, preferences for environmental goods and services are likely *not* to be complete.

There are also concerns related to preferences being stable, which they quite often aren't.

Furthermore, and this is linked to the complete preferences, the hypothetical market environmental goods and services is not a market under perfect competition. The existence of externalities is one reason for this, which is why environmental economists try to value externalities. But the condition of perfect knowledge isn't there either. The reason is simple; we still don't have all the information about environmental degradation and risks associated with the use of, for example, chemicals.

Nevertheless, economic valuation is still the best available option when trying to allocate resources to protect the environment or human health. Why?

Because some sort of valuation and ranking of options always have and always will take place in decision making. The choice is between using economic values derived in a consistent and transparent way (environmental economics approach), or to use arbitrary and random economic or other values estimated in a case-by-case setting. And the authors of this chapter are in favour of a transparent approach that is open for improvements.

6 Identification of Impacts and Their Stressors

When a chemical is emitted to the environment, it is distributed into different environmental matrices depending on the properties of the substance. When distributed in the environment, different organisms, including humans, can be exposed to the substance via different exposure routes such as ingestion, inhalation and dermal exposure. Depending on both species and substance characteristics, the exposure to a substance can give rise to different impacts.

In this section, the process of identifying impacts and the substances causing the impacts, here called stressors, will be discussed in more detail.

6.1 Impacts on Human Health and the Environment

When identifying impacts to human health or the environment and their stressors, there are two main approaches that can be used. One of these approaches focuses on the emission of a substance, called stressor, and tries to determine which impacts that can occur due to the emission of the substance (stressor to impact). The other approach instead focuses on an observed impact and tries to identify which stressor that caused the impact (impact to stressor).

6.1.1 Stressor to Impact Approach

The stressor to impact approach is used when the impact of a substance is unknown. It is, for example, used in the guidance on information requirements and chemical safety assessment developed by the European Chemicals Agency [28] for the implementation of REACH.

When determining the impact of a stressor using this approach, there are two main steps, exposure assessment and hazard assessment [28]. The exposure assessment is aimed to determine the concentrations of a substance that a certain organism can be exposed to due to the emission of a certain amount of a substance. The first step is the release estimation. The release estimation aims to determine how much of a substance that is emitted, where the emission takes place, to which environmental matrices and how the emissions are distributed over time. Next, the environmental fate of the emitted substance is determined using multimedia environmental models which are based on substance characteristics as well as the properties of the receiving environment [29]. Depending on which type of model used, the environmental fate can be determined with different level of detail. Finally, exposure estimation is performed where it is determined which organisms that can be exposed to the emitted substance and in what concentrations.

The second step when determining impacts is the hazard assessment [28]. During the hazard assessment, the impact caused by the exposure to a substance is determined [30]. This is often done using in vitro or in silico testing. The results of the hazard assessment are often presented as dose–response functions.

For more information on exposure and hazard assessment, see ECHA [30–34].

6.1.2 Impact to Stressor Approach

The impact to stressor approach is used when an impact has been observed but the stressor causing the impact is unknown. This approach is often used when studying impacts on human health, for example within the field of epidemiology. This approach is the backwards version of the stressor to impact approach. Here, the impact is known. Here, the stressor is identified by studying the affected organisms, for example their daily routines, their food intake or by sampling their surrounding environment for possible stressors.

6.2 Economic Impacts

Some environmental degradation can actually be bad for business. The classical example is the laundry firm sited right next door to the coal power plant. Environmental degradation does often have these types of impacts which need to be quantified. Economic impacts can be either large-scale or small-scale impacts. Examples of large-scale impacts are loss of work hours and loss in productivity, investment in cleaning equipment, etc.

7 Economic Tools for Analysis

Valuation of environmental impacts can consist of both monetary values and non-monetary weights to make it easier to estimate total effects from different products and projects.

7.1 Cost–Benefit Analysis

In CBA both cost and benefits are given a monetary value and then compared. Effects on, e.g. the environment, time use and health are examples of externalities that are monetized in a CBA. These are then compared with technical abatement costs, etc. in order to calculate net benefits of the studied scenario or policy. By doing this, the analysis provides policy relevant results describing whether a scenario provides a net benefit for society or not. The analysis can also identify the most beneficial scenario out of a number of scenarios.

A CBA usually considers all costs and benefits to the society as a whole.

The value for society of a studied scenario or policy is described by the net social benefit (NSB):

$$\mathrm{NSB} = B - C,$$

where B is social benefits and C is social costs.

The major steps in a CBA are usually [35]:

1. Specify the set of alternative projects/programs
2. Decide whose benefits and costs count (stakeholders)
3. Catalogue the impacts and select measurement indicators (units)
4. Predict the impact quantitatively over relevant time period
5. Monetize all impacts (convert all costs and benefits)
6. Discount benefits and costs to obtain present values (discount rate)
7. Compute the net present (NVP) of each alternative
8. Perform sensitivity analysis
9. Make a recommendation based on the NPV and sensitivity analysis

7.2 Impact Pathway Approach

The impact pathway approach was developed within the ExternE project series and is commonly used today to assess transport externalities [2]. The method is a bottom-up approach in which environmental benefits and costs are estimated by following the pathway from source emissions via quality changes of air, soil and water to physical impacts, before being expressed in monetary benefits and costs. The impact pathway approach is acknowledged as the preferred approach when it comes to air pollution and noise costs. Figure 2 shows the impact pathway methodology, whose principles are: emissions and inventories, dispersion modelling of the emissions, exposure calculation to the emission calculations involving the impact calculation on human and ecosystem of the emissions, and external costs calculation of damage.

To illustrate the concept of external (or damage) cost, we can first look at the emissions from Waste of Electric and Electronic Equipment (WEEE) to the air. The different points leading to the evaluation of emission's impact are the following [36]:

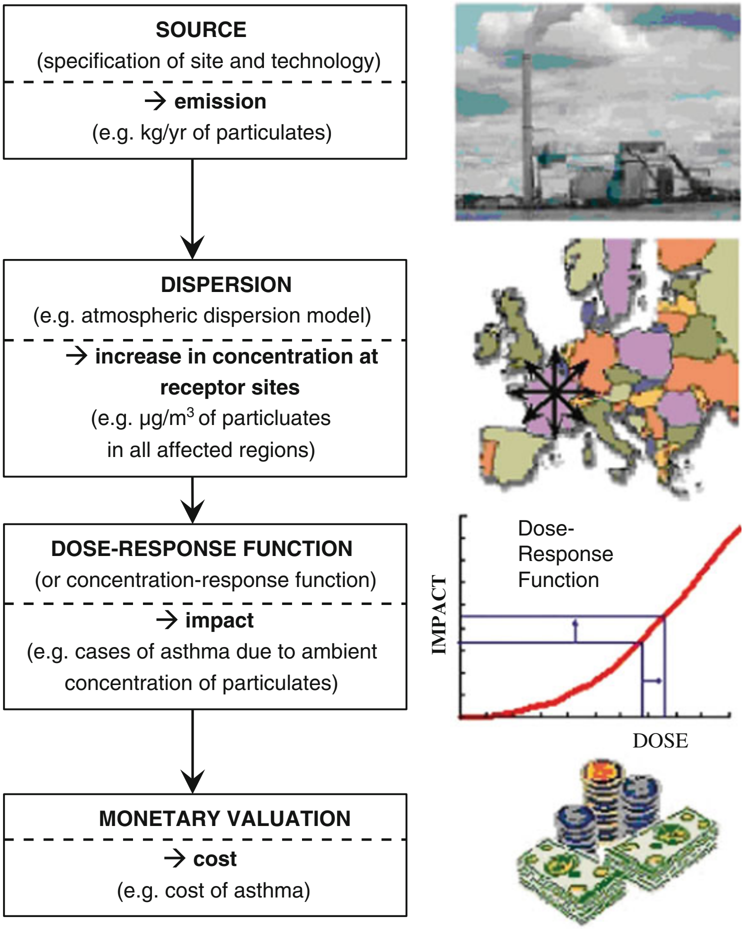

Fig. 2 The impact pathway approach [2]

1. *Emissions and inventories* are in the case of air pollution related to the assessment of the level of pollutants released from various sources. That is to say emission specification of the relevant technologies and pollutants. The determination of emission factors of different substance in WEEE road transport is often the product of national, EU and international research.
2. *Dispersion modelling of the emissions* concerns how air pollutants disperse in the ambient atmosphere. This step is also called environmental fate analysis, especially when it involves more complex pathways that pass through the food chain. The pollutants dispersed to the atmosphere are in general modelled using dispersion models.

3. *Exposure calculation to the emission calculations involving impact of emissions on humans and ecosystem of the emissions* means the impact calculation of the dose from the increased concentration. The impact calculation is followed by calculation of impacts (damage in physical units) from this dose, using a dose–response function. The impact of WEEE substances on health and the environment is location specific and is based on conditional, that is to say the way the WEEE is taken care of. Hence, the exposure assessment relates to the population and the ecosystem being exposed to the externalities.
4. *Impact*: the exposure response relations are based on epidemiological studies.
5. *External cost of damage* is where economic valuation of these impacts i.e. external costs and their value is performed [2]. Evaluation of impacts on both the humans and the ecosystem is based on valuation studies, in order to monetize the external effects.

The ExternE methodology has been applied on many studies analysing environmental, energy and transport policies, both at a national and European level. The relevance on transport externalities has been focused on emissions, dispersion modelling and updating of dose–response functions. Noise and accidents have also been analysed in addition to air pollutions. With this method, aggregated external cost in addition to marginal external cost of transport can be estimated. The external cost estimations from the transport sector are depending on the mode of the transportation in question and where it takes place since the emissions released differ as well as the location of the emissions [2].

7.3 EPS Method

The EPS (environmental priority strategies in product design) system was initiated in 1989 by Volvo Automotive Company, IVL Swedish Environmental Research Institute and the Swedish Industry Federation. The current version was developed at the Centre for Environmental Assessment of Product and Material Systems (CPM) [37, 38].

The EPS system was initially developed to be used within the product development process as a tool to help assess the environmental performance of products. The system is based on LCA (Life Cycle Assessment) methodology and uses inventory data (kg of substance X), characterization factors (impact/kg of substance X) and weighting factors (cost/impacts) to calculate the external costs or values of a product. By multiplying the characterization factor with the weighting factor, an impact index is obtained (cost/kg of substance X) which describe the cost/values related to the emission per use of a kg of a certain substance.

The first version of the model was developed in 1991–1992. In the EPS system, the impacts are expressed in terms of socio-economic costs (or values) occurring by unit effects of damage to five safeguards subjects: human health, biological diversity, ecosystem production, natural resources and aesthetic values. The latest version was published in 1999 [37, 38].

For abiotic stock resources, the resource value is set as equal to the production and environmental cost for a sustainable alternative. For fossil oil, gas and coal, these alternatives are rapeseed oil, biogas and charcoal, respectively. For metal (metal ores), the production and environmental costs to upgrade low-quality ores (sustainable supplies), such as silicate minerals, to a quality similar to present day ores, using a bioenergy-driven process (near-sustainable process), is used as the resource value.

8 Examples of Valuation of Impacts

In order to illustrate how the results finally turn out, examples for external costs induced by lead emissions and environmental and human health end points are presented here. The example presenting the external costs of lead emissions is more elaborate so as to give the reader an opportunity to follow a typical line of reasoning, while the generic table on typical external costs can be used as examples of final results from economic valuation studies.

8.1 Economic Valuation of Lead Emissions

Lead (Pb) is used for many applications, for example in electronic goods such as cathode ray tube (CRT) televisions and as a stabilizer in PVC. Pb is one of the oldest known and most studied occupational and environmental toxins. Despite the many studies, there is still debate regarding the toxic effects caused by Pb [39].

In studies of acute effects on humans caused by exposure to Pb, nephrotoxic effects as well as gastrointestinal effects have been observed [40]. Encephalopathy can affect both children and adults. Acute encephalopathy has been shown to increase the incidence of neurological and cognitive impairments.

Chronic exposure to Pb has been shown to cause anaemia, neurotoxic effects, such as reduced cognitive performance and reduced peripheral nerve conduction velocity, and nephrotoxicity. Children are more sensitive to exposure to Pb than adults, especially during the first 2 years of life [41]. For children, exposure to lead can cause growth retardation, affect the neuropsychological development and cause encephalopathy [39]. Adverse reproductive effects due to lead exposure have been observed for both men and women. Exposure of pregnant women to low concentrations of lead is associated with miscarriages and low birth weights [40].

According to Spadaro and Rabl [41], damage costs of IQ decrement is likely the dominant part of the total damage costs of Pb. The dose–response function has been quite well characterized for Pb, for example by Schwartz [48] in a meta-analysis, who found that the IQ decrement is 0.026 IQ points for a 1 μg/L increase of Pb in blood. Spadaro and Rabl identified two possible ways of linking blood levels of lead to exposure. One of the methods connects incremental exposure of Pb in air to

Table 1 External costs for loss of IQ points

Endpoint	Unit	External cost	Reference
Severe nuisance	ELU/person-year	10,000	Steen [38]
Loss of one IQ point	€/IQ point	3,000	Lutter [3]
Loss of one IQ point	€/IQ point	8,600	GREENSENSE project, 2004 cited in Spadaro and Rabl [41]
Loss of one IQ point	€/IQ point	10,000	Spadaro and Rabl [41]
Loss of one IQ point	€/IQ point	14,500	Grosse et al. [42]
Loss of one IQ point	€/IQ point	15,000	Muir and Zegarac [4]

increases of Pb in blood levels, while the other method relates blood levels to ingested dose of Pb.

Combining the dose–response function with the exposure/blood level relations, Spadaro and Rabl [41] derived two possible characterization factors of 0.268 and 0.59 IQ points decrement per kg emitted Pb.

External costs for loss of an IQ point have, for example, been derived by Lutter [3], Grosse et al. [42], Muir and Zegarac [4], see Table 1. The range of external costs for the loss of one IQ point was estimated to 3,000–15,000 €/IQ point. Using an average of 10,000 €/IQ point in combination with the two characterization factors given above, as in the study by Spadaro and Rabl [41], gives a damage cost of 2,680–5,900 €/emitted kg Pb. External costs for emission of lead were also derived in the EPS system [38]. Damages caused by emissions of Pb were estimated with IQ decrement. In the EPS system the loss of IQ points is classified as severe nuisance which is measured in YOLL (person-years). A Swedish case and a global case were derived. The Swedish case was based on Swedish emission data and epidemiological data from 1990. Based on the Swedish case, a characterization factor of 1.58×10^{-4} person-years/emitted kg Pb is obtained. For the global case, global emissions for 1983 estimated by UNEP [43] and epidemiological data from USA were used. These data yield a characterization factor of 0.291 person-years/emitted kg Pb. According to the EPS system, the cost for severe nuisance is 10,000 €/person-year. This gives a damage cost of 1.58–2,910 €/emitted kg Pb. The Swedish value is considerably lower than the external costs derived by Spadaro and Rabl [41], while the global estimation is very close to Spadaro and Rabl's estimations.

8.2 Example of Economic Valuation Results Linked to Environmental and Health End Points

Table 2 presents results from three different methods and studies that have performed large-scale inventories on external costs associated with environmental and human health impacts [37, 38, 44, 45]

Table 2 External costs for different environmental and human health impacts

Safeguard object	Endpoint	Unit	EPS (Euro/unit)	LIME (Euro/unit)	ExternE $[\text{Euro}_{2000}]$/unit
Human health	Life expectancy	YOLL	85,000		40,000
	Life expectancy	DALY		97,000	
	Fatal cancer due to radio nuclides	Case			1,120,000
	Value of prevented fatality	Case			1,500,000
	Cough days	Case			38
	Work loss days (WLD)	Day			295
	Severe nuisance	YOLL	1,000		
Ecosystem production capacity	Crop growth capacity	kg	0.15		0.093–0.237
	Fish production capacity	kg	1		
Biodiversity	Species extinction	Per specie	1.10E+11		
	Species extinction	Per specie		4.8E+10	

8.3 Illustrative Cost–Benefit Analysis of Flame Retardants in Furniture

Let us consider the use of flame retardants in furniture, which has been a standard additive approximately since the 1970s. Flame retardants are added to reduce flammability and therefore to prevent fire. In Sweden there should be some 6 million couches which we will use for this simple example. Each couch needs some 0.5 kg of flame retardant.

It is assumed that the annual life years gained from using flame retardants equal X (external benefits). And the value of each life year lost avoided is €40,000 [45].

The costs of using flame retardants equal the extra production costs, are assumed to some 4 €/kg.

The external costs of using the flame retardants are caused by long-term adverse impacts in the aquatic environment (reduction in fish production capacity) and severe nuisance in humans (T) and potentially disturbance in human development (Z). There are as of yet no economic values derived for the latter two but we express the values as Y and U. For reduction in fish production capacity the value from the literature is 1 € per kilogram fish [37, 38]. And in our example, we assume that the production capacity is reduced by some 10 tonnes of fish.

The CBA then shows that flame retardants are good for society if:

$$40000X > 4 \times 0.5 \times 6000000 + 10000 \times 1 + T \times Y + Z \times U.$$

Our example also shows that the T, Y, Z and U need to be estimated in order to see the welfare impact of using flame retardants in furniture. See this as a call for data.

Since flame retardants have been recognized as not desirable (although not properly quantified in economic valuation), there is now work on replacing flame retardants with other additives with the same functionality.

The substitution of flame retardants is assumed to cost some 8 €/kg substitute and the substitute is equally effective with respect to decreasing flammability.

Assuming that equal mass of additives is needed, the CBA shows that it is good for society to replace flame retardants in furniture if:

$$(8 - 4) \times 0.5 \times 6000000 < 10000 \times 1 + T \times Y + Z \times U.$$

Note that the cost for life years is left out of the equation since the impact on fire is the same between the two types of flame retardants.

CBA can be used also when the definite outcome is unknown but when there are estimates. The T and Z in the equation might be two possible outcomes with different prices (Y and U). Pretend that the probability of T is 0.3 and that the probability of Z is 0.7. The equation above would then be

$$(8 - 4) \times 0.5 \times 6000000 < 10000 \times 1 + 0.3 \times T \times Y + 0.7 \times Z \times U.$$

where $0.3 \times T \times Y + 0.7 \times Z \times U$ is equal to the *expected value* of the environmental and human health impacts considered.

As is seen, this example shows that flame retardants might be good for society (from a socio-economic perspective) even if they cause a number of adverse environmental and human health impacts as long as the value of the avoided mortality impacts is larger. Replacement of flame retardants should only be done (from an economic perspective) if the replacement cost is smaller than the avoided environmental and human health values.

9 Discussion

Economic valuation of environmental and human health impacts is one tool available for the management of chemical additives in society. There are other tools, but it is mainly economic tools that give an answer to whether it is good or bad for society to perform a certain action. One might not agree with the moral code supporting utility and profit maximization, but it is a moral code of sort. It thereby allows for the economic tools such as CBA to provide answer on what is the right course of action. It also stresses the importance of inclusion of all parameters related to the benefits and costs associated with the use of chemicals. Chemicals are serving society with a number of positive functions, and these must be taken into account when performing CBA.

A strong focus on estimating external costs from chemicals is motivated since there has been a severe lack of information and knowledge in this area, but the external costs must be complemented with benefit assessment in order for a CBA to provide a useful result. An external cost estimate only provides partial results and should not be used as policy support in itself.

As we have pointed out in this chapter current economic methods and background assumptions leave room for substantial improvements. And improvements are being made in all areas, although it takes time for these improvements to enter into the applied versions of economic analysis. But larger attention is definitely needed for analysis based on other assumptions than utility-maximizing behaviour where the preferences are complete and stable and where all actors on the market have perfect knowledge.

The negative aspects of chemical additives appear to be getting more and more attention in the public debate. Results linking chemical additives to adverse environmental and human health impacts are being produced. But more results are needed. More economic valuation studies are needed to support analysis as well as impact analysis on parameters such as human fertility, animal reproduction and animal productivity. Of big concern for the authors of this chapter is the need to know more about diffuse exposure from the use of products containing chemical additives.

Also, and this is where it gets very tricky, stressors are likely to be influencing each other. In other words, there is a possibility that “cocktail effects” exists. These “cocktail effects” are likely caused by a large number of lifestyle factors (food intake, stress, sleep, exercise, socio-economic factors, status) as well as by pollutants (air pollutants, water contaminants, diffuse exposure to chemicals). More knowledge is desperately needed about the potential existence of “cocktail effects”. Current limit values of chemicals and other pollutants are usually derived from a single-pollutant impact measurement, but in reality humans are exposed to all of the above-mentioned factors to varying degrees. So sensibilities to chemicals derived from a laboratory environment might understate the “real life” sensibility to the same chemical. Identification and quantification of “cocktail effects” are the major challenges for both the scientific and economic research communities.

10 Buzz Words

Table 3 summarize a number of terms that often occur in the context of economic valuation.

Table 3 Buzz words within environmental economics

Buzz word	Quick explanation
YOLL (years of life lost)	The number of deaths caused × the standard life expectancy at the age of death
YLD (year lost due to disability)	The number of incidents × disability weighting factor × the average duration of the case until remission or death
DALY (disability adjusted life year)	How many years of life that is lost due to premature death and morbidity. Normally: DALY = YOLL + YLD
QALY (Quality adjusted life year)	Years that would be saved following an intervention
HALY (health adjusted life year)	A generic term that includes the two most popular measures, the QALY and the DALY [46]
VSL (value of statistical life)/value of prevented fatality (VPF)	The monetary welfare average value assigned to not dying prematurely
Dose response function	The relation between experienced dose and environmental and human response
Exposure response function	The relation between exposure to an environmental stressor and the environmental or human response
Stressor	Substance causing adverse environmental and/or human health impact

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RISKCYCLE and EU Legislation

Uwe Lahl and Barbara Zeschmar-Lahl

Abstract RISKCYCLE is an artificial word which addresses the risks associated with the global recycling streams. As part of materials like waste paper, plastic, and electronics, pollutants and chemical additives are transported abroad, e.g., they are exported to emerging and developing countries. Here these pollutants/additives can cause risks for humans and the environment especially if treatment/recycling is performed on a lower technical standard. The specific risks that can occur have been studied in an international EU-funded research program, which is the basis of this publication.

At the end of such a project with important results, it is also the question: How can these results become part of a solution for this problem? For this purpose we have analyzed, which EU regulations have the ability to cover RISKCYCLE, namely for waste (WEEE, RoHs), product design (ecodesign), and chemicals (REACH). Finally, all regulations contain segments that are suitable to address RISKCYCLE. But the European chemicals legislation is the best sector to integrate the RISKCYCLE problem because of its sophisticated instrumental equipment.

It is shown that REACH today in principle has already many necessary instruments to tackle RISKCYCLE. So within the registration procedure of chemicals, the registrants have to include RISKCYCLE exposure scenarios. The guidance documents for the registration procedure cover the waste sector in a way that risks identified in connection with waste export in developing countries should be quantified and if necessary managed. But it is open, how these provisions are considered in reality.

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Therefore the authors give some recommendations, how within REACH RISKCYCLE aspects could become a more binding part of the regulation.

Keywords Legislation, REACH, Recycling, RISKCYCLE, Waste exports, WEEE

Contents

1 Background

While analyzing the outcome of RISKCYCLE project [1] one of the main points noticed is that selected hazardous pollutants (chemical additives) that are contained in consumer and industrial products, are ultimately circulated globally due to the products' waste/recycling path. These global pollutant cycles are likely to pose risks to humans and the environment, but for a final evaluation of the impacts, many basic data are lacking.

This article analyzes the question "How can the outcome of the project RISKCYCLE influence European legislation?" In fact, there are many possible ways in which the outcomes of the project RISKCYCLE can influence EU regulation.

First, the *Ecodesign Directive* is a possibility to implement more precautionary approach against risks posed by hazardous chemicals.

The second possibility is the European *waste legislation,* which includes the Restriction of Hazardous Substances Directive (RoHS). The RoHS Directive is closely linked with the Waste Electrical and Electronic Equipment Directive (WEEE) which sets collection, recycling, and recovery targets for electrical goods and is part of a legislative initiative to solve the problem of toxic e-waste.

And third, *REACH* (regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals), the European new chemicals legislation, has interrelation to the waste sector and therefore to the project.

2 Ecodesign Directive

2.1 Basics

The Ecodesign Directive is the regulation that sets standards for products (products, goods) at EU level. Thus, for the RISKCYCLE issue, principle regulations could be established for the pre-consumer phase, so that only those chemical additives may be used that do not cause problems in a sustainable closed substance cycle.

Originally only energy consuming products were considered as part of the EU Ecodesign Directive. The scope of the Directive was extended in 2009 to the range of products that are related to energy consumption (such as windows, insulation).

The EU Commission may establish minimum standards to improve efficiency of energy-related products. Although energy is the focus of the Directive, other kinds of resource consumption are considered, too. This is illustrated by the evaluation methodology *MEEuP* (*M*ethodology for the *E*codesign of *E*nergy-*u*sing *P*roducts), which is basic for the implementation of the Ecodesign Directive [2]. Under the heading *MEErP* (*M*ethodology for the *E*codesign of *E*nergy-*r*elated *P*roducts) this method is actually passing an evaluation and completion process due to the expansion of the scope of the Directive [3]. The Eco-Report 2011 is an Excel-based pre-computation method that allows for products to be assessed in terms of their resource efficiency [4]. From this it is clear which indicators are to be applied in future implementations of the Ecodesign Directive.

The European Commission has adopted a formal working plan for the implementation of the Directive. The current working plan 2009–2011 sets out an indicative list of products and product groups, which are processed successively and in the end are also regulated (air-conditioning and ventilation systems; electric and fossil-fuelled heating equipment; food-preparing equipment; industrial and laboratory furnaces and ovens; machine tools; network, data processing, and data storing equipment; refrigerating and freezing equipment; sound and imaging equipment; transformers; water-using equipment) [5]. The new working plan 2012–2014 is in the vote [6].

The regulation of each type of product group is preceded by an expert study (preparatory study), which is then scrutinized intensively in a stakeholder process.

How can the Ecodesign Directive be further developed to handle the RISKCYCLE-topic? So far, pollution issues are involved in the context of product evaluation and the derivation of product standards, but rather in the sense of LCA to capture the energy side and the other relevant environmental indicators. The topic of mercury in compact fluorescent lamps (CFL) has made it clear that pollution issues can be quite important in the context of this Directive. However, relevant limits for energy saving lamps were first set by a waste-related regulation, namely the Annex of the WEEE Directive [7].

Currently (2012) there is an internal discussion within the Commission on the evaluation of the Ecodesign Directive. One of the positions taken is to expand the scope of the directive a second time to broaden its field of application. There are some voices proposing to include the pollution issue in the context of setting product standards. Decisions are expected in late 2012.

2.2 Conclusion

The Ecodesign Directive can include selected pollutants in life cycle assessment considerations (connected with the topic resource efficiency). This does, however, not cover the topic RISKCYCLE.

At present it is unclear whether the scope of the Ecodesign Directive will be extended a second time and whether the problem of pollutants in products will be included. Since the focus of the policy will remain clearly on the energy aspect, it is not expected that, even with expansion of the scope, the Ecodesign Directive can make a relevant contribution to solving the problem highlighted in RISKCYCLE.

3 Waste Legislation

3.1 Basics

In the past, product-related standards in the European waste law were rare. This changed with the triumphal success of everyday electronic gadgets and the associated increase in e-scrap. The EC Directive 2002/96/EC – better known as the WEEE directive – aimed to combat the increasing amount of e-waste from electrical and electronic devices [8]. Goal is the avoidance, reduction, and environment-friendly disposal of increasing amounts of electronic waste through extended producer responsibility. This goal has been hindered by a number of pollutants that are included in the devices (RISKCYCLE).

For this purpose, the WEEE Directive has been complemented with an additional directive that limits the use of certain pollutants in these products. The EC Directive 2002/95/EC on the *R*estriction *o*f the use of certain *H*azardous *S*ubstances in electrical and electronic equipment (RoHS Directive) ([7], recast 2011 [9]) restricts the use of the six harmful substances/substance families lead, mercury, hexavalent chromium, polybrominated biphenyls (PBB), and polybrominated diphenyl ethers (PBDE) to 0.1% and cadmium to 0.01% w/w per homogenous material in equipment and components, but with several exemptions for a wide range of applications (Annex III and IV).

In particular, the RoHS Directive has been proven in Europe. Those substances are now banned from the products (below the limit values). In addition, the international equipment manufacturers have switched their production, not limited to Europe, but made for the world market. This in turn has led to the creation of laws similar to the RoHS regulation in other regions of the world.

3.2 Conclusion

In the sector of electrical and electronic equipment, the RoHS Directive, as explained, has successfully resulted in reduction of hazardous chemicals in line with goals of the RISKCYCLE project and has reduced many problems. This raises the question whether the RoHs Directive can offer a further contribution for solving the problem. This would require an extension of the scope of the Directive in two aspects:

- Expansion of product scope, including other products in addition to electrical and electronic equipment
- Extension of the catalog of restricted substances (Annex II of Directive)

Article 6 of the RoHS Directive (recast 2011 [9]) says: "*1. With a view to achieving the objectives set out in Article 1 and taking account of the precautionary principle, a review, based on a thorough assessment, and amendment of the list of restricted substances in Annex II shall be considered by the Commission before 22 July 2014, and periodically thereafter on its own initiative or following the submission of a proposal by a Member State . . .*".

Thus, the door would be open for this extension. Whether it succeeds also to extend the scope of the Directive to other RISKCYCLE-related products is doubtful. No such advances are known.

Furthermore, the instrumentation of the RoHS Directive has to be considered in this context. The Directive is targeting a clearly structured business sector with very few clear substance bans (or more precisely: limits). For the regulated pollutants in turn very unique risk considerations are possible. Without an extension of the instrumentation to a more sophisticated control system, the complex (chemical) process cannot be reproduced in other sectors.

4 REACH: The European Chemicals Legislation

REACH has now been in force for 5 years. REACH is setting the legal frame for the chemical sector. But REACH also gave a task, which is to work off for more than 15 years: a "safety check" for all existing chemicals.

This "safety check" is in the first approach a check the responsible manufacturer or importer has to do in his own responsibility. In a second approach, it is to some extent also a check which is done by the competent authorities, especially the European Chemicals Agency (ECHA) and the national authorities.

For this, the manufacturer and the importer have to register the chemicals they are placing on the European market. The registration is mandatory for all chemicals that are sold in a volume of more than 1 Mg/a. With the registration the manufacturer and the importer have to provide a special registration dossier. This dossier should cover all necessary information to do the "safety check." To be precise, the structure of the dossier has to follow well-defined requirements, which will not be explained in this article. More information is offered here [10, 11].

Meanwhile the first "tranche" of the registration is done for all chemicals with a market volume of more than 1,000 Mg/a and for chemicals which have a high concern out of hazardous reasons (e.g., carcinogenic, mutagenic, or toxic to reproduction (CMR)). By the REACH deadline of 30 November 2010 for the first tranche, 24,675 registration dossiers were submitted for 4,300 substances including nearly

3,400 phase-in substances [12]. In the coming years the rest of the existing chemicals have to be registered. Currently the evaluation of the dossiers takes place.

The REACH regulation states that after a 5-year period there should be an evaluation of the regulation itself. First the commission has to give a report about the lessons learned: "*The Commission will launch a review which will consist of the legally required reviews and reports: (a) the review of ECHA (Article 75.2), (b) the review to assess whether or not to amend the scope of REACH in order to avoid overlaps with other EU legislation (Article 138.6), and (c) a general report from the experience acquired in the operation of the regulation (Article 117.4) including a review of the requirements relating to registration of low tonnage substances (Article 138(3)) and the information submitted by the Member States and ECHA in their respective reports on the operation of REACH (Art.117(1)(2)(3)).*" [13].

This evaluation is on the way. The different stakeholders have made their proposals regarding what should be modified or supplemented. Our proposals like improvement of transparency, installation of a positive list, and a household product database (HPDB) have been published some weeks ago, including the topic REACH and RISKCYCLE [14]. This article only covers the topic "RISKCYCLE," but more in depth.

5 REACH and RISKCYCLE

5.1 REACH Regulations on Waste

The RISKCYCLE project deals with chemicals, but with those beyond their actual use phase, when they have entered the phase after end of service life, that means the waste phase. But is this area not considered legally outside the scope of REACH and more covered by waste legislation? The answer to this question is quite clear. Without doubt REACH covers the waste period, too. Thus, REACH is also suitable, in principle, to implement the findings of RISKCYCLE by legislation or regulation.

As Article 2(2) of REACH provides that "*waste as defined in Directive 2006/12/EC is not a substance, mixture or article within the meaning of Article 3 of this Regulation*," REACH requirements for substances, mixtures, and articles do not apply to waste. However, as soon as a material or a waste "ceases to be waste," it becomes instead a product in the eyes of the EU's legislators and is falling under the REACH regulation.

5.2 REACH Regulations on Recovered Materials

Waste fractions leaving the recycling process of waste as a recovered material have to fulfill the obligations of the REACH regulation, but with certain privileges. Article 2(7d) provides under certain conditions for an exemption from registration (Title II), downstream user regulations (Title V), and evaluation (Title VI) [10]:

> 7. The following shall be exempted from Titles II, V and VI:
>
> (d) substances, on their own, in preparations or in articles, which have been registered in accordance with Title II and **which are recovered in the Community if**:
>
> (i) the substance that results from the recovery process is the same as the substance that has been registered in accordance with Title II; and
> (ii) the information required by Articles 31[1] or 32[2] relating to the substance that has been registered in accordance with Title II is available to the establishment undertaking the recovery.

This means, if the recovered material is identical to a substance already registered and if the information on hazardous properties is available, e.g., from the safety data sheet, a registration is no longer mandatory.

But when does a material or a waste "cease to be waste?" The End-of-waste status is specified in Article 6 of the revised Waste Framework Directive 2008/98/EC:

> 1. Certain specified waste shall cease to be waste … when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with the following conditions:
>
> (a) the substance or object is commonly used for specific purposes;
> (b) a market or demand exists for such a substance or object;
> (c) the substance or object fulfills the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products; and
> (d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.
>
> The criteria shall include limit values for pollutants where necessary and shall take into account any possible adverse environmental effects of the substance or object.
>
> 2. … End-of-waste specific criteria should be considered, among others, at least for aggregates, paper, glass, metal, tyres and textiles.

ECHA points out that some materials currently considered as waste might in future be considered to have "ceased to be waste" [15]. These materials will then be out of the scope of waste legislation, and – if not covered by an exemption – will potentially fall under REACH. Clarification of end-of-waste criteria is a matter for waste legislation. In accordance with the general principle of subsidiarity of the European Union law, and following the revised Waste Framework Directive, Member States may decide case by case whether certain waste has "ceased to be waste," where end-of-waste criteria have not been set at Community level. Member States have already worked for use of this regulation, like, e.g., the Waste Quality Protocol in England, Wales, and Northern Ireland [16].

The Commission is working on establishing end-of-waste criteria for a number of specific recyclable materials including metal scrap of copper, aluminum and iron, waste paper, waste glass, compost, and plastics. Based on the results of two frontrunner studies, ferrous scrap and aluminum scrap in 2010, the first

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[1] Requirements for Safety Data Sheets.

[2] Duty to communicate information down the supply chain for substances on their own or in preparations for which a safety data sheet is not required.

End-of-Waste Regulation (333/2011/EC) has been adopted [17]. It applies to the EU since 9 October 2011. Following JRC/SUSPROC, based on a second round of technical studies on waste paper, copper and copper alloy scrap, as well as waste glass (glass cullet), regulations for end of waste on these materials are currently being prepared in comitology. Further studies are performed on biodegradable waste and waste plastics, and the development of end-of-waste criteria on aggregates and waste-derived fuels is in discussion [18].

5.3 REACH Regulations on Waste Life Cycle Stage of Substances

REACH requirements for substances, mixtures, and articles do not apply to waste itself. "*Nevertheless manufacturers and importers of substances, downstream users and potentially recipients of articles have a number of duties under REACH related to substances in waste. Waste-related information must be included in the registration dossier for all substances, including those for which no CSR and/or SDS*[3] *is required (<10 t/a) or which are not classified as dangerous.*" [19].

With regard to the outcome of RISKCYCLE, the obligations for products containing hazardous substances are of great concern, as a risk characterization is mandatory. Following Article 14(4) of REACH, the chemical safety assessment (CSA) shall include the following additional steps if the substance meets the criteria for classification as dangerous in accordance with Directive 67/548/EEC or is assessed to be a PBT (persistent, bioaccumulative and toxic) or vPvB (very persistent and very bioaccumulative) substance:

(a) Exposure assessment including the generation of exposure scenario(s) (or the identification of relevant use and exposure categories if appropriate) and exposure estimation
(b) Risk characterization

For these substances, "*the waste life stage of the substance needs to be covered by suitable exposure scenarios, the corresponding exposure estimation and the related risk characterisation. The conditions ensuring control of risk in the waste life stage of the substance need to be documented in the chemical safety report (CSR) and also communicated in the supply chain by means of the extended safety data sheet.*" [19].

Article 3(37) of REACH defines exposure scenarios as "*the set of conditions, including operational conditions and risk management measures, that describe how the substance is manufactured or used during its life-cycle and how the manufacturer or importer controls, or recommends downstream users to control, exposures of humans and the environment [. . .]*".

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[3] Chemical safety report and/or safety data sheet.

The CSA has to cover the whole life cycle of the substance in the exposure assessment. Following Annex I paragraph 5.2.2 of REACH the waste stage is to be assessed where relevant: "*The emission estimation shall consider the emissions during all relevant parts of the life-cycle of the substance resulting from the manufacture and each of the identified uses. The life-cycle stages resulting from the manufacture of the substance cover, where relevant, the waste stage.* ***The life-cycle stages resulting from identified uses cover, where relevant, the service-life of articles and the waste stage****. The emission estimation shall be performed under the assumption that the risk management measures and operational conditions described in the exposure scenario have been implemented*." Furthermore, following Annex I paragraph 5.1.1 of REACH, the Risk Management Measures of an Exposure Scenario shall in particular include, where relevant, a description of "*the waste management measures to reduce or avoid exposure of humans and the environment to the substance during waste disposal and/or recycling*."

5.4 Risk Management Measures of Exposure Scenarios

ECHA's Guidance on information requirements and CSA, Chapter R.18, gives detailed information about exposure scenario building and environmental release estimation for the waste life stage.

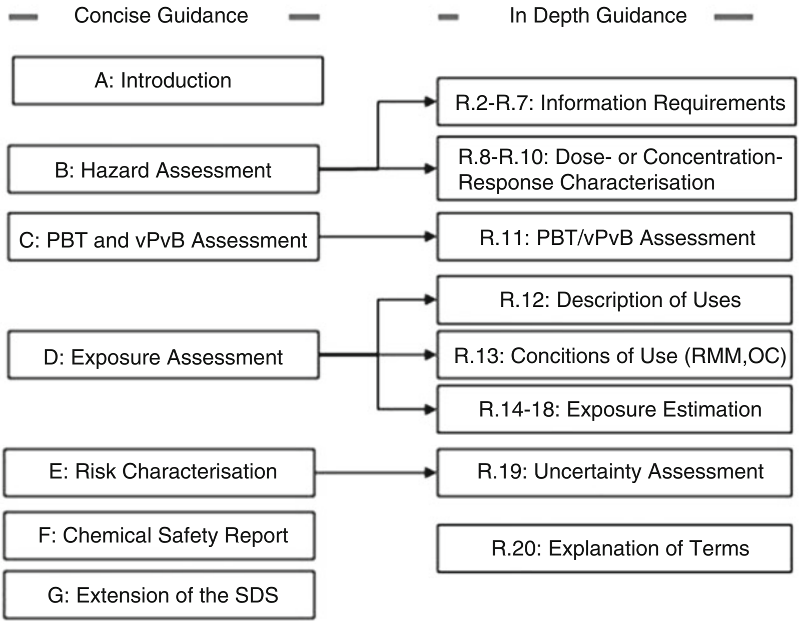


Fig. 1 Structure of the Guidance [20]

This Guidance is part of a series of guidance documents that aim to help all stakeholders with their preparation for fulfilling their obligations under the REACH Regulation. The Guidance consists of two major parts: Concise guidance (Part A to G) and supporting reference guidance (Chapters R.2 to R.20) (see Fig. 1).

Figure 2 illustrates the workflow and location in the guidance of the relevant information for Chapter R.18 [19].

Registrants can choose which kind of approach they want to use for the quantitative exposure assessment for the waste life stage. The guidance contains examples for calculation of releases at local and at regional scale, as they are driven by the operational conditions and risk management measures relevant for the different uses. The Assessment of distribution and fate of the substance in the environment mainly driven by substance properties, once the substance has been released to the environment, is only addressed in Guidance R.16 [21], as this step is independent of the life cycle stage. The guidance contains in addition workflows for the generic and the specific approach.

In the following, the approach for the releases at regional scale is described. Figure 3 provides an overview of waste generation during the life cycle of a substance and examples of related possible sources of information.

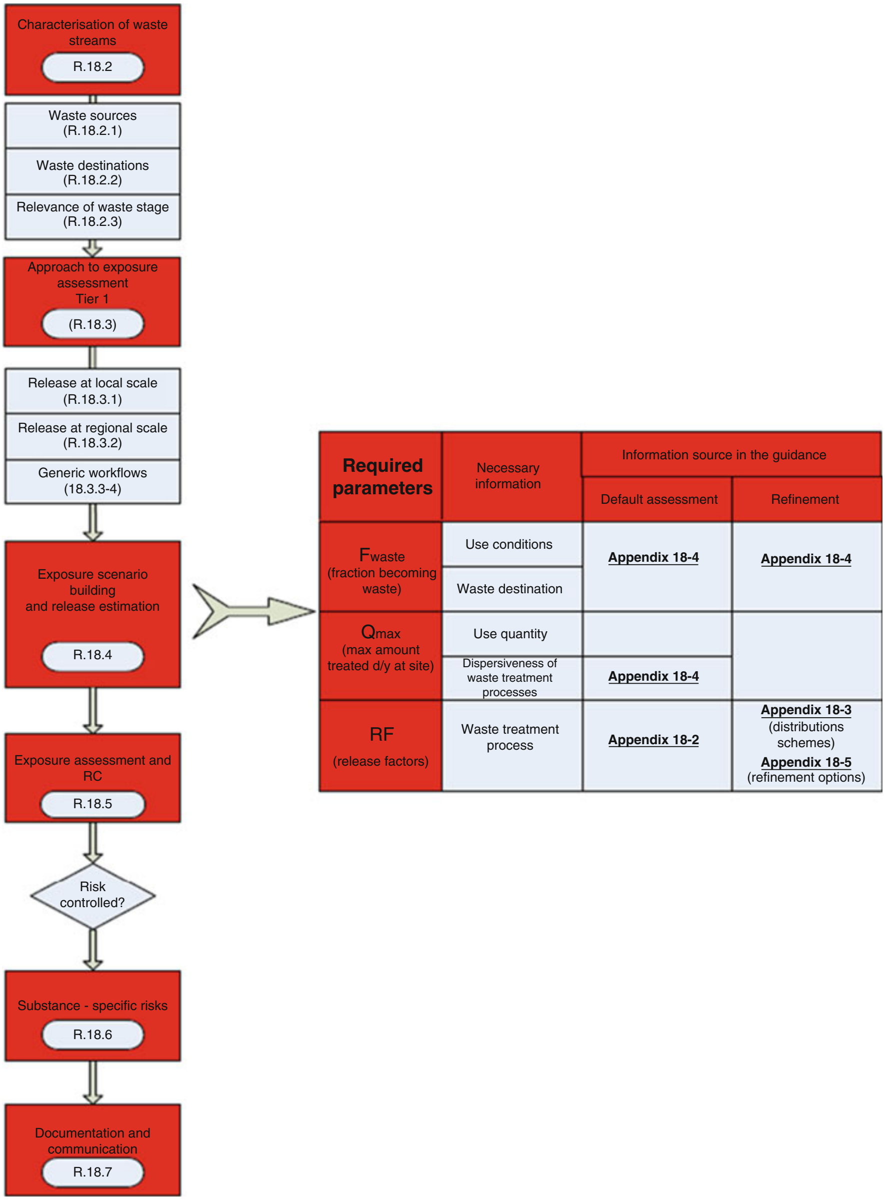
For calculation of the waste life stage's contribution to the release of the substance at regional scale, a standard model of a European region with about 20 million inhabitants and defined parameters (e.g., size, volume of water, soil, sediments and biota, etc.) is used; details are given in Chapter R.16: Environmental Exposure Estimation [21].

> In order to calculate the regional releases from waste treatment in the default conservative approach (Tier 1), again two cases are distinguished: i) Waste from manufacture and industrial uses and ii) waste from dispersive uses and article service life. The fraction of the registrant's total amount per use assumed to be treated in the region ($Q_{\mathrm{max,regional}}$) is different for the two cases: For manufacture and industrial uses the total use and related waste amount is assumed to occur in one region. For dispersive use and article service life, it is assumed that 10% of the registrant's total volume occurs in the region for use and related waste treatment [19].

At regional scale all the releases occurring at the different life cycle stages are summed up. Figure 4 shows the input parameters and the results of the release assessment at regional scale. The outputs are the annual amounts of substance released to the different environmental compartments (regional air, regional water, regional soil).

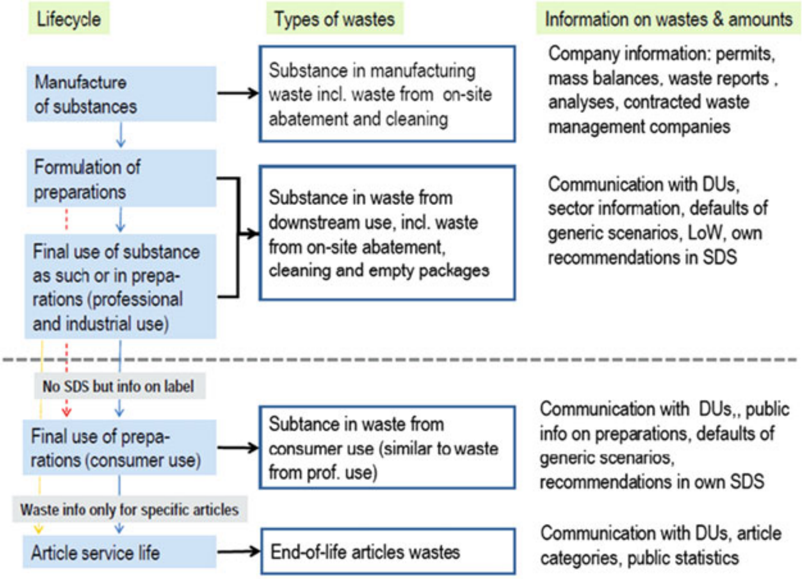
As an alternative to these calculations, the registrant may choose to make a generic release estimate. Here, conservative default values are used for identifying waste amounts and fractions entering into the three main waste streams. "*Furthermore, generic exposure scenarios can be selected containing default release factors and assumptions on implemented risk management in the processes.*" [19].

Figure 5 shows the workflow for a generic approach. "*In order to simplify and structure the exposure assessment of the waste stage, the current assessment approach distinguishes three main waste streams, each of which is connected*



Required parameters	Necessary information	Information source in the guidance	
		Default assessment	Refinement
F_{waste} (fraction becoming waste)	Use conditions	**Appendix 18-4**	**Appendix 18-4**
	Waste destination		
Q_{max} (max amount treated d/y at site)	Use quantity		
	Dispersiveness of waste treatment processes	**Appendix 18-4**	
RF (release factors)	Waste treatment process	**Appendix 18-2**	**Appendix 18-3** (distributions schemes) **Appendix 18-5** (refinement options)

Fig. 2 Chapter R.18: illustration of the workflow and location in the guidance of the relevant information [19]



LoW = List of Waste (established by Commission Decision 2000/532/EC), DU = downstream user, SDS = Safety Data Sheet

Fig. 3 Types of waste generated along the life cycle of a substance [19]

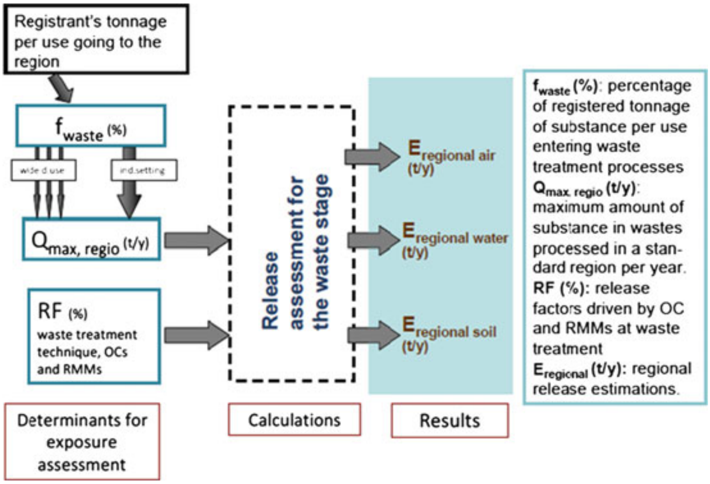


Fig. 4 Determinants and results of regional release estimation for the waste stage [19]

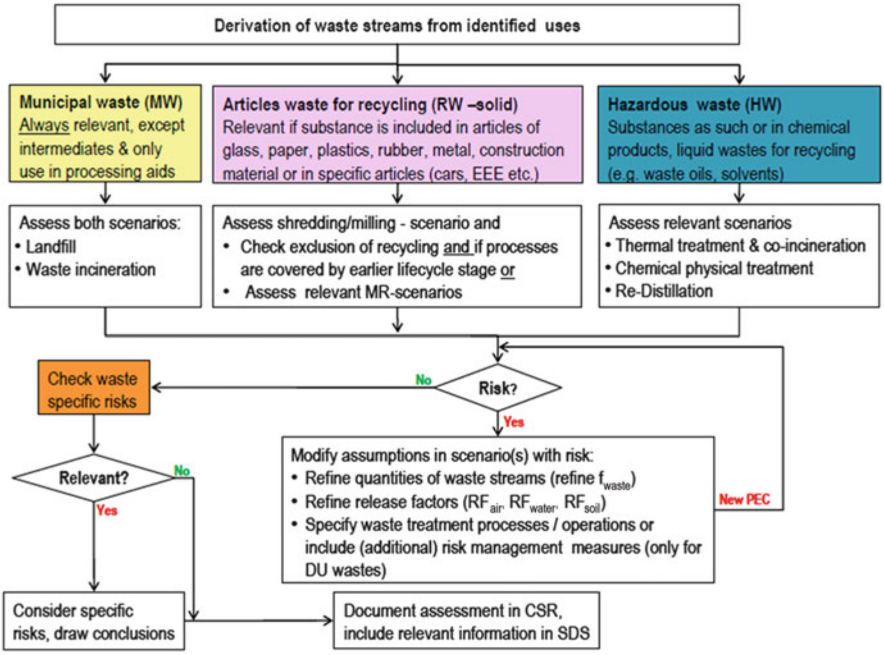


Fig. 5 Workflow for generic approach [19]

with the most typical waste treatment processes: municipal waste (MW), recycling waste (RW) and hazardous wastes (HW) (see Section R.18.2.2)." [19]

5.5 Results

The research project RISKCYCLE has compiled relevant information highlighting the risks of the chemicals that are recycled in regional and global systems. Many of these risks are being provoked due to the fact that manufacturers of chemicals or other items did not make efforts to pursue the item and its chemicals along its way in the product cycle up till the waste stage. The waste stage is not being appropriately taken into consideration in life cycle assessments.

It has been approximately 5 years since the European law on chemicals REACH came into force. It was implemented to audit the risks of all chemicals on the market by their sales volume and hazardousness. The essential aim of this security check is to determine so-called "exposure scenarios," which facilitates the assessment of the occurrence of unacceptable or dangerous exposure created by the evaluated chemical. If these risks are identified, measures are to be taken to reduce the exposure by restrictions on usage or by issuing a ban.

This information is to be submitted to the authorized ECHA for the purpose of substance registrations (details see above in clause 3.4). The essential information should be recorded in the factsheet (SDS) of each chemical including exposure scenarios in case they are substantial. This article describes the importance of the waste stage in the drafting of exposure scenarios. The waste phase is to be included in the calculation of exposure. As part of the implementation of REACH, guidance documents were developed with detailed recommendations which describe how this is to be done. Important aspects of this procedure are explained above.

As a consequence of the implementation of REACH, many problems described in the RISKCYCLE project would become relevant. These described gaps in knowledge are in parts to be extracted from the registration dossiers. The information will be gained depending on the processing status of REACH registrations. Currently, only the so-called first tranche of hazardous chemicals and also chemicals with a market volume of more than 1,000 Mg/a have been registered. Further tranches will follow the next few years.

The analysis of the currently available registration dossiers indicates that they have some serious shortcomings. It is yet unknown whether the mandatory registration of the waste stage in the dossier has been sufficient.

6 Prospect

All three routes (Ecodesign, RoHS, and REACH) are feasible for influencing European legislation by the outcome of the project. There is one argument that indicates REACH is the most promising route: the outcome of RISKCYCLE is a “complex chemical matter.” This is the original domain of REACH!

The instrumentation of REACH is differentiated and targeted to this complex regulatory field. And the waste phase, as shown, is explicitly subject to exposure scenario building, which in turn is the basis for substance evaluation and the resulting management measures to be derived.

For this it must be questioned whether the stipulations in REACH and in the relevant guidance documents are sufficient to solve the explained problem of RISKCYCLE. The represented stipulations for the determination of exposure scenarios in the waste stage are, in our view, sufficiently detailed as well as extensively and professionally prepared to solve the problems of RISKCYCLE through REACH implementation.

Problematic is the implementation of REACH within the personal responsibility of the registrant for his registration dossier. Our thesis is that the quality problems that are currently often deplored at the main registration pathways are likely to become even more serious on “side roads.” And from the perspective of a chemical manufacturer the waste stage is commonly seen as such a side road. To solve this, we have three suggestions:

1. The RISKCYCLE issue should be explicitly noted in the regulatory text to raise awareness among the registrants of this topic.

2. The ongoing analysis of registration dossiers should be considered and performed with sensitivity to the waste stage. This should also be done for the selection of substances of very high concern (SVHC, candidate list). For this purpose this task should be designated to the ECHA.
3. A previous proposal given in the process of designing REACH could be helpful: the introduction of quality assurance mechanisms in REACH regulation. This proposal could not be implemented due to the lack of majority during the political decision process on structuring REACH. But today's situation shows that such a mechanism is needed. Quality assurance mechanisms could be arranged privately. Before a registration is submitted the file could be proofed by an independent expert for completeness and defined content requirements. Without such an examination a registration would be incomplete.

The auditors themselves may be obliged to undergo an approval process for independent and high quality work. Since the amendments to REACH are currently on the European political agenda, 2012 would be a convenient time to introduce these three proposals.

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Part II
Case Studies

Two Sides of One Coin: Relations Between Hazardous Substances and Valuable Resources

Henning Friege

Abstract Many hazardous substances of today had been looked at as valuable chemicals some decades ago. At present, management especially in the case of scarce, non-renewable resources is of growing importance. The experiences collected with the management of contaminants might be helpful also for valuable resources. This is demonstrated using two well-documented examples, Cd and PCBs. Pt serves as a counterexample to prove if the DPSIR method can be applied to contaminants and resources without fundamental changes. Some of the countermeasures introduced to control environmental contaminants may also be applied to save non-renewable resources.

Keywords Cadmium, DPSIR method, Hazardous waste, PCBs, Platinum, Resources

Contents

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1 Introduction

Resource conservation and resource recovery are an issue of growing importance on the agenda of international policy [1]. With respect to the basic rules of sustainable management of substance chains, “the consumption of non-renewable resources should be limited to levels at which they can either be replaced by physically or functionally equivalent renewable resources or at which consumption can be offset by increasing the productivity of renewable or non-renewable resources” [2, 3]. Societies all over the world are far away from complying with this rule. Increasing amounts of non-renewable resources may lead to regional or worldwide scarcities already indicated by a steep increase of the prices for some specific resources. This is especially true for some rare metals. Many of these elements have never been used in industrial scale before the last decades of the twentieth century. Now, the demand is rising rapidly for industrial use mostly for very interesting technologies and private consumption mostly in electric and electronic devices. These metals are either found in extremely low concentrations in minerals or are mixed up with other elements with similar physical and chemical properties. Therefore, separation processes are difficult and energy consuming. Especially rare earth metals and the elements of the platinum group (PGM – platinum group metals) are only mined in few areas in the world. Therefore, the supply with these elements is endangered by technical, economical and political obstacles. The European Commission started strategic work on resources [4, 5] focussing on

- A globally free market for non-renewable resources
- More extraction of minerals in Europe
- Higher efficiency in the use of resources and recycling

2 Outline of the Problem

Waste management is expected to contribute to resource conservation by the recycling of used goods. There are a lot of experiences with the recycling of resources from used goods (paper, cardboard, glass bottles, plastic packaging…) made of renewable as well as of non-renewable resources. All these goods have a more or less homogeneous composition based on easily available materials. The recovery of scarce resources from waste turns out to be far more difficult. This may be easily explained by the general dilemmas of waste management [6, 7], i.e.

- The entropy dilemma, i.e. small concentrations of valuable substances in used products leading to complicated and energy consuming recovery processes
- The dissipation dilemma, i.e. high dissipation of products being an obstacle for collection

- The double role of waste and valuables, i.e. contamination of used items containing valuable resources by dangerous compounds
- Different opportunity costs for waste disposal for people with different inducing informal collection activities
- A time lag between the production of a good and its final fate as waste leading to lack of specific secondary resources during the useful life of the items

Quite a number of useful chemicals introduced some decades ago later turned out to be hazardous and have therefore been substituted by other substances. Very often, the following phases are observed:

- Placing the substance on the market for few applications
- More and more application fields
- Hazardous properties published; public pressure against further use
- Substitution of the substance in question by less hazardous alternatives
- Adaption of concentration limits (emission, food...) in case of persistent compounds
- Ban of the substance often with a transition period depending on the application area
- Phasing out of products containing the substance in question (going to the waste bin)
- Special treatment requirements for waste including the hazardous substance

Especially in the case of solid substances, waste management is responsible for the clean-up of the technosphere, i.e. collection and disposal of the chemical in question. With respect to hazardous compounds in used goods, tools have been developed to phase out these goods for special recycling procedures or safe disposal.

The experience collected with hazardous compounds in waste shall be compared with the problem of scarce resources in waste using well-known examples. The comparison must be extended to other phases of the “life cycle” of products, because waste management is only a part of substance chain management. The instruments used for the management of hazardous chemicals will be analyzed using some examples to answer the question if they could also be useful for scarce resources.

3 Cadmium

Cadmium (Cd) has a number of interesting technical characteristics. Plating with Cd yields high protection against corrosion also in saline environment. CdS, CdO, CdSe, and mixed salts are thermally stable pigments showing bright and luminous colours. Cd stearate turned out to be an excellent stabilizer for PVC against sun light. Ni/Cd is an electric cell with a battery voltage of 1.2 V. Recently, CdTe has been introduced as semi-conducting material in photovoltaic (PV) thin layer cells.

In the twentieth century, Cd was declared to be an element of strategic importance by the U.S. government (cited from [8]) due to its importance for plating (marine applications) and accumulators. The atomic structure of Cd resembles zinc (Zn) and also calcium (Ca). Zn ores contain Cd in low concentrations. Therefore, Cd is normally obtained as a by-product of Zn smelting, but is also found in the dust of copper and lead smelters. Small concentrations of Cd are found in phosphate minerals depending on the origin (Morocco/Sahara ~60–120 ppm, North America, Russia ~20 ppm with respect to P_2O_5 [9]). Traces of Cd are also found in coal and oil thus leading to emissions from treatment of fuel and power stations.

From the 1950s on, there were findings that Cd is toxic for humans in low concentrations. The important target organs are kidney and liver, Cd accumulating mainly in the adrenal cortex. Its half-life in humans ranges between 10 and 30 years. Cd and CdO are assessed to be potent carcinogens. Some years ago, the tolerable weekly intake (TWI) has been decreased by a European group of experts to 2.5 μg/kg b.w. (body weight) [10]. The mean intake of Cd by German citizens is about 1.5 μg/kg b.w.; in special groups like vegetarians with high food consumption or smokers the TWI might be exceeded [11].

The production peak (world wide production ~20,000 Mg) was attained in the 1980s. In 2004, the overall production in Europe was about 4,600 Mg, nearly half of the production volume being exported [12]. The production figures mean isolation of Cd as a pure metal. Besides that, Cd is found as an impurity in commercial Zn products and as part of the waste from Zn smelters.

To address the root of the problem, chemical policy focuses on the substance itself: With respect to the inherent hazards of Cd-containing products, all highly entropic applications like pigments, stabilizers, and plating have been banned. Following the Battery directive [13], more than 0.002% Cd (w/w) in accumulators is prohibited with the exception of medical appliances, military use, alarm systems and cordless electric tools. In electric and electronic devices, Cd concentrations may not exceed 0.01% as stipulated by the RoHS Directive [14, 15]. This is not valid for PV cells: the amount of CdTe used in this field is increasing enormously. Today, CdTe semiconductors in thin layers and Ni/Cd accumulators are the most important application areas for Cd in Europe, the first increasing, the latter decreasing. The concentration of Cd in Zn and products containing Zn is restricted by quality requirements defined in the European standards EN 1179 (for refined Zinc metal) and EN 10240 (for Zinc coatings of steel, e.g. pipes). To reduce emissions from production and recycling, limit values have been set up for waste water, exhaust gas, and sludge from waste water purification to be used as fertilizer. There are also threshold values for environmental compartments like surface water. Cd concentrations in food are also strictly limited to protect the consumers, who are exposed especially by the consumption of liver, kidney, mushrooms and bread. As to the remaining appliances, recovery after use is important:

- Ni/Cd accumulators are collected with respect to the Battery Directive, the collection target being 25% with respect to the amount of batteries sold. As to Germany, in 2009 1,141 Mg Ni/Cd accumulators were collected and 802 Mg sold [16]. As the time of sale is not known, recovery quota cannot be calculated from these figures. In 2004, the relation between used Ni/Cd accumulators collected and Ni/Cd accumulators sold was about one third [17]. With respect to all types of batteries and accumulators sold, the European collection target will be enhanced up to 35% (starting in 2012). In Germany, the collection has reached 44%. It is reasonable to assume that about 50% or more of Ni/Cd accumulators are not collected separately. A compulsory deposit for Ni/Cd batteries has therefore been discussed to enforce the return.

– CdTe cells have to be collected after use following the latest revision of the WEEE Directive, the collection target corresponding to other e-waste [18]. Until 2016, the yearly collection target of 4 kg per inhabitant remains valid. Starting in 2016, the collection target for used electrical and electronic equipment will reach 45% (65% after 2019) of the products sold with respect to the average of three foregoing years. Considering the long lifetime of PV cells, this regulation is not practical without further provisions. As PV cells have been integrated into the WEEE regulation [18], producers are enforced to give a take-back guarantee independent of the average useful life of the devices. Some producers already started the setup of a voluntary take-back system before the amendment to avoid a legally binding rule [19].

Complete balances based on the analysis of material streams containing Cd in relevant amounts have not been published in the literature in the last years with few exceptions which are based on data from the beginning of the century [12, 20]. Therefore, the actual mass flow of Cd into the technosphere and its further fate in the environment after use cannot be described quantitatively. The overall emissions from German point sources sum up to about 2 Mg in the year 2009 [21] being very small as compared to the Cd flows from products. Among the point sources, power stations and steel mills are remarkable where Cd is emitted as a contaminant from fuel or from scrap. Part of the emissions originates from recycling of scrap including high levels of non-ferrous metals like Cu, Zn, Pb where Cd is an accompanying element. According to the register [21], there is no WtE plant among the important point sources.

Dissipated products containing Cd like pigments, stabilizers and plated compounds will be found in normal waste. As outlined above, this might be also valid for ~50% of the batteries. The concentration of Cd in municipal waste ranges from 6.1 (rural areas) to 11.1 (cities) g/Mg dry waste [22]. This relatively large mass flow of approximately >100 Mg is split up by disposal in MWIs, the amount of Cd leaving the stack as flue gas is $<1\%$ as compared to the input [23, 24]. Normal MWIs with a mean input of 6,700 mg Cd per Mg waste have very low emissions of about 4.6 mg per Mg input [25]. Cd retained in flue ash is going to underground mines, the other part remains in bottom ash.

Long-lasting measurements of the environmental background contamination (particulate matter and air in areas far away from cities and industry) and analytical data of food and biota prove that the transport into the environment is slowly decreasing. The actual emissions in Europe decreased from 500 Mg/year (1990) to about 250–280 Mg/year (2005–2008) [26], diffuse sources becoming more and more important. In areas far away from remaining point sources, resuspended particles add up to about 50% of the immission. Having these trends in mind, future Cd immissions may remain constant.

The view at Cadmium changed with time starting from a valuable resource and ending up as a toxic element with a limited number of applications not substituted by alternative products. The decontamination of the technosphere works to a certain extent. Due to the character of Cd as trace contamination of phosphate fertilizers and of Zn ores and fossil fuels, there is no final solution for the environmental contamination. Due to the restrictions issued in many countries, there is reason to fear that Cd could end up in unknown material streams. From an analysis of the refining of Zn ores in 2002, it has been concluded that about one quarter of Cd generated as by-product (~7,000–8,000 Mg) could not be found either in the products analyzed or in the emissions from the process [27].

4 Polychlorinated Biphenyls

The production of polychlorinated biphenyls (PCBs) started in 1930 driven by the need for hardly inflammable isolation material for capacitors and transformers. PCBs were also introduced as heat exchanger fluids because of its good thermal conductivity. Its stability against heat led to application in mines as hydraulic fluids. Due to recognition about toxic and cancerogenic properties starting with the Yusho disease in 1968 and scientific findings about the enormous accumulation of PCBs in marine sediments and biota, pressure against this group of substances sharply increased. Therefore, the use and/or the production of PCBs were banned in industrialized countries, first in Japan. PCBs number among the persistent organic pollutants banned world wide (POP convention). Today, the PCB contamination of German citizens by food is in the range of the TWI, in special groups also above the TWI [28]. The body burdens decrease slowly [29].

Some typical areas of former use are presented in Table 1 with an assessment of the problems coming up with the separation of used products containing PCBs. The overall production was about 1.5 Mio Mg until the end of the eighties. Many production lines ceased already until 1980. In Europe, PCBs were banned first for "open" [30], then for "closed" applications [31]. But many of the closed applications turned out to be open in reality, as has been demonstrated for hydraulic fluids used in German coal mines, where up to two third of the annual consumption of PCBs were lost [32].

About one third of the overall production was applied in buildings used as additives to dyes and joint sealers. Normally, the use of PCBs in the materials is not (more) known to the inhabitants or users of the houses. Only in the case of secondary contamination of ambient air or food detected by chance or by systematic search, those buildings were decontaminated. Spreading of PCBs into the environment was accelerated by mixing of used hydraulic or heat exchanger fluids

Table 1 Some important applications of PCBs in relation to waste management

	Type of PCB used	Type of application	Intended way/normal way of disposal	Separation from other items
Isolating agent in transformers	Cl $\geq$ 54%	"Closed"	Special waste	Easy
Hydraulic fluid in mining equipment	Tri- and Tetra-CBs	"Closed"	Special waste/waste water from mine draining	Difficult in underground mines
Isolating agent in small capacitors	Cl $\leq$ 42%	"Closed"	Waste from electric and electronic equipment/ household waste	Possible in state-of-the-art sorting plants
Additive to joint sealer	All technical mixtures	"Open"	Hazardous waste/ mixed construction waste	Possible in state-of-the art dismantling processes

with waste mineral oil which was refined and used as marine diesel. To stop this contamination pathway, oil with more than 50 mg/kg PCBs has to be treated as PCB waste [33].

In the case of transformers and industrial hydraulic equipment, PCBs were used together with steel, copper and other valuable materials. An exchange of PCB containing equipment at once short after the PCB ban

- Would have led to stranded investments
- Would have overloaded the disposal capacities available at that time

Therefore, closed-loop appliances, i.e. transformers and large capacitors, with PCB concentrations over 50 mg/kg could be operated further until 2000, in case of a special exemption also until 2010. These devices could be easily identified by a compulsory label. It is assumed that an overwhelming percentage of these items were separately disposed. Instead of disposal of the complete devices, isolating fluids can be exchanged by other chemicals. The complete cleaning of contaminated transformers is somewhat difficult and should be done very carefully to avoid PCB impurities after refilling with other liquids [34]. These impurities originate from PCB oil adsorbed on copper windings and on the walls as a sort of tailing which leads to increasing concentrations in the new isolation fluid. Therefore, most of the transformers and large condensers were stored in salt mines as complete devices. Due to increasing copper prices, a lot of transformers already disposed under ground have been brought back to treatment plants in the last years. If the contaminated fluids are completely removed in a cleaning process, this might be a good method to save resources. But again, the cleaning procedure turned out to be unsafe. A company specialized on this treatment was closed down in 2011 because of remarkable pollution of its workers and contamination of the facility [35].

Small capacitors containing PCBs and "electrolyte capacitors containing substances of concern" must be separated in sorting plants according to the WEEE Directive [36]. These capacitors with a unit weight between 100 and

300 g (a third of this being PCBs) [37] have been used until the end of the 1970s, may be also later (imported domestic appliances). From a technical point of view, more than 95% of all PCBs in electronic waste can be separated by the first step in a sorting plant [38]. In a report of the German government, it is assumed that about 3.5 Mg capacitors contaminated with PCBs were separated and disposed in 2008 in sorting plants [39]. In some e-scrap sorting facilities, PCB contaminations were detected [40, 41] probably due to accidentally destroyed capacitors.

It is assumed that most small items containing PCBs, sealers, dyes, etc. have been disposed with household or construction waste. Due to numerous dissipative applications, on the one hand, and high persistence of PCBs, on the other hand, the contaminations will last for further decades.

5 The DPSIR Approach

The most important measures introduced to avoid spreading of Cd and/or PCBs into the environment may be summed up as follows:

- The ban of applications being open to the environment
- The prohibition of mixing up the contaminants with other chemicals
- The introduction of strict emission limits for production and disposal facilities
- The definition of concentrations for waste (in the case of PCBs) to be kept separately
- The introduction of quality levels (e.g. in the case of Cd/Zn and for used oils)
- The limitation of transfer of the contaminants via sewage sludge used as fertilizer

Limit values for food and fodder do not decrease the environmental burden. Indeed, regulations of this type are a signal for the public enforcing the producers to avoid contaminations in the chain of food production. Thus, the food industry is acting as a steward influencing other industries: the pressure against unsafe management of contaminated by-products and waste increases. The labelling of large devices including the contaminant serves as a caution signal leading to safe handling of these devices to avoid accidents.

Experiences of this type are the basis of the DPSIR (“driving forces – pressure – state – impact – response”) approach (Fig. 1), which has been introduced in environmental policy as a link between ecological problems and economic and social responses [43].

The examples reported above may be described in terms of the DPSIR framework. Production and use of Cd or PCBs, respectively, are *driving forces*, whereas the *pressure* has grown by emissions from production, waste disposal and particularly from dissipative use in open systems (Cd: erosion of plating material or pigments. . ., PCBs: evaporation from sealers. . .). Concentrations of the substances in question analyzed in environmental compartments represent the *state* of the

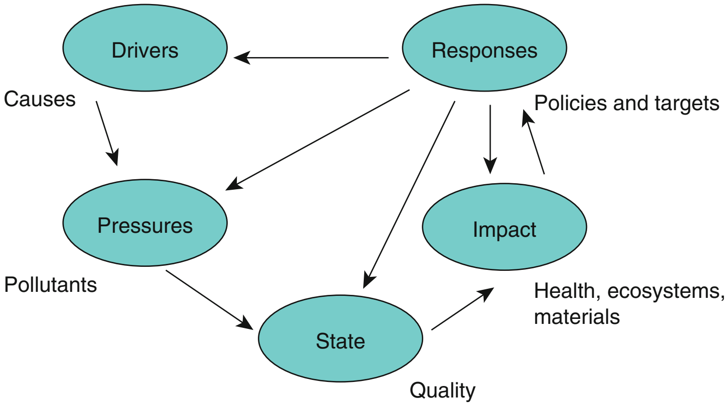

Fig. 1 The DPSIR scheme [42]

contamination. The burden of man and biota as well as harmful effects may be taken as *impacts* caused by environmental pollution. All measures taken to decrease the emissions of these substances, to recall products containing Cd or PCBs or to reduce environmental contamination are interpreted as *responses* relating either to direct impacts or to pressures or to the source of the problem, i.e. the driving forces mentioned. Actions taken against Cd and PCBs as well as the specific objectives are summarized in Table 2.

It is obvious that the driving forces causing the widespread use of a substance do not change, when the substance in question turns out to be hazardous. To look deeper into the potential comparability between valuable and hazardous compounds, Platinum (Pt) may serve as an example. Mining of Pt is energy consuming and causes enormous heaps of rock. The overall consumption worldwide is about 200 Mg/year. (For a detailed material flow analysis, see [44] and the literature cited therein.) In contrary to contaminants, the "impact" mainly results from the scarcity of Pt. Very similar to the contaminants presented here, "pressure" results also from dissipative uses leading to significant losses [45]. Increasing Pt concentrations are found in soil in the vicinity of highways caused by emissions from catalysts ("state"). Due to its high adsorption to soil, the mobility of Pt is low as compared to many other metals. Organometallic molecules with Pt acting as central element are found in waste water indicating considerable risk because of the physiological effects of cis Pt complexes used as anticancer drugs. (For more details see [45] and literature cited therein.) So, we can realize that "pressure", "state", and "impact" for a valuable resource resemble the situation found for hazardous substances. In the case of Pt, there is a flowing transition from "valuable" to "hazardous" characteristics. Pt is therefore referred to as a "green polluter" [44] or as a "Janus faced" element [45]. In the case of valuable resources widely used, the high anthropogenic material flow represents the most important pressure driven by production and consumption. Therefore one might differ between system-turnover-based indicators and impact-based indicators [44], the first relating to the input

Table 2 Experiences with Cd and PCBs compared with Pt in the framework of the DPSIR approach

		Cd	PCBs	Pt	Comparison between hazardous and valuable substances
D	Needed for economically important application fields	+++	(+++)	+++	Comparable
D	By-product from the synthesis of other substances or contamination of a valuable product	+++	+	–	Different
P	Emissions of the substance from production, processing, recycling	(+++)	(+)		Not investigated for Pt
P	Application areas open to the environment or dissipative use	++	(++)	++	Comparable
P	High dispersion in the environment and highly accumulative	+++	+++	++	Comparable
P	Huge amount used	(++)	(+++)	+++	Comparable
S	Significant concentrations in samples from the environment	+++	+++	+	Partially comparable
S	Dispersion of a toxic substance	+++	+++	+	Pt: this depends on the molecular structure
S	Anthropogenic production significant as compared to geogenic flow	+++	+++	+++	Comparable
S	Contamination of sinks (soil, sediment, atmosphere…)	+++	+++	+	Partially comparable
I	Contamination of food	+++	++	+	Partially comparable
I	Impacts on man	+++	+++		Different by today's knowledge
I	Impacts on other biota	+++	+++		Pt: Not investigated
I	Impacts on environmental systems	+	+		Pt: Not investigated
I	Scarce resource	–	NR	++	Completely different from today's view
I	Obstacle for recovery of other valuable resources	+++	++	NR	Different
R	Emission limits for the substance from production and recycling processes	+++	+		Different
R	Limit values for food and feed	+++	+++	NR	Different
R	Limit values for workplaces	++	++	NR	Different
R	Substitution and/or closed loops for some products	+++	+++	++	Comparable
R	Ban for some/all applications	+	+++		Matter of policy
R	Special methods for disposal and/or recovery	++	++	+++	Comparable

Explanation of the table: +++ very important, ++ important, + less important, – not valid. *D* Driving forces, *P* Pressures, *S* State, *I* Impact, *R* Response, *NR* not relevant for this example. Data in brackets refer to former use or emissions in the technosphere, the latter relating to the output into the environment. In the case of Pt, we can indentify both. The view at Cd – see above – has changed from input problems (scarcity) to output problems (environment) as impact.

The cases of Cd, PCBs, and Pt are compared in Table 2 following the empirical DPSIR approach. Considering many similarities and some differences between valuable and hazardous compounds, it is interesting to look for common "responses". As to the life cycle, substitution is a big issue for scarce as well as for hazardous materials. In the case of hazardous substances, substitution is mostly driven by legal issues, i.e. prohibition of certain appliances. In the case of scarce resources, substitution is normally driven by the market. For many scarce metals, signals indicating shortage in the long run may come too late to avoid wasting non-renewable resources. The demand for rare metals needed for "green technologies" is increasing continuously sometimes doubling within a few years (see for example [46, 47]). It is therefore reasonable to enforce the substitution of these resources, especially in the case of dissipative and/or open uses as it is found for Pt.

In the time lag between placing of a chemical on the market and regulations after scientific findings about potentially hazardous properties, the chemical is spread out in numerous application areas. In this case, waste management has the role of a vacuum cleaner for the technosphere. In the case of a scarce resource, the situation is very similar. Considering waste management as part of the "response", both groups might be managed in a similar way, i.e. separate collection of devices which include hazardous or scarce substances also as a minor component. It is therefore useful to establish regulations fitted to the type of waste in question. From the collection, recycling, and disposal of waste from electric and electronic devices we have learned that the difficulties are comparable for waste containing valuable resources and hazardous compounds, respectively [48]. There is one important exception: If the prices of the resource in question are high and only little efforts are needed for the separation from normal waste, the informal sector will start cherry picking thus disturbing public initiatives. The introduction of take-back systems well known for batteries which are enforced by deposits could be a solution for the collection of dissipated devices containing small amounts of scarce materials.

6 Conclusions

From an empirical evaluation of the tools used to minimize the emissions, the environmental contamination, and the exposure of man by hazardous chemicals one may conclude that the following strategies could also be applied to save scarce resources:

- The prohibition of use in dissipative application fields is the most important step to reduce the distribution in the technosphere and to minimize the spread into the environment.

- The concentrations of hazardous substances in waste are often limited with respect to different disposal methods. This could also be discussed for valuable resources to avoid mixing up of products containing the resource with other waste items. If this dilution cannot be avoided, disposal in landfills or reuse as part of construction material will lead to non-retrievable losses.
- Compulsory return especially of devices used commercially is very helpful for the recovery of hazardous materials as well as goods with valuable resources. In the latter case, economic incentives are needed as well.
- Strict labelling requirements for appliances containing hazardous substances lead to attention in handling those devices especially if safety at work is affected. But in case of valuables, this might produce opposite effects. (The message "don't waste this product – valuables included" will encourage people to keep the useless product instead of dropping it into the correct recycling bin).
- Labels indicating correct disposal may also be helpful, but are very often ignored if there is no obvious danger for the waste producer in case of acting against the label's advice. In the future, invisible identification tags like the RFID technique could help to sort out the devices in question from the waste stream.
- For persistent hazardous substances, inventories covering production, trade, application fields, and disposal are extremely helpful to identify sources and sinks in the technosphere and in the environment. Data covering the flows of valuable resources are necessary as well and should be documented by the responsible parties dealing with these resources. Material balances based on the inventories are helpful also to get an idea of unknown sources and undetected leakages in the technosphere, even if the figures sometimes might be questionable.
- The DPSIR scheme is a reasonable approach also in the case of valuable resources, if we define the impact as (potential) shortage of a resource. This is an input-oriented problem caused by high anthropogenic flows of a scarce non-renewable resource.

More examples should be checked using this approach to learn from the management of hazardous substances for the management of resources.

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Toxicological Characterization of Waste-Related Products Using Alternative Methods: Three Case Studies

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Abstract The characterization of toxicological impact of chemicals and mixtures from environmental matrices is a critical point in the assessment of adverse effects induced in human and ecological targets. In fact, the toxicity of most of the environmental mixtures is still under investigation due to the possibility of synergic or antagonistic effects of the components. Moreover, in some cases, the toxicity of identified chemicals is not already well known and it could be an additional matter of concern.

Encouraged by recent legislations all over the world aimed to protect human health and environment, alternative methods have proved their abilities to assess the toxicity of chemicals. Hence, a possible solution to the characterization of the toxicological and ecotoxicological risk of the chemicals could be represented by the application of in silico and in vitro techniques.

However, only a limited number of studies using alternative methods (testing and non-testing) are present in the scientific literature but the studies are increasing and becoming more important and spread day by day, in particular for the evaluation of mixtures derived from environmental matrices.

Among the possible solutions, in vitro assay and QSARs models are the most applied approaches in the field of environmental research and risk assessment.

In this chapter three case studies are introduced as examples of the application of alternative methods for the toxicological characterization of waste-related products.

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The first case is an integrated approach based on chemical analyses, risk assessment, and in vitro assays for the investigation of the toxicity of a leachate produced by a modern industrial landfill in Italy.

The second example focuses on qualitative evaluation of cancerogenic potential of some perfluorinated compounds using both QSARs models and an in vitro cell transformation assay.

Finally, a QSAR evaluation of different chemicals from waste-related products and recycling is shown in order to underline how in silico models can be used as a valid tool to fill in the gaps and to obtain information on toxicological profile and physicochemical information on compounds. In particular, a focus on compounds suggested by EU project "Riskcycle" is presented.

Keywords Alternative methods, Chemical carcinogenicity, Mixtures, Toxicological profile

Contents

1 Introduction

The assessment of acute and chronic adverse effects induced by chemicals in both human and ecological (plants, animals, ecological chains, and ecosystems) targets is one of the most important scopes of environmental toxicology and sciences. In particular, the evaluation of the risk derived from the exposure to complex mixtures from environmental and diet sources is a challenging task which needs strategies, efforts, and time to reach the objectives of health protection.

Moreover, nowadays there are still thousands of chemicals, including industrial xenobiotics, natural products, and pesticidal active and inert ingredients, with the potential for significant human exposures but for which toxicity information is either limited or nonexistent [1]. The requirements arising from the regulation and the need to better characterize the toxicological, ecotoxicological, and environmental properties of an increasing number of chemicals have the consequence of an increased number of animal experiments to provide answer to these data needs.

The data gap could be solved conducting animal testing in rodents and other species which requires high cost and time: thousands of animals are used to perform a complete set of regulatory tests for a single chemical and costs millions of dollars [2].

Carcinogenicity and chronic, reproductive, and developmental toxicity are the most animal-consuming studies.

However, this request of more animal testing faces several issues. There is an ethical concern on the millions of animals used every year for experiments. These tests are also those more expensive, and thus this poses questions about the costs for these experiments and the resources to cover them. Many of these tests, especially the chronic ones, require long times, years in some cases. The number of available laboratories in Europe to cover this potential request is insufficient. For all these reasons, some European regulations foresee the use of methods alternative to animal tests, such as the REACH legislation, and actually the cosmetics directive foresees the complete ban of animal tests for cosmetics by 2013.

Alternative methods includes “any method that can be used to Replace, Reduce or Refine the use of animal experiments in biomedical research, testing or education” [3]. The term “alternative” includes all procedures which can completely replace the need for animal experiments, reduce the number of animals required, or diminish the amount of distress or pain suffered by animals in meeting the essential needs of man and other animals [4].

Replacement consists in the use of non-sentient organisms (e.g., microorganisms, metazoan parasites, and higher plants) as possible alternatives of higher animals for experiments, also the including stages of development where it is recognized that organism is able to feel pain. Experiments using these materials could be defined “absolute replacement” when no higher animals were required at any stage or “relative replacement” if methods require non-sentient material with animal origins. The Reduction occurs when a method reduces the number of animals needed to perform a specific assay, while still achieving the same level of information (best quality information with the smallest possible number of animals). Refinement is referred to all changes in protocols that reduce the incidence or severity of distress experienced by laboratory animals.

An important point, made by the European Centre for the Validation of Alternative Methods (ECVAM), is that these 3 aspects (3Rs) should not be considered as alternatives that could replace each other, but as parts of an integrated system which should lead to progress in the development of non-animal tests and testing strategies. Another important key point recently defined by ECVAM is that the use of existing information *must be maximized* instead of testing methods.

For this purpose some useful data can be:

- The production volume
- The reasons for uses
- The studies of occupational or environmental exposure
- The physicochemical properties of chemicals (for example stability, solubility, pH, octanol-water partition coefficient, protein binding)

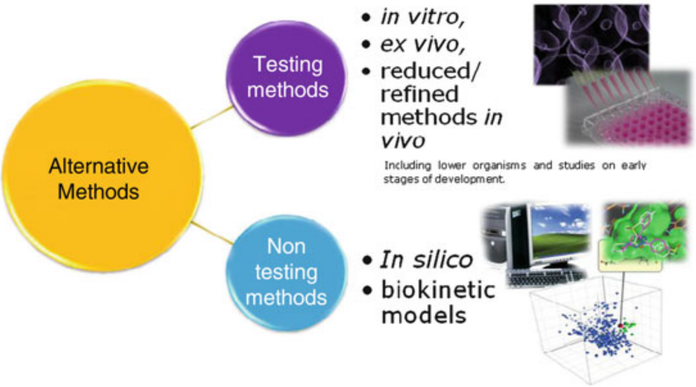

Fig. 1 Classification of alternative methods

- Epidemiological investigations
- Post-marketing surveillance for medicines, cosmetics and household or agricultural products

Alternative methods could be classified into *testing* (ATMs) and *non-testing methods (ANTMs)* (Fig. 1) [5]. The first class includes experiments on lower organisms (bacteria, fungi, plants, invertebrate animals), studies on vertebrates at early stages of development (before they become sentient/protected animals) and studies on in vitro systems of various kinds (including whole perfused organs, tissue slices, cell, tissue and organotypic cultures, and subcellular fractions). The second group is represented by predictions based on structure-activity relationships (SARs) (qualitative and quantitative mathematical models, and the use of read-across data from related chemicals) or the biokinetic modeling of physiological, pharmacological, and toxicological processes.

Among the possible alternative methods, in vitro assay (for ATMs) and quantitative structure-activity relationships (QSARs) models (for ANTMs) are the most applied approaches in the toxicological and ecotoxicological evaluation of chemicals' profiles, even in the field of environmental research and risk assessment.

Encouraged by recent legislations all over the world aimed to protect human health and environment, alternative methods have proved their abilities to assess the toxicity of chemicals. Hence, a possible solution to the characterization of the toxicological and ecotoxicological risk of the chemicals could be represented by the application of in silico and in vitro techniques.

However, only a limited number of studies using alternative methods (testing and non-testing) are present in the scientific literature but the studies are increasing and becoming more important and spread day by day, in particular for the evaluation of mixtures derived from environmental matrices.

In this chapter, three case studies are introduced as examples of the application of alternative methods for the toxicological characterization of waste-related products.

The first case is an integrated approach based on chemical analyses, risk assessment, and in vitro assays to investigate the toxicity of a leachate produced by a modern industrial landfill in Italy.

The second example focuses on qualitative evaluation of carcinogenic potential of some perfluorinated compounds (PFCs) using both QSARs models and an in vitro cell transformation assay (CTA).

Finally, a QSAR evaluation of different chemicals from waste-related products and recycling is shown in order to underline how in silico models can be used as a valid tool to fill in the gaps and to obtain information on toxicological profile and physicochemical information on compounds. In particular, a focus on compounds suggested by EU project “Riskcycle” is presented.

2 Alternative Methods for the Study of Landfill Leachate Toxicity

Solid wastes constitute an important and emerging environmental problem at a global scale. A recent study from Bakare et al. suggests that the production of solid wastes varies from 0.5 to 4.5 kg per person per day in different regions of the world [6]. It is therefore clear that proper management of the waste problem must be nowadays at the center of the management policies of each nation in order to reduce the local and the global impact.

The most common methods for dumping off wastes are the storage in landfills or the incineration in incinerator plants.

Between these two solutions, landfills are considered the most widely practiced methods for the disposal of municipal solid waste (MSW): actually up to 95% total MSW collected worldwide is disposed off in landfills [7]. Landfilling is a fundamental step in any waste management strategy but it can constitute a hazard for the environment in the long time. Generally, landfills will produce mainly two kinds of by-products: a highly toxic leachate and a significant amount of landfill gases. Gas components can be partly used to produce energy while liquid residues could not be used for energetic purpose. Leachate and gas control measures are very important in order to reduce the overall environmental impact from a waste disposal site [8]. The need to protect the environment from potential landfill emissions makes risk assessment a decision tool of extreme necessity [9].

Landfill leachate is generated by the infiltration and percolation of water (not only mainly rainfall but also groundwater, runoff, or flood water) into and through the waste layers of a landfill site. From a toxicological point of view, leachate is the results of a combination of physical, chemical, and microbial processes in which pollutants transfer from the waste material to the percolating water, creating a water-based solution that may be harmful to organisms, including human and environmental receptors. In fact, due to its intrinsic properties and composition, small amounts of leachate could pollute large volume of groundwater, rendering

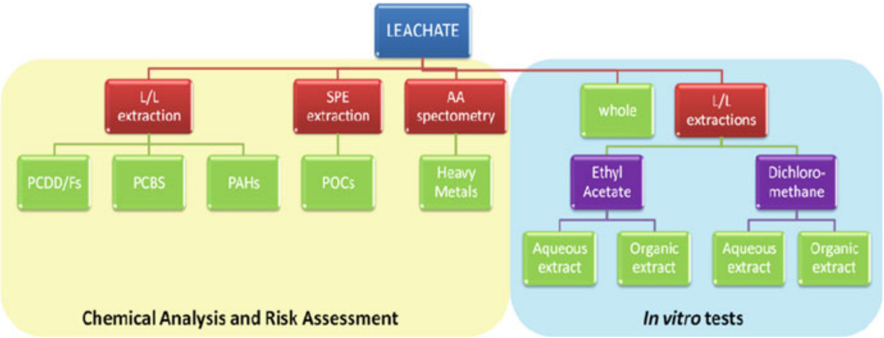

Fig. 2 Design of the experiment for the investigation of leachate toxicity (modified from [17])

them unusable for domestic and many other purposes. More than 200 organic compounds have been identified by previous studies in municipal landfill leachates: inorganic salts, heavy metals, and xenobiotic organic compounds [10–12].

Different international legislations and guidelines have been released to underline and highlight the role of ecotoxicological and toxicological risk assessment (ERA and HRA) methodologies in the last 20–30 years [13–16]. These technical methodologies could also be applied for the assessment and the evaluation of pollutants from landfills, facing one of the major environmental issues in Europe due to the large number of sites and to the importance of groundwater protection.

A recent study published by Baderna et al. in 2011 describes a combined method to investigate the toxicity of an industrial landfill's leachate which is based on a triad approach including chemical analyses, risk assessment, and in vitro assays [17]. Moreover, to verify the applicability and the robustness of the proposed method, the approach was applied on a real case study: a controlled, ISO-14001 certified landfill for nonhazardous industrial waste and residual waste from the treatment of MSW in northern Italy for which data on the presence of leachate contaminants are available from the last 11 years.

First step of the approach is the chemical characterization of leachate using well-established analytical techniques (Fig. 2): GC-MS for polar organic compounds (POCs), HRGC-MS for PCDD/Fs, PCBs and PAHs [18], atomic absorption spectrometry for heavy metals and ion chromatography for ammonia.

Regarding POCs, eight compounds (see Table 1) were selected as "indicators" from the qualitative analysis of leachate due to their frequent detection, to their abundance, and to their absence in groundwater wells monitored upstream the landfill. The selected compounds include plasticizers or their degradation products, insect repellent and natural compounds resulting from anthropogenic pollution.

Levels of analyzed compounds were comparable with those reported in previous studies with the exception of cadmium, ammonia, 2(3H)benzothiazolone, and bisphenol A, which were higher than the published data regarding long-term composition of MSW landfill leachate from some European MSW landfills while

Table 1 Selected polar organic compounds (POCs) for the quantitative analysis

Indicator POCs
2-Phenyl-2propanol
2-Ethyl hexanoic acid
2,2,6,6-Tetramethyl-4-piperidinol
Nicotine
Bisphenol A
α,α,α,α-Tetramethyl-1,4-benzenedimethanol
N,*N*-Diethyl-m-toluamide
2(3H)-Benzothiazolone

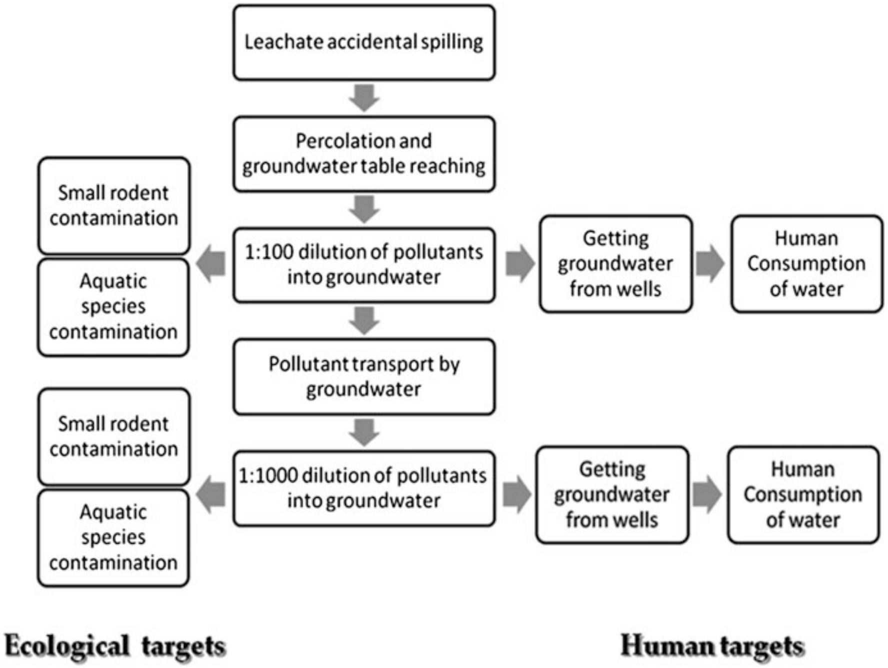

Fig. 3 The hypothesis for the risk assessment (modified from [17])

no comparative data are reported in the literature for other compounds with recognized carcinogenic potential such as dioxins, PCBs, and PAHs.

Data from chemical characterization were used to estimate possible adverse effects on humans and the environmental receptors. Following previously published works [11, 19], a hypothetic scenario was set up to assess the risk posed by these non-conventional matrix: an accidental leachate release into groundwater resulting in 1:100 and 1:1,000 dilutions of the leachate compounds, which have been subjected to dilution as the leachate mixes with the groundwater (Fig. 3).

Human risk assessment (HRA) was done applying guidelines from the Italian Institute for Environmental Protection and Research (ISPRA) and selecting water ingestion as route of exposure for human health assessment [20]. According to the guidelines, for each compound, chronic daily intake (CDI), Hazard Index (HI) for toxic compound and Cancer Risk (CR) for carcinogenic effects were calculated and exposures associated with $HI<1$ and $CR<1E\text{-}6$ were deemed negligible.

For the ecological assessment, risk analysis was based on the traditional PEC/PNEC ratio (Hazard Quotient) where PEC is the predicted environmental concentration (resulting from chemical analysis) and PNEC the predicted no-effect concentration. Ecological assessment for aquatic species was based on rainbow trout or fathead minnow while terrestrial assessment was based on small rodents like mice rats and rabbits. Exposures associated with $HQ<1$ were considered negligible.

Reference toxicological values for HRA for the selected pollutants were obtained from ISS/ISPESL [21] and IRIS [22] databases or derived from animal in vivo studies (rat or mouse) and using appropriate safety factors while PNEC concentrations were obtained from previously selected peer-reviewed freely available databases [23] such as ECOTOX [24], ChemIDPlus advanced [25] and specific reviews.

The first innovation introduced by the work is the approach used in the case of missing data: human toxicological and ecotoxicological values were predicted using freely available QSAR models like Toxicity Estimation Software Tool (T.E.S.T.) v 3.2 [26] and ToxBoxes [27] (nowadays ToxBoxes is no longer free).

The evaluation of risk has underlined the possible adverse effects both on human health after the exposure to drinking water contaminated by landfill leachate and on small rodents and aquatic species at the hypothesized condition: for humans, the estimated toxic effects of the raw leachate are mainly due to the levels of ammonia and cadmium and carcinogenic effects are induced by arsenic first and then by PCBs and PCDD/Fs while ecological potential risk is mainly attributable to the concentration of inorganic compounds, in particular ammonia for small rodents, cadmium, ammonia, and heavy metals for fishes.

The second innovative peculiarity is the application of HRA-oriented in vitro investigation: a human in vitro model has been used to obtain more information on the effect of leachate exposure and toxicity accounting of not only the toxicity of hydrophilic and lipophilic compounds but also the effects of whole leachate as a complex mixture.

Researchers focused on the metabolically competent human hepatoma cell line HepG2 as a model of human liver. HepG2 cells are a well-known hepatoma cell line that retains many of the morphological characteristics of liver parenchymal cells. This model is often used as a useful tool for HRA/ERA-oriented chemical risk assessment due to the expression of antioxidant and xenobiotic metabolizing enzymes (in particular phase I and phase II enzymes responsible for the bioactivation/detoxification of various xenobiotics) that can be induced or inhibited by dietary and non-dietary agents [28–30].

Screening assays were used to study the effects on cell proliferation and cytotoxicity of whole leachate and relative organic and hydrophilic extracts on cell model after 24–72 h of exposure.

According to the authors, no study has previously been setup to investigate the potential hepatotoxicity of leachate using in vitro models. Results from the in vitro study (Fig. 4) clearly indicate that the inhibition of cell proliferation by the raw

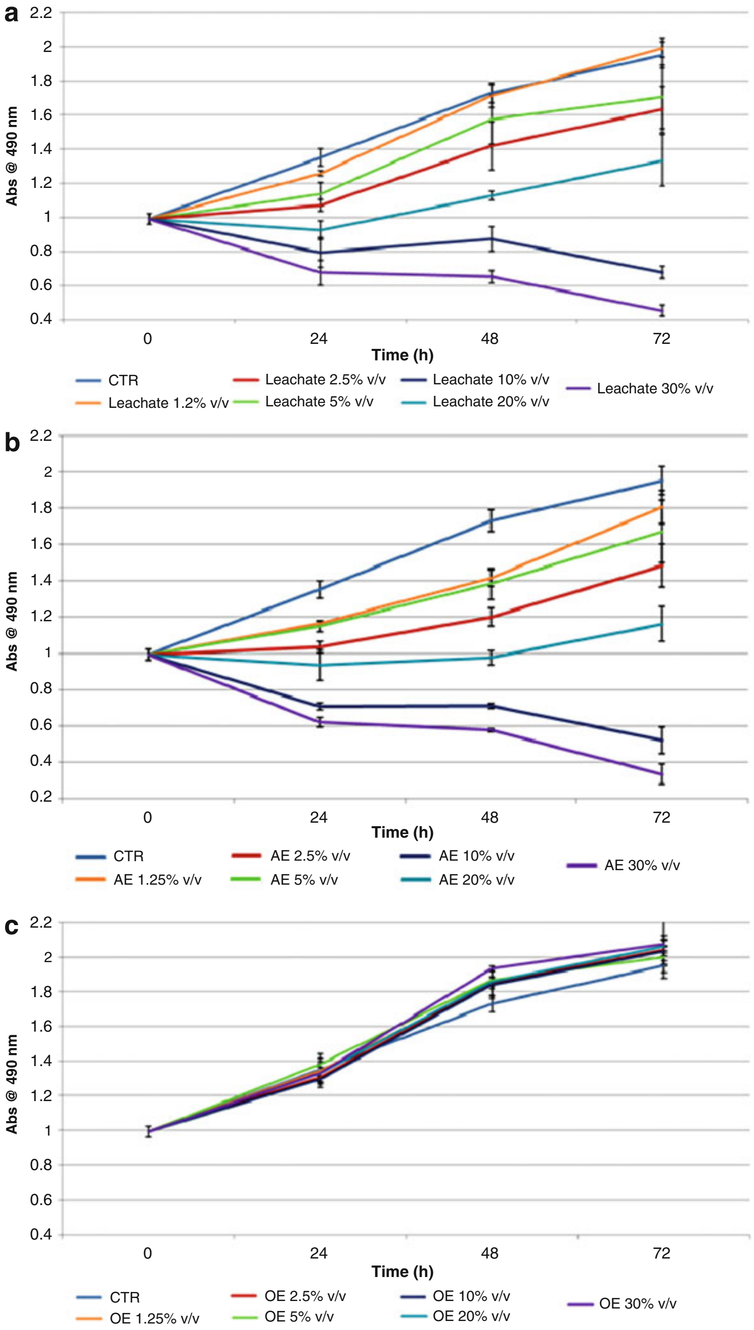

Fig. 4 Leachate toxicity: effects of whole leachate (**a**), aqueous/hydrophilic phase (**b**) and organic/lipophilic phase (**c**) on HepG2 cells (modified from [17])

leachate is induced by the hydrophilic components that remain, after organic extraction, in the aqueous phase such as ammonia and heavy metals, while the organic components do not show any effect.

Another peculiarity of the study is that the use of a biological system has allowed the authors to hypothesize a possible mechanism of action of the leachate as a mixture, hypothesis that could have been drafted on the basis of the only knowledge derived by chemical analysis. Researchers suggest that leachate inhibits cell proliferation at low doses probably inducing a reversible cell cycle arrest that becomes irreversible at high doses, probably due to leachate-induced oxidative stress. This activity is mainly due to the chemical compounds extracted in the aqueous phase. Similar effects were noticed by previous investigations on other human cells (human peripheral blood lymphocytes and a human breast cancer cell line, MCF-7) [31, 32], supporting the hypothesis that cells that survive the initial insult from leachate constituents maintains the potential to proliferate until the effects on cell metabolism lead to death.

Summarizing, this first example of toxicological characterization of waste-related products using alternative methods clearly suggests that:

- Chemical characterization alone is not sufficient to understand the overall toxicity of conventional and unconventional environmental matrices;
- Risk assessment of landfill leachate, which is traditionally based on chemical analyses of specific compounds, is not sufficiently developed to take into account interactions among chemicals in the complex mixtures;
- Bioassays and in vitro human models can be used to characterize the toxicity of leachate integrating the biological effects of all its constituents, in contrast to chemical analyses;
- The evidences provides by ERA and HRA seems to be confirmed by in vitro results;
- Each of the three above-mentioned components has advantages and disadvantage which could be offset by the integration of different approaches.

The study on the landfill leachate, shown here as an example application of the method, has demonstrated how information derived from individual approaches provides a valuable support to one another.

3 Qualitative Evaluation of Carcinogenic Potential of Some PFCs Using In Silico and In Vitro Methods

Carcinogenicity is one of the toxicological endpoints that pose the highest concern for human health. Nowadays, protection against cancer resulting from exposure to chemicals in the environment is a critical goal in public health management.

According to the definition provided by Pitot [33], “carcinogen” is an agent whose administration to previously untreated animals leads to a statistically significant increased incidence of neoplasms of one or more histogenetic types as compared with the incidence in appropriate untreated animals.

The occurrence of cancer is complex and not yet completely clarified process: a tumor is formed by millions of clones originating from one initial cell that has accumulated genetic and epigenetic alterations leading to the transformation into a cancer cell. The possible factors involved in neoplastic transformation of cells and the subsequent development of cancer are manifold: in addition to endogenous factors (e.g., genetic predisposition, immune system damage, and chronic inflammation), there are indeed numerous exogenous or environmental factors which serve as causative or tumor-promoting agents. Exposure to chemicals, dietary habits, lifestyle, viruses, and radiation are important examples of exogenous factors.

After the exposure to carcinogens, the occurrence of cancer is the final stage of sequential processes. Studies using animal models, in vitro models and epidemiological studies have shown that the pathogenesis of cancer is a multistep process which can be divided, at least, into three distinct phases: initiation, promotion, and progression. Initiation is the first stage of carcinogenesis and it is caused by irreversible genetic mutations that make a normal cell more susceptible to malignant evolution and immortality. In the promotion stage, the initiated cell interacts with a tumor promoting agent that does not directly interact with the cellular DNA but it is nevertheless able to induce different cascades of biological effects resulting in cellular new properties.

The progression is the third and final stage of carcinogenesis: cells derived from the original initiated cell, whose growth was accelerated in the promotion step, acquire full malignant phenotype, by accumulating more genetic damages, most of them affecting genes of cell cycle and growth control. The progression phase is irreversible. Malignant cells appear morphologically different: they are genetically unstable, grow faster, and acquire the ability to invade surrounding tissues and to metastasize.

Several chemicals can act as initiators and/or promoting agents participating actively in the process of carcinogenesis and also producing synergistic effects when taken simultaneously via multiple routes of exposure.

Exposure assessment of general population and workers to carcinogens is therefore a critical prerequisite for risk assessment to ensure an adequate level of health protection. Since cancer represents the world's leading cause of death as well as the highest economic toll among diseases, due to premature death, disabilities, treatments, not only would cancer prevention mean to increase life expectancy and quality, by reducing loss and suffering, but also to lower its huge economic impact.

In recent decades, the development of chemical, biochemical, and biological techniques has allowed the creation of analytical tools which can be used to facilitate the identification of the mechanisms involved in neoplastic transformation. Animal models remain, however, the most widely used approach of investigation. Cancer bioassays are usually conducted in rodents (rats and mice) and the experimental protocol takes 18–24 months and it is followed by extensive histopathological and statistical analysis. The procedure is time and money-consuming and the extrapolation of results from animal model to humans is often difficult. Although many human carcinogens have been predicted on the basis of results from animal models, it is often pointed out the representativeness of the animal model for human carcinogenicity. Species-specific susceptibility, different metabolism, and especially the treatment schedule at very high doses of chemicals are the most debated points. Animal are often treated at doses that are not representative of real human exposure. High doses may lead to impairment of the natural mechanisms of defense of the organism, such as DNA repair and metabolic detoxification, that may be overwhelmed by high chemical concentrations. Moreover, while the effects induced by genotoxic compounds are commonly considered to be linear with the applied dose, even at low exposures, non-genotoxic compounds behavior is quite unpredictable.

In recent years, the scientific community has focused on the need to develop alternative methods to animal experiments, including cell-based in vitro methods and in silico models, based on statistics and informatics.

In vitro models could be used to study the molecular mechanisms involved in the process of neoplastic transformation and as screening tools for the classification of the carcinogenic potential of a substance. Among the in vitro tests available to the scientific community, the CTA may represent an important tool for the identification of carcinogens, particularly those that are not identifiable by classic mutagenicity tests such as the Ames test.

Compared to animal assays, CTA is faster and cheaper. In vitro CTAs have been shown to involve a multistage process that closely resembles some stages of in vivo carcinogenesis and have the potential to detect both genotoxic and non-genotoxic carcinogens.

One of the most used transformation protocol is represented by the BALB/c 3T3 model, which shows a high correlation with the in vivo carcinogenesis and is able to discriminate between substances that act at different stages of carcinogenesis process, as initiating or promoting agents. BALB/c 3T3 cells are immortalized mouse embryonic fibroblasts that are adapted to grow in vitro culture, where they can divide indefinitely, while retaining some characteristic properties of normal cells, like the inhibition of cell division occurring when cells reach the confluence (contact inhibition). The treatment with a potential carcinogenic agent induces the loss of contact inhibition.

Cells do not stop their proliferation upon reaching confluence, pile up in “stacks (foci)” of morphologically transformed cells that can be considered as an endpoint of neoplastic transformation (Fig. 5).

The possible use of the BALB/c 3T3 CTA is mentioned in various recent testing strategies including the supplemental data for pharmaceuticals and the guidance on information requirements and chemical safety assessment for REACH [34, 35].

In this chapter we will introduce and discuss the use of alternative methods to evaluate the carcinogenic potential of some PFCs. In detail, in silico (QSAR) models and BALB/c 3T3 CTA will be used to investigate the issue.

PFCs are a large group of chemicals characterized by a fully fluorinated hydrophobic chain and an hydrophilic head. These compounds are often used as coating

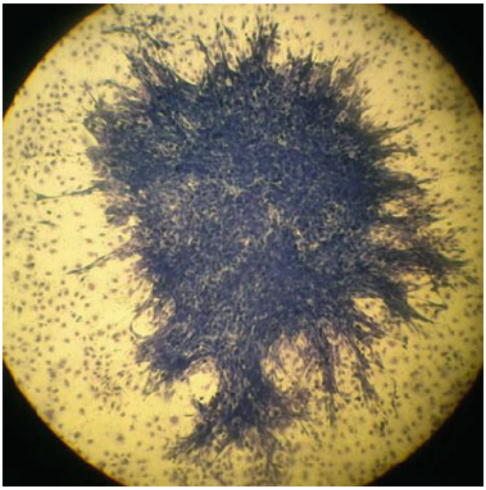

Fig. 5 BALB/c 3T3 cell transformation assay: example of focus induced in BALB/c 3T3 clone A31-1-1 after exposure to a carcinogenic compound. Cells are stained with Giemsa stain

agents (textile products, packaging products, cookware, and food contact papers) due to their ability to repel both water and oils. Nowadays they are internationally recognized as global contaminants [36–38].

Several studies have suggested that some critical adverse effects like peroxisome proliferation, hepatotoxicity, immunotoxicity, and developmental toxicity may be associated with chemical exposure to PFCs, particularly to PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid), two ubiquitous persistent organic pollutants with possible environmental and human health risks.

Only a very limited number of strong evidence is present in the scientific literature and guidelines about the correlation between PFCs and cancer [39–41].

3.1 QSARs Approach and Results

For the in silico evaluation of carcinogenic potential of PFCs, 16 compounds were selected (see Table 2).

For each selected PFC, a profile was edited including the name of the compound, its CAS (Chemical Abstracts Service) number and the SMILES (Simplified Molecular Input Line Entry System) formula.

Using SMILES as input, carcinogenic potential was evaluated using four different internationally recognized QSARs models: VEGA, ToxTree, Lazy structure-activity relationships (Lazar), and Deductive Estimation of Risk from Existing Knowledge (DEREK) for Windows. VEGA, ToxTree, and Lazar are freely available models while DEREK requires an annual fee.

Table 2 Selected perfluorinated compounds (PFCs) for the QSARs analysis

ID	Acronym	Name	CAS	SMILES
1	PFOS	Perfluorooctane sulfonic acid	1763-23-1	C(C(C(C(C(C(C(C(S(=O)(=O)O)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)(F)F
2	PFOA	Perfluorooctanoic acid	335-67-1	C(C(C(C(C(O)=O)(F)F)(F)F)(F)F)(C(C(C(F)(F)F)(F)F)(F)F)(F)F
3	PFNA	Perfluoro-n-nonanoic acid	375-95-1	O=C(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
4	PFBS	Perfluorobutanesulfonic acid	375-73-5	OS(=O)(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
5	POSF	Perfluorooctanesulfonyl fluoride	307-35-7	C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(C(C(C(S(=O)(=O)F)(F)F)(F)F)(F)F)(F)F
6	PFOSA	Perfluorooctanesulfonamide	754-91-6	S(=O)(=O)(C(C(C(C(C(C((F)(F)C(F)(F)C(F)(F)C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)N
7	PFDA	Perfluorodecanoic acid	335-76-2	C(C(C(C(C(C(O)=O)(F)F)(F)F)(F)F)(F)F)(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F
8	PFHxA	Perfluorohexanoic acid	307-24-4	O=C(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
9	PFBA	Perfluorobutanoic acid	375-22-4	C(C(C(O)=O)(F)F)(C(F)(F)F)(F)F
10	PFUnDA	Perfluoroundecanoic acid	2058-94-8	C(C(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)(F)F)(C(C(C(C(=O)O)(F)F)(F)F)(F)F)(F)F
11	PFDoDA	Perfluorododecanoic acid	307-55-1	O=C(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
12	PFHxS	Perfluorohexane sulfonate	355-46-4	O=S(=O)(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
13	PFHpA	Perfluoroheptanoic acid	375-85-9	O=C(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
14	PFTA	Perfluorotetradecanoic acid	376-06-7	O=C(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
15	PFPeA	Perfluoro-n-pentanoic acid	2706-90-3	O=C(O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
16	PFOSAA	N-Ethyl-N-((heptadecafluorooctyl) sulfonyl)glycine potassium salt	2991-51-7	C(C(C(C(S([N@@](CC(=O)[O-])CC)(=O)=O)(F)F)(F)F)(F)F)(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F.[K+]

VEGA platform (http://www.vega-qsar.eu/) provides a series of QSAR models for regulatory purposes, including mutagenicity, carcinogenicity, developmental toxicity, skin sensitization, Fathead Minnow LC50 at 96 h, Bioconcentration factors (BCF), persistence, and LogP.

The VEGA Carcinogenicity Classification Model provides a qualitative prediction of carcinogenic potency according to specific requirements of chemical regulation and extends the original freely available CAESAR model (http://www.caesarproject.eu/software): based on Counter Propagation Artificial Neural Network algorithm, the output of the neural network is if predicted compound could be carcinogenic or non-carcinogenic compounds based on artificial neural network algorithm [42]. Moreover, VEGA checks some Structural Alerts (SAs) in the compound structure providing a remark about the presence of some fragment related to a possible carcinogenic activity, if some SAs matches are found.

As a result, VEGA creates a PDF file that contains all the information about the prediction, including the final assessment of the prediction, the list of the six most similar compounds found in the training and test set of the model, the list of all Applicability Domain indices and a reasoning on SAs with a brief explanation of their meaning.

Lazar (http://lazar.in silico.de/predict) is a k-nearest-neighbor approach to predict chemical endpoints from a training set based on structural fragments [43]. It derives predictions for query structures from a database with experimentally determined toxicity data [43]. Model provides prediction for four endpoints: Acute toxicity to fish (lethality): Fathead Minnow Acute Toxicity (LC50), Carcinogenicity, Mutagenicity, and Repeated dose toxicity.

Focusing on carcinogenicity model, predictions could be done using six different models based on DSSTox datasets to make a qualitative evaluation of carcinogenicity on hamster, mouse, rat, and cells.

Toxtree (http://toxtree.sourceforge.net/) is a full-featured and flexible open source application which can be used to estimate various kinds of toxic hazard by applying a decision tree approach.

The platform includes different decision trees for the following endpoints: the estimation of Threshold of Toxicological Concern (TTC), aquatic modes of action [44], skin and eye irritation and corrosion, mutagenicity and carcinogenicity [45], in vivo micronucleus assay, identification of Michael Acceptors and biodegradation potential [46].

Regarding the carcinogenicity model, Toxtree includes a decision tree for estimating carcinogenicity and mutagenicity based on the "Benigni/Bossa rulebases" which estimate potential carcinogenicity and mutagenicity using SAs and different QSAR models.

In the latest version of Toxtree, another rulebase has been implemented for the in vivo micronucleus assay (ToxMic rulebase) which identifies 30 SAs from the Benigni-Bossa rulebase for genotixic carcinogenicity and five alerts specific for the micronucleus assay [47]. The occurrence of micronucleus in cells, tissue, or blood is linked to irreversible mutations which can also lead to cancer.

DEREK [48] is an expert knowledge base system which predicts carcinogenicity merging a series of rules based on laboratory studies on different species [49]. DEREK studies substructures known to have adverse toxicological properties SAs, looking for matches to substructures in the target molecule. The presence of an alert is related to the carcinogenicity of the compound processed. Potentially toxic substructures (toxicophore) are identified by matching patterns of atoms and bonds in the rule base to the target molecule. Each possible toxicophore is then further evaluated by “reading” from the rule base a list of scope and limitations questions.

Results of the QSAR analysis are shown in Tables 3, 4 and 5.

Results from VEGA underline the presence of 13 compounds with carcinogenic activity and only two non-carcinogenic compounds (perfluorobutanesulfonic acid and perfluorotetradecanoic acid). It is crucial to underline that for each selected PFCs, VEGA provides a remarks about the “performance” of the prediction: in fact, the model indicates that all the analyzed compounds are out of the VEGA applicability domain.

Analyses from Toxtree indicate that no alerts for carcinogenicity were identified in the selected PFCs applying the Benigni-Bossa rulebases for carcinogenicity while some positives matches has been registered regarding the presence of SAs for in vivo induction of micronuclei for each PCFs, except for POSF (perfluorooctanesulfonyl fluoride).

Regarding Lazar, different modules were applied. No evidence of carcinogenic potential was recorded using the modules for multi cells (1), rat (2), single cell (3), and hamster (6), while different results were obtained using ISSCAN (4) and mouse (5) modules. Results from ISSCAN underline the presence of carcinogenic potential in ten PFCs while the module on mouse is not able to perform a prediction on five compounds due to the absence of enough similar compounds in the dataset but no evidence of carcinogenic potential was recorded for the other 11 compounds, according to the above-mentioned modules.

Finally, results from DEREK clearly suggest that all the selected PFCs are non-carcinogenic compounds. It is important to underline that in our application of DEREK a compound was considered “non-carcinogenic” if the response was “Nothing to report,” although this is not the intended use of the “Nothing to report” output of the Derek for Windows software [50].

3.2 BALB/c CTA Approach and Results

The analyses using the LAZAR module 4 and VEGA have indicated that perfluorooctanoic acid (PFOA) and perfluoro-n-nonanoic acid (PFNA) could be compounds with carcinogenic potential.

So, to verify this hypothesis a CTA was set up using BALB/c 3T3 clone A31-1-1 cells.

Table 3 QSARs analysis of PFCs using VEGA and ToxTree

	VEGA		TOXTREE	
			Benigni Bossa rulebase for carcinogenicity	SAs for in vivo micronucleus assay in rodents
Compounds	Response	Note	Response	Response
PFOS	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFOA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFNA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFBS	Non positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
POSF	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	No alerts for the micronucleus assay
PFOSA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFDA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFHxA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFBA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFUnDA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFDoDA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFHxS	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFHpA	Positive		No alerts for carcinogenic activity	Positive SAs for the micronucleus assay

(continued)

Table 3 (continued)

	VEGA		TOXTREE	
			Benigni Bossa rulebase for carcinogenicity	SAs for in vivo micronucleus assay in rodents
Compounds	Response	Note	Response	Response
PFTA	Non Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFPeA	Positive	Compound is out of model Applicability Domain	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay
PFOSAA	–	Molecule has disconnected structure	No alerts for carcinogenic activity	Positive SAs for the micronucleus assay

Note: VEGA version 2.1.3; ToxTree Version 2.5.0 - August 2011

Table 4 QSARs analysis of PFCs using Lazar

	LAZAR					
	1	2	3	4	5	6
Compounds	Response	Response	Response	Response	Response	Response
PFOS	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Not enough similar compounds in training dataset***	Non-carcinogen
PFOA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFNA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Non-carcinogen***	Non-carcinogen	Non-carcinogen
PFBS	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Not enough similar compounds in training dataset***	Non-carcinogen
POSF	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Not enough similar compounds in training dataset***	Non-carcinogen
PFOSA	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Not enough similar compounds in training dataset***	Non-carcinogen
PFDA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFHxA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFBA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFUnDA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFDoDA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFHxS	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Not enough similar compounds in training dataset***	Non-carcinogen
PFHpA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFTA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFPeA	Non-carcinogen	Non-carcinogen	Non-carcinogen	***Carcinogen***	Non-carcinogen	Non-carcinogen
PFOSAA	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen	Non-carcinogen

Note: 1 - DSSTox carcinogenic potency DBS MultiCellCall; 2 - DSSTox carcinogenic potency DBS Rat; 3 - DSSTox carcinogenic potency DBS SingleCell; 4 - DSSTox ISSCAN; 5 - DSSTox carcinogenic potency DBS Mouse; 6 - DSSTox carcinogenic potency DBS Hamster

Table 5 QSARs analysis of PFCs using DEREK

DEREK	
Compounds	Response
PFOS	Non-carcinogenic
PFOA	Non-carcinogenic
PFNA	Non-carcinogenic
PFBS	Non-carcinogenic
POSF	Non-carcinogenic
PFOSA	Non-carcinogenic
PFDA	Non-carcinogenic
PFHxA	Non-carcinogenic
PFBA	Non-carcinogenic
PFUnDA	Non-carcinogenic
PFDoDA	Non-carcinogenic
PFHxS	Non-carcinogenic
PFHpA	Non-carcinogenic
PFTA	Non-carcinogenic
PFPeA	Non-carcinogenic
PFOSAA	Non-carcinogenic

CTAs are possible in vitro alternatives to the standard approach for the assessment of carcinogenicity (the 2-year bioassay in rodents), which have been shown to be a multistage process able to model the most important stages of in vivo carcinogenesis [50]. CTAs are faster and more economic than in vivo assay and they could be a valid and useful screening tool for chemicals.

Actually, the BALB/c 3T3 test is mainly used:

- To screen chemicals for their potential carcinogenicity
- To provide useful ancillary information when the biological significance of the bioassay result is uncertain
- To clarify in vitro genotoxic positive results by weight of evidence
- To screen for non-genotoxic carcinogens
- To demonstrate differences and similarities across a chemical class
- To screen for efficacy of chemopreventive agents
- To investigate tumor promotion activity
- For mechanistic studies of carcinogenicity

The endpoint of the BALB/c CTA is the carcinogenic conversion from non-tumorigenic immortality to tumorigenicity resulting in focus formation and anchorage-independent growth [51].

Focusing on PFOA and PFNA, the evaluation assay was set up in two phases:

- Cytotoxicity assay to evaluate the PFCs' toxicity and to select the concentrations for the transformation assay
- Transformation assay

As the first step, the toxicity of PFOA and PFNA was assessed using the colony formation assay (Fig. 6): cells at the density of 250 cells/plate were seeded in

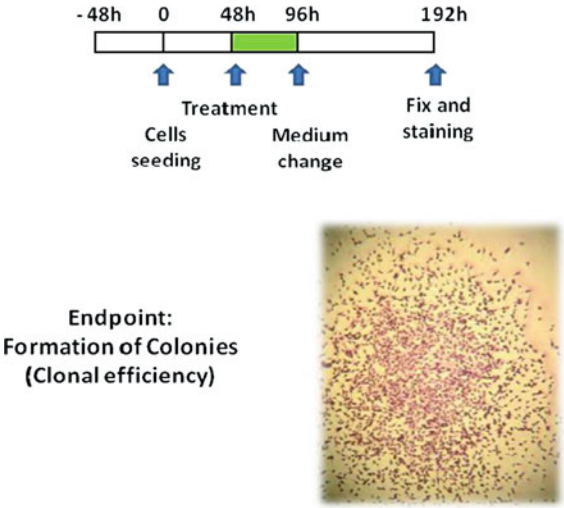

Fig. 6 BALB/c 3T3 cell transformation assay: Colony formation assay

60 x 15 mm Petri dishes and, after two days, were treated with different doses of PFCs dissolved in DMSO. Five replicates for each concentration were done. After 2 days treatment medium was removed and cells were replenished with fresh medium. Cells were maintained in culture for ten days, then fixed with methanol, stained with 10% aqueous Giemsa and scored for colony formation. Only colonies containing more than 50 cells were counted. Untreated BALB/c 3T3 cells and vehicle-treated cells were used as negative controls. Results were expressed as relative clonal efficiency (RCE) which estimates the per cent reduction of cell clonal efficiency in treated groups as compared to that of the relative control (vehicle-treated cells). Results of cytotoxicty assay are reported in Fig. 7. A dose response relationship was obtained for both compounds. However, since PFNA is more toxic than PFOA, no colonies were recorded after 250 μM PFNA treatment, while a similar evidence was achieved only at the highest assayed dose of PFOA (1,000 μM).

Based on these results, compounds were tested at five doses for CTA (Fig. 8). Cells were seeded at a density of 3 × 104 cells/60 mm dish, incubated for 48 h and then exposed to the tested compound at concentrations previously determined by the cytotoxicity test. Ten replicates were carried out for each treatment.

Untreated BALB/c 3T3 cells and solvent-treated cells were used as negative controls. Positive controls were represented by cells treated with the well-known carcinogen 3-MCA (2.5 μg/mL). After 48 h, cells were replenished with fresh normal culture medium and maintained in culture for 4–6 weeks, with biweekly medium changes. Cells were then fixed with methanol, stained with 10% aqueous Giemsa, and scored for foci formation. In order to calculate the number of cells

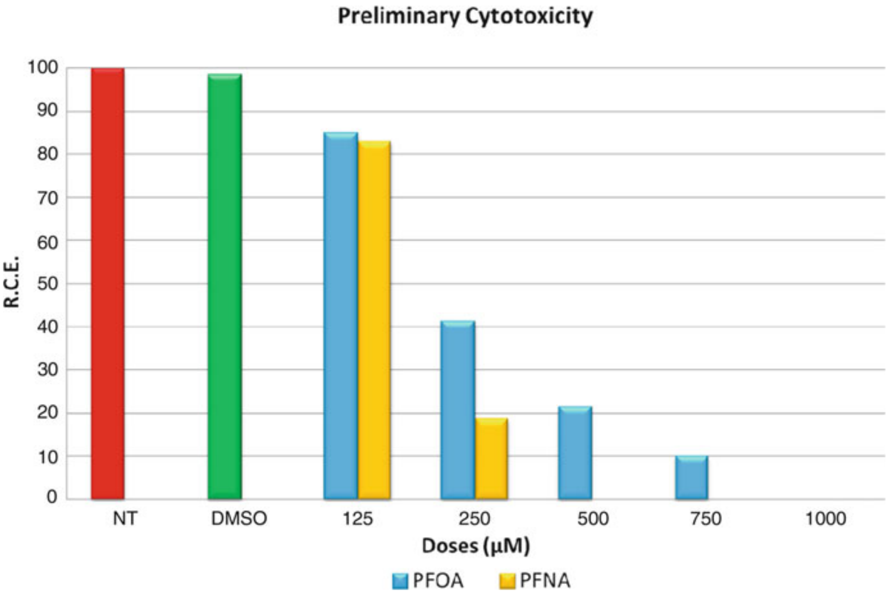

Fig. 7 BALB/c 3T3 cytotoxicity assay: red bar (NT) is untreated cells while green bar (DMSO) is the vehicle control

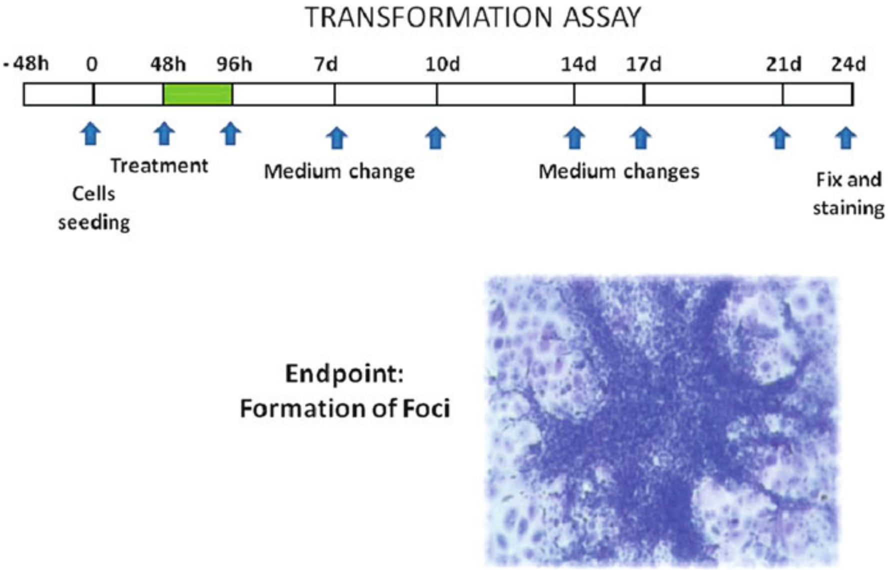

Fig. 8 BALB/c 3T3 cell transformation assay: transformation assay protocol

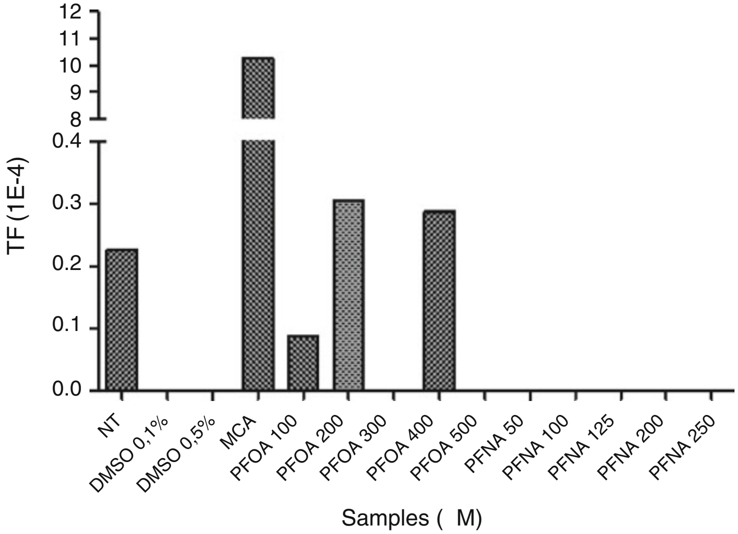

Fig. 9 BALB/c 3T3 cell transformation assay: transformation frequency of PFOA and PFNA. Red bar is the control group (untreated cells)

surviving the chemical treatment, colony-forming efficiency assays were also performed in parallel with the transformation test.

The scoring of foci was carried out according to the recommended guidelines. Only foci considered as positive (type III), showing deeply basophilic, dense multilayering of cells, random cell orientation at all parts of the focus edge, invasion into the surrounding contact-inhibited monolayer, and domination of spindle-shaped cells, were counted.

Data was reported as transformation frequency (TF), calculated on the cells that survived after chemical exposure. TF is expressed as a function of the total number of foci per treatment divided by the number of surviving cells estimated from the clonal efficiency observed in the cytotoxicity assay performed in parallel with the transformation test [52].

Results are reported in Fig. 9: no significant increase of TF was recorded after exposure to PFOA (100–500 μM) and PFNA (50–250 μM) suggesting that both compounds do not have carcinogenic potential.

3.3 Conclusions

The potential for a compound to induce carcinogenicity is a crucial consideration when establishing hazard and risk assessment of chemicals and pharmaceuticals in humans [53]. To date, the standard approach to assess carcinogenicity at a regulatory level is the 2-year bioassay in rodents. According to the recent REACH legislations, the use of alternative methods for carcinogenicity is strongly recommended for the screening of chemicals.

Among possible alternative, QSARs models and the BALB/c 3T3 in vitro CTA represent a possible solution. An example of the application of these methodologies is reported in this chapter focusing on the evaluation of PFCs.

Most results from QSARs models underline that selected PFCs do not have a carcinogenic profile. Only a model, VEGA, not only suggests the presence of compounds with carcinogenic activity but also clearly indicates that all the analyzed compounds are out of the VEGA applicability domain.

To verify the prediction from in silico approach, a BALB/c 3T3 CTA was performed on PFOA and PFNA. Results from in vitro assay confirm the response from QSARs models.

Results from this preliminary study suggest that a combined approach based on alternative methods could be positively applied to chemical screening in order to reduce the number of animal testing for carcinogenicity studies.

It is important to underline that the use of different models is strongly recommended in case of QSARs evaluation in order to face the limitation of their applicability domain and to produce a reliable judgment.

4 Comparative QSAR Evaluation of Toxicological Properties of Chemicals Suggested by EU Riskcycle Project

One of the aims of EU project Riskcycle is to assemble and evaluate existing information on the chemicals and especially the additives used in consumer and industrial products with a special focus on the fate and behavior of these additives in six product sectors: textile, electronics, plastics, leather, paper, and lubricants [54].

Selecting from scientific literature and reviews, Riskcycle researchers have defined a preliminary list of 16 additives of interest which will be analyzed and evaluated for a waste-related risk assessment: chosen compounds include perfluorinated and brominated compounds, phthalates, phenols, and some heavy metals (Table 6).

Within the project we also evaluated alternative methods as tools to obtain information on the toxicological and physicochemical profile of the pollutants. In this paragraph, an example of the application of QSARs models is reported: a comparison is done between predicted values from different models or between QSARs evaluation and experimental values from internationally recognized databases.

From the preliminary list of 16 compounds of concern, 14 compounds have been selected for the application of in silico methods because metals, and generally inorganic compounds, cannot be subjected to QSARs analysis.

Different toxicological endpoints which can be useful for a risk-oriented profiling have been evaluated:

Table 6 RISKCYCLE selected compounds

ID	Name	Acronym	SMILES	CAS	Sector
1	Perfluoro octane sulfonate	PFOS	OS(=O)(=O) C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	2795-39-3	Lubricants
2	Perfluoro octanic acid	PFOA	OC(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	335-67-1	
3	(4-Nonylphenoxy)acetic acid	NPAA	CCCCCCCCCC1=CC=C(CCC(O)=O)C=C1	3115-49-9	
4	Hexabromo cyclododecane	HBCDD	C1C(CC(CC(CC(CC(CC1Br)Br)Br)Br)Br)Br	256937-99-4	Textiles
5	5-Chloro-2-(2,4-dichloro-phenoxy)-phenol (biocide)	Triclosan	OC1=CC(Cl)=CC=C1OC1=C(Cl)C=C(Cl)C=C1	3380-34-5	
6	Di-(2-ethylhexyl)-phthalate	DEHP	c1(c(C(OC[C@@H](CCCC)CC)=O)cccc1)C(CC[C@@H](CCCC)CC)=O	117-81-7	Plastics
7	Lead	–	[Pb]	7439-92-1	
8	2,2’,4,4’,5-Pentabromo-diphenyl ether	BDE 99	c1(cc(c(cc1Br)Br)Oc1ccc(cc1Br)Br)Br	60348-60-9	Electronics
9	2,2’,4,4’,6-Pentabromo-diphenyl ether	BDE 100	BrC1=CC=C(OC2=C(Br)C=C(Br)C=C2Br)C(Br)=C	189084-64-8	
10	Decabromodiphenylether	–	BrC1=C(Br)C(Br)=C(OC2=C(Br)C(Br)=C(Br)C(Br)=C2Br)C(Br)=C1Br	1163-19-5	
11	Triphenylphosphate	TPP	O=P(OC1=CC=CC=C1)(OC1=CC=CC=C1)OC1=CC=CC=C1	115-86-6	
12	Mercury	–	[Hg]		
13	Nonylphenol	NPE	CCCCCCCCCC1=CC=C(C=C1)O	25154-52-3	Leather, paper
14	Bisphenol A	BPA	CC(C)(C1=CC=C(O)C=C1)C1=CC=C(O)C=C1	80-05-7	
15	Isothiazolinones (biocides)	–	CN1SC(Cl)CC1=O	26172-55-4	
16		–	CN1SC=CC1=O	2682-20-4	

- Genotoxicity/Mutagenicity (Ames Mutagenicity)
- Carcinogenicity
- Developmental toxicology
- Skin sensitization
- Bioconcentration factors (BCF)
- Aquatic toxicity: *Daphnia magna* 48 h LC50 and fathead minnow (fish) 96 h LC50
- Acute toxicity: rat oral LD50

For a comparison, to obtain multiple values of each parameters six different models have been applied: CAESAR, Toxtree, T.E.S.T., Lazar, and ECOSAR, which are freely available, and ToxSuite (ACD/Labs) [55].

QSAR models addressing five endpoints relevant for REACH legislation have been developed by the European funded CAESAR research project [56]. These models are focused on BCF in fish, mutagenesis, carcinogenesis, developmental toxicity, and skin sensitization. The developed models have been implemented into a Java-based applet available through the Internet.

A similarity check is also implemented to compare the queried substances with those used to develop the model and to verify how accurate their predicted values were.

Toxtree [57] can be used to estimate various kinds of toxic hazard by applying a decision tree approach.

The platform includes different decision trees for the following endpoints: the estimation of TTC, aquatic modes of action, skin and eye irritation and corrosion, mutagenicity and carcinogenicity, in vivo micronucleus assay, identification of Michael Acceptors and biodegradation potential.

Regarding the carcinogenicity model, Toxtree includes a decision tree for estimating carcinogenicity and mutagenicity based on the “Benigni/Bossa rulebases” which estimate potential carcinogenicity and mutagenicity using SAs and different QSAR models.

The US EPA T.E.S.T. is a downloadable program to estimate different toxicological endpoints and physicochemical properties from molecular structure using a variety of QSAR methodologies [58].

T.E.S.T allows you to estimate the value for 96 h fathead minnow LC50, 48 h *Daphnia magna* LC50, 48 h *Tetrahymena pyriformis* IGC50, Oral rat LD50, Bioaccumulation factor, Developmental toxicity, Ames mutagenicity, Normal boiling point, Density, Flash point, Thermal conductivity, Viscosity, Surface tension, and Water solubility.

Lazar [59] derives predictions for four endpoints: Fathead Minnow Acute Toxicity (LC50), Carcinogenicity, Mutagenicity, and Repeated dose toxicity.

Focusing on carcinogenicity model, predictions could be done using six different models based on DSSTox datasets to make a qualitative evaluation of carcinogenicity on hamster, mouse, rat, and cells.

The US EPA Ecological Structure Activity Relationships (ECOSAR™) Class Program estimates the aquatic toxicity of industrial chemicals, in particular focusing on acute (short-term) toxicity and chronic (long-term or delayed) toxicity for fish, aquatic invertebrates, and green algae using SARs [60]. Model is included in the Estimation Program Interface (EPI) Suite, a Windows®-based suite of physical/chemical property and environmental fate estimation programs developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation (SRC) [61].

ACD/Tox Suite is a collection of software modules that predict probabilities for basic toxicity endpoints. Predictions are made from chemical structure and based upon large validated databases and QSAR models, in combination with expert knowledge of organic chemistry and toxicology. ToxSuite modules for Acute Toxicity, Genotoxicity, Skin Irritation, and Aquatic Toxicity have been used.

The Acute Toxicity LD50 module provide predictions of LD50 (mg/kg) values for rats and mice according to various routes of administration including oral ingestion [62]. Moreover, experimental values (if present) and similarity to test compound are shown for the five most similar structures from the training set.

The Ames test module of Genotoxicity predictor provides qualitative evaluation of the mutagenic potential of compounds calculating by the probability of a positive Ames test results [63]. Moreover, it is possible to visualize the genotoxic potential of atoms or fragments of the compound's structure by a dual-color mapping (red is involved in genotoxicity, green is not involved).

The Irritation module estimates the potential of selected compound to cause eye or skin irritation in standard rabbit Draize test [64].

Finally, the Aquatic Toxicity module predicts fish and daphnia toxicity providing LC50 values (mg/L) for *Pimephales promeals* (Fathead minnow) and *Daphnia magna* (Water flea). Experimental values (if present) and similarity to test compound are shown for the five most similar structures from the training set [65].

Results from the QSARs analyses are reported in Tables 7–14.

Table 7 shows the predictions relating to the mutagenicity. The models gave homogeneous and consistent results. Only exceptions are the predictions of Toxsuite on HBCDD and Methylisothiazolinone which are in contrast with the predictions of other models and with experimental data. Moreover, no predictions are provided by Lazar for Isothiazolinones due to the absence of not enough similar compounds in the training dataset.

Table 8 summarizes the carcinogenicity predictions. The models gave overall consensual results. It is important that the different values from Toxtree models reflect the capabilities of the models to provide prediction for non-genotoxic (Toxtree 1) and genotoxic carcinogenicity (Toxtree 2). Also Lazar is able to predict carcinogenic potential on six systems, so differences in the results are due to the difference on analyzed target biological models.

Results from the application of QSARs models for Developmental Toxicity are reported in Table 9. CAESAR bold values indicate that descriptors for these compounds have values outside the descriptor range for the compounds of the training set, suggesting that predictions are not reliable. Focusing on reliable results, obtained predictions are quite controversial underlining the need of more models for this endpoint.

Table 7 Results from QSARs: mutagenicity

ID	Compound	T.E.S.T	CAESAR	ToxSuite	Lazar	Experimental
1	PFOS	No	No	Negative	Negative	
2	PFOA	No	No	Negative	Negative	
3	NPAA	No	No	Negative	Negative	
4	HBCDD	No	No	Positive	Negative	Negative
5	Tridosan	No	No	Negative	Negative	
6	DEI-P	No	No	Negative	Negative	Negative
7	BDE99	No	No	Negative	Negative	
8	BDE100	No	No	Negative	Negative	
9	Decabromodiphenylether	No	No	Negative	Negative	Negative
10	TPP	No	No	Negative	Negative	Negative
11	NPE	No	No	Negative	Negative	
12	BPA	No	No	Negative	Negative	Negative
13	Kathon CG 5243	Yes	Yes	Positive	–	Positive
14	Methylisothiazolinone	No	No	Positive	–	

Table 8 Results from QSARs: carcinogenicity

ID	CAESAR	ToxTree (1)	ToxTree (2)	Lazar (1)	Lazar (2)	Lazar (3)	Lazar (4)	Lazar (5)	Lazar (6)
1	No	No	No	No	No	No	No	–	No
2	No	No	No	No	No	No	Yes	No	No
3	No	No	No	No	No	No	No	No	No
4	No	Yes	No	Yes	Yes	Yes	–	–	–
5	No	Yes	No	Yes	Yes	Yes	Yes	No	No
6	No	No	No	No	No	No	Yes	No	No
7	No	Yes	No	Yes	–	Yes	Yes	No	No
8	No	Yes	No	Yes	–	Yes	Yes	No	No
9	No	Yes	No	Yes	Yes	Yes	Yes	No	No
10	No	No	No	No	No	Yes	No	No	No
11	No	No	No	No	No	No	Yes	No	No
12	No	No	No	No	No	No	Yes	No	No
13	Yes	No	Yes	–	–	–	No	Yes	–
14	No	No	Yes	–	–	–	–	Yes	–

Table 10 includes the results for skin irritation. No clear results have been obtained. All models are in agreement only for the absence of irritative potential of BDE 100. Multiple results from ToxTree are due to the five different alerts used by the model (Schiff base formation, SNAr, Acyl transfer agent, skin sensitization, and Michael acceptor). A global evaluation of ToxTree data could suggest that all the analyzed compounds are not able to induce skin sensitization. These predictions are in clear contrast with that obtained by applying CAESAR and in partial agreement with the results of Toxsuite.

Results from the application of models for BCF in fish (LogBCF) are reported in Table 11 with some comparison experimental values from models training set. Bold

Table 9 Results from QSARs: developmental toxicity

ID	Compound	T.E.S.T	CAESAR
1	PFOS	No	No
2	PFOA	Yes	No
3	NPAA	Yes	No
4	HBCDD	Yes	**Yes**
5	Triclosan	Yes	No
6	DEHP	Yes	No
7	BDE99	Yes	No
8	BDE100	Yes	**No**
9	Decabromodiphenylether	Yes	No
10	TPP	Yes	**No**
11	NPE	No	No
12	BPA	Yes	No
13	Kathon CG 5243	Yes	**Yes**
14	Methylisothiazolinone	Yes	**No**

Table 10 Results from QSARs: skin irritation

ID	CAESAR	ToxTree (1)	ToxTree (2)	ToxTree (3)	ToxTree (4)	ToxTree (5)	ToxSuite
1	Inactive	No	No	No	No	No	Yes
2	Active	No	No	No	No	No	Yes
3	Active	No	No	No	No	No	Yes
4	**Inactive**	No	No	No	Yes	No	Yes
5	Active	No	No	No	No	No	No
6	Active	No	No	No	No	No	No
7	Inactive	No	Yes	No	Yes	No	No
8	Inactive	No	No	No	No	No	No
9	Active	No	Yes	No	Yes	No	No
10	**Active**	No	No	No	No	No	No
11	Active	No	No	No	No	No	No
12	Active	No	No	No	No	No	No
13	Active	No	No	No	Yes	No	No
14	Active	No	No	No	Yes	Yes	No

values from CAESAR indicate the presence of chemical features in the compound (for example O linked to Ar and 3 Br/Cl linked to Ar or 10 F atoms in the molecule) that might be associated with a lower reliability of the predicted value. Generally, the predicted data have different levels of concordance. Evaluations for six compounds (5, 10, 11, 12, 13, and 14) present a high degree of agreement while the predictions for the other compounds are quite variable. It is important to underline that in most cases the analyzed BCF model are conservative if compared to the experimental data: predicted values are higher than experimental ones resulting in overestimated bioconcentration potential. Moreover, it is interesting that also experimental values present a high degree of variability.

Table 11 Results from QSARs: BCF

ID	T.E.S.T	CAESAR	EOOSAR	Experimental	
1	3.12	1.7	0.5	3.73	–
2	2.54	2.53	0.5	3.12	–
3	1.37	2.09	1	–	–
4	2.19	1.59	3.76	–	–
5	2.58	2.71	2.808	1.67	1.7171
6	1.36	1.51	3.234	1.99	2.7694
7	3.29	1.94	4.18	–	–
8	34	1.94	3.801	–	–
9	2.07	1.02	1.62	1.2	3.38
10	2.14	2.12	1.871	2.48	2.281
11	2.19	2.89	2.093	2.55	2.58
12	1.76	1.97	1.858	1.39	1.8415
13	0.86	0.08	0.5	–	–
14	0.46	0.06	0.5	–	–

Table 12 Results from QSARs: 48 h LC50 Daphnia

ID	Compound	T.E.S.T	ECOSAR	ToxSuite	Experimental	
1	PFOS	N/A	20.094	0.096		–
2	PFOA	N/A	9.114	1.6		–
3	NPAA	2.57	0.954	8.5		–
4	HBCDD	1.65	0.006	7		–
5	Tridosan	0.38	0.991	0.37		–
6	DEHP	1.44	0.00147	10	11	–
7	BDE99	0.0217	0.006	0.14		–
8	BDE100	0.0569	0.006	0.14		–
9	Decabromodiphenylether	0.0571	0.00000236	0.00087		–
10	TPP	0.0719	1.042	0.0014		1
11	NPE	1.84	0.067	1.3	0.38	–
12	BPA	3.86	5.039	1.6	3.5	12.81
13	Kathon CG 5243	7.53	4787.144	14		–
14	Methylisothiazolinone	13.69	9060.711	22		–

The evaluation for aquatic toxicity on daphnids and fish is reported in Tables 12 and 13. Bold values indicate that compounds are out of the model applicability domain (ECOSAR) or that the prediction is not reliable. ECOSAR and ToxSuite are able to predict all the selected compounds while T.E.S.T. fails in prediction for the daphnia toxicity of perfluorinated compounds (PFOS and PFOA). Tables 12 and 13 include also a limited number of experimental results provided by the model training dataset (some data are extracted from USEPA Ecotox database). Predicted results are in agreement for five compounds only (2, 3, 5, 13 and 14) for both endpoints while the predictions for the other compounds are highly variable.

Table 13 Results from QSARs: 96 h LC50 fathead minnow

ID	Compound	T.E.S.T	EOOSAR	ToxSuite	Experimental	
1	PFOS	30.88	24.648	16		–
2	PFOA	28.2	10.662	130		–
3	NPAA	1.23	0.964	0.36		–
4	HBODD	0.21	0.004	0.00013		–
5	Tridosan	0.31	1.244	0.24	0.32	–
6	DEHP	0.0474	0.00117	0.43	16	–
7	BDE99	0.1	0.005	0.0024		–
8	BDE 100	0.0434	0.005	0.0043		–
9	Decabeomodiphenylether	0.00157	0.00000094	0.000000097		–
10	TPP	0.79	1.303	2.4	0.88	0.93
11	NFE	0.37	0.072	0.13		0.27
12	EPA	3.15	7.16	2.6	4.6	4.65
13	Kathon CG 5243	31.18	11008.46	94		–
14	Methylisothiazolinone	101.55	22113531	330		–

Table 14 Results from QSARs: Oral Rat LC50 (mg/kg b.w.)

ID	Compound	T.E.S.T	ToxSuite	Experimental	
1	PFOS	238.47	1500		
2	PFOA	225.47	420	430	
3	NPAA	3924.02	7900		
4	HBCDD	1908.39	850		
5	Triclosan	65.76	2800	3700	3695.8
6	DEHP	37293.36	27000	30000	
7	BDE99	581.16	2200	5000	
8	BDE100	761.76	2600		
9	Decabromodiphenylether	660.5	1500		
10	TPP	1070.28	2700	3500	3496.37
11	NPE	2021.42	1900	1620	1618.8
12	BPA	3147.1	1900	3250	3247.32
13	Kathon CG 5243	680.71	590		
14	Methylisothiazolinone	2868.62	580		

Focusing on compounds with experimental data, we can underline that

- T.E.S.T. and ToxSuite are very conservative on prediction of aquatic toxicity;
- ECOSAR often underestimates values for daphnids and fish.

Results for the prediction of oral toxicity on rat are shown in Table 14. Bold values indicated that prediction is not reliable. Table includes also a limited number of experimental results provided by the model training dataset (some data are extracted from ChemID database). Globally, values show a high degree of concurrence. The only exceptions are the predictions of triclosan and methylisothiazolinone toxicity: for triclosan, prediction made by T.E.S.T. is more conservative than ToxSuite and experimental values while for methylisothiazolinone predicted values from T.E.S.T and ToxSuite are variable.

5 Conclusions

This chapter describes some examples of application of alternative methods for the study and characterization of the toxicity of some compounds of environmental significance.

Among the possible techniques, in vitro assays and QSARs models are the most relevant ones. Both tools have advantages and disadvantages which could be offset by the integration of different approaches.

The investigation on leachate shown in the first paragraph suggests that, focusing on risk assessment, chemical characterization alone is not sufficient to understand the overall toxicity of conventional and unconventional environmental matrices. Furthermore, risk assessment of complex mixtures, which is traditionally based on chemical analyses of specific compounds, is not sufficiently developed to take into account interactions among chemicals in the complex mixtures. A possible solution is the use of bioassays (on simplified models like daphnids, algae, and worms) and in vitro cell models which can integrate the biological effects of all mixture, in contrast to chemical analyses.

The second example focused on the evaluation of carcinogenic potential of PFCs. This property is one of the most important endpoint for hazard and risk assessment of chemicals and pharmaceuticals in humans. Traditionally, this investigation requires time and money efforts because the standard approach to assess carcinogenicity at a regulatory level is the 2-year bioassay in rodents. Highlights from the revision underline that QSARs models and the BALB/c 3T3 in vitro CTA could be very useful in reducing the number of compounds (and doses) which should be tested for the screening of the carcinogenic potential. These results in a significant reduction of animal consume which can be translated in both economic and temporal saving.

Finally, results reported in the third part from evaluation of Riskcycle compounds of concern suggest that the use of different QSARs models for the same endpoint is a good practice to reduce the variability of the response.

Clearly, for some endpoints the models are more reliable. This is due to the higher number of compounds available to build up the model and to the complexity of the toxicological process which is modeled. Thus, for instance, models for genotoxicity can refer to many thousands of chemicals with experimental values, and the process is relatively simple. Conversely, reproductive toxicity is a much more complex endpoint and the number of chemicals with experimental data is limited (a few hundreds).

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LCA Case Study on Printed Matter

Henrik Fred Larsen

Abstract Previous product life cycle assessments (LCAs) on offset printed matter all point at paper as the overall dominating contributor to the impacts from the life cycle of this product category. The dominating role of paper is primarily founded in the energy-related impact categories: global warming, acidification and eutrophication. These former studies focus on impacts related to energy and the chemical-related impact categories, comprising ecotoxicity and human toxicity, are not included at all or only to a limited degree. In this chapter we present a newer case study that includes these chemical-related impact categories by making use of knowledge about emissions from the printing industry combined with knowledge about the composition of the printing materials used during the production of offset printed matter. The results show that the relative importance of the paper-related energy consumption is significantly reduced when chemical emissions combined with toxicity-related impact categories are included in the impact assessment. By including results from a survey on the presence of hazardous chemicals in the Danish printing industry, some of the potential additives/impurities that may appear in the recycled paper are identified.

Keywords Additives, Chemicals, Impurities, Life cycle assessment (LCA), Paper, Printing industry, Recycling

Contents

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Abbreviations and Symbols

AOX	Adsorbable organic halides
APE	Alkylphenol ethoxylates
BPA	Bisphenol A
CMR	Carcinogenic, mutagenic and reprotoxic
COD	Chemical oxygen demand
DTU	Technical University of Denmark
ECHA	European Chemicals Agency
EDS	Endocrine-disrupting substances
eqv	Equivalents
EU	European Union
FP7	EU Seventh Framework Programme
ILCD	The International Reference Life Cycle Data System
LAS	Linear alkyl benzene sulphonates
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
MSDS	Material safety data sheets
NMVOC	Non-methane volatile organic compounds
NPE	Nonylphenol ethoxylates
PBT	Persistent, bioaccumulative and toxic
PE	Person-equivalents
PET	Person-equivalents targeted
REACH	Registration Evaluation, Authorisation and Restriction of Chemicals
SVHC	Substances of very high concern
TOC	Total organic carbon
VOC	Volatile organic carbon
vPvB	Very persistent and very bioaccumulative
WWTP	Wastewater treatment plant

1 Introduction

Until recently only a few life cycle assessment (LCA) studies [1–7] have been done on printed matter, and most of them focus on energy consumption. However, one of the newer and most comprehensive case studies [8, 9] actually includes toxic impacts from chemical emissions – mostly printing chemicals like printing ink and glue of which some components may accumulate in recycled paper. Though recycling is included in this case study, there is, however, no special focus on the additives/impurities in the recycled paper. Anyway, the study shows that potential toxic impacts from the production and use of chemicals like pigments, solvents, metals, AOX and biocides may play a very important role in the LCA impact profile of printed matter. This chapter deals with LCA on printed matter and focuses on the potential importance of chemical emissions, including additives/impurities, for the LCA impact profile. Highly problematic additives/chemicals that might stay/accumulate in the paper when recycled are addressed. The main part of the research reported here is based on two studies performed by the author, i.e. an LCA on printed matter [8, 9] and a Danish printing industry substitution project including a survey on occurrence of hazardous substances [10]. In Fig. 1 the life cycle of printed matter is illustrated by the cycle of the main raw material paper.

2 Methodology

The method used in the LCA case study on printed matter [8, 9] is described in Sect. 2.1. As regards general LCA methodology it is described in [34]; however, methodology on life cycle impact assessment (LCIA) is further detailed below in Sect. 2.1. Regarding the substitution project [10] the description of the method used and the main results are part of the chapter “Case Study on Printed Matter in Denmark” in Volume I of “Global Risk-Based Management of Chemical Additives” [11]. Results from the substitution project [10] are only included here to the degree relevant for the LCA of printed matter.

2.1 LCA Case Study

The goal of the LCA case study on printed matter [8] was to identify the distribution of potential environmental impacts (hot spots) and resource consumption during the life cycle of generic sheet fed offset printed matter produced at a European model printing house. The functional unit is 1 ton of sheet fed offset printed matter (books, pamphlets, brochures, etc.).

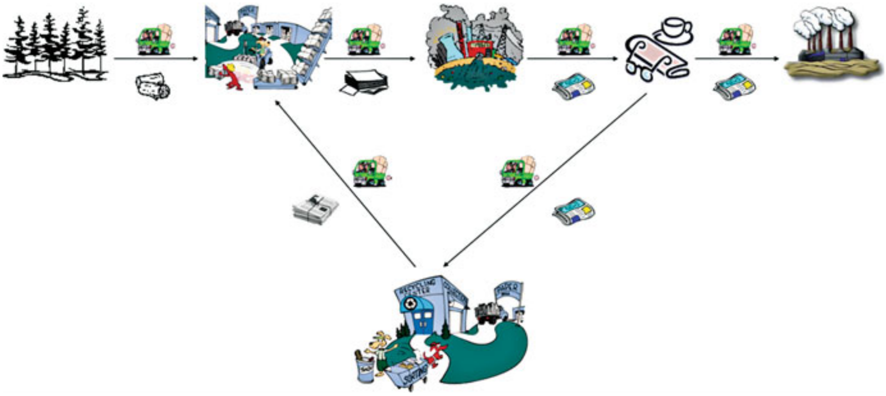

Fig. 1 Life cycle of printed matter – focus on paper

The scope of the case study is depicted in Fig. 2. In the inventory, average data on emissions and consumptions, typically based on 5–10 data points (depending on the parameter) from a total of 71 Danish and Swedish printing houses and European literature values, are used (foreground data). For the upstream and downstream emissions and consumptions (background data), inventory data from databases like "EDIP LCV tool" [12] and literature like BUWAL [13] and data from Swedish paper mills [14] have been used. In the main scenario, it is assumed that 53% of the paper is recycled and the rest incinerated (Danish situation in year 2000).

For the impact assessment, the midpoint method EDIP97 [15] was used, and the following impact categories were included:

- Global warming
- Ozone depletion
- Acidification
- Nutrient enrichment
- Photochemical ozone formation
- Chronic human toxicity via water
- Chronic human toxicity via soil
- Chronic ecotoxicity in water
- Chronic ecotoxicity in soil
- Acute human toxicity via air
- Acute ecotoxicity in water
- Hazardous waste
- Nuclear waste
- Slag and ashes
- Bulk waste
- Resource consumption

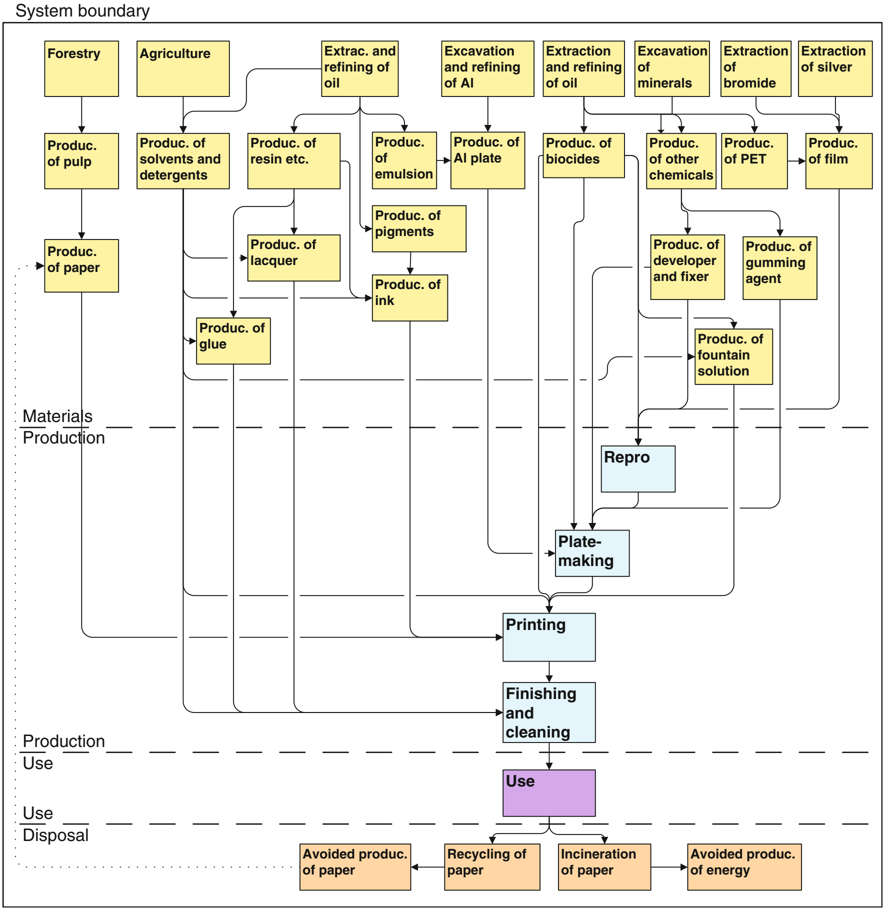

Fig. 2 Scope of case study on printed matter

As focus in this chapter is on additives/chemicals and emissions, the impact category on resource consumption is not included. Results regarding resource depletion may be found in the case study report [8].

An average of the impact potentials for the four impact categories on chronic (eco)toxicity, i.e. chronic human toxicity via water, chronic human toxicity via soil, chronic ecotoxicity in water and chronic ecotoxicity in soil, is defined as the common impact category "persistent toxicity" [16] and used when calculating normalised and weighted results.

Besides the two steps classification and characterisation, which are mandatory according to ISO 14042 [17], the LCIA in this case study also includes the optional steps normalisation and valuation (weighting).

During classification the emissions mapped in the inventory are assigned to the relevant impact categories, e.g. carbon dioxide and methane emissions are assigned to global warming, and the methane emission is also assigned to photochemical ozone formation. Then during characterisation a total impact potential is calculated for each impact category, by summing up the results of each assigned emission quantity multiplied by its corresponding characterisation factor within that impact category. The characterisation factor is a substance, emission and impact category-specific factor expressing the potential impact on the environment or humans of emitting 1 kg of the substance in question. For example, regarding carbon dioxide (CO_2) emissions, the characterisation factor is 1 kg CO_2-equivalents (eqv)/kg CO_2 emitted to air, and for methane (CH_4), being 25 times more potent, the corresponding factor is 25 kg CO_2-eqv/kg CH_4 emitted to air, both as related to the impact category on global warming.

The calculated impact potentials are normalised within each impact category in order to give an impression of their relative magnitude. The normalisation is achieved by dividing the case study impact potentials by reference information on the background impact from society's total activities, i.e. the total impact potential in the reference region divided by the number of citizens in that region. For example, for global warming, the reference information or normalisation reference for the year 1990 is 8,700 kg CO_2-eqv/person/year, meaning that in 1990, greenhouse gases equivalent to 8,700 kg CO_2 were emitted to air, on average, for each citizen worldwide. The normalisation reference therefore represents the annual impact of an average person. The normalised results are hereby expressed in units of person-equivalents (PE).

The weighting factors for the individual impact categories are based on the Danish political targets for the reduction of impact within regional and local impact categories (e.g. ecotoxicity, acidification), whereas weighting of the global impact categories (global warming and ozone depletion) is based on international conventions and plans of action for reduction. The reference year is 1990 and the target year is 2000, meaning that if the political target is to reduce the impact within a certain impact category by 20% during that period, the weighting factor becomes 1.3 ($1/(1 - 0.2) = 1.3$). The weighted normalised impact potentials are simply calculated by multiplying the normalised impact potentials by the corresponding weighting factor and expressed in targeted person-equivalents (PET).

For normalisation and weighting, the EDIP normalisation references regarding the year 1990 and the EDIP weighting factors regarding the target year 2000 [16] were used.

The case study was done in accordance with the ISO 14040 series [17–20] and peer-reviewed. More details about the methodology used and the peer review may be found in the work by Larsen et al. [8, 9].

3 Results of the LCA Case Study

The normalised and weighted impact profile for the case study is shown in Fig. 3. The potential impacts are divided into nine phases/steps, mainly related to the process steps at the model printing house and the paper production, incineration

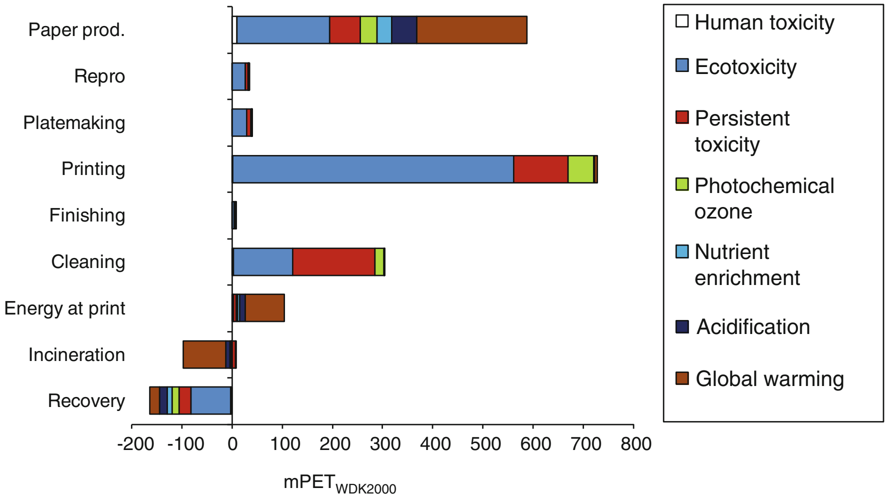

Fig. 3 LCA impact profile on sheet fed offset printed matter (functional unit: 1 ton). Weighted potential impact (milli-person-equivalents targeted), shown on the *x*-axis. Only seven impact categories, i.e. human toxicity, ecotoxicity, etc. were shown here

and recycling ("recovery"), see Fig. 2. Only seven impact categories are shown, as ozone depletion is insignificant and the four waste-related categories (bulk waste, slag and ashes, etc.) are almost entirely related to paper production. Results including all impact categories may be found in Larsen et al. [8, 9].

As is evident from Fig. 3, paper production contributes significantly (about 30% of total) to the impact profile but is not at all dominating like in former studies (60–80% of total) focusing on energy consumption and only including chemicals and potential toxic impacts to a limited degree. If the toxicity-related impact categories are excluded in this case study, the contribution from paper is increased to 67% of total, which is at the level of the former studies.

The dominating potential impact in the impact profile (Fig. 3) is ecotoxicity, i.e. acute ecotoxicity in water. For this category, the printing process accounts for more than half and paper production below one-fifth of the total. This impact category is dominated by contributions from emissions of tetradecane (printing and cleaning at the production stage) and contribution from emissions of synthesis chemicals (e.g. 3,3-dichlorobenzidine) at the synthesis of pigments (material stage). Emission of strontium related to energy production (especially for production of paper, i.e. heavy fuel oil for production of pulp) and emission of biocides at the model printing house contribute less, but significantly.

The second most contributing impact category is persistent toxicity with the cleaning step (e.g. emissions of hexane) at the printing house being the main contributor followed by the printing step (e.g. emissions of isopropyl alcohol) and paper production (e.g. emissions of strontium and mercury). For human toxicity (acute human toxicity air), the contribution is minor and mainly related to energy production, i.e. emissions of nitrogen oxides and sulphur dioxide.

Global warming is the third most contributing impact category in the impact profile shown in Fig. 3. It is highly dominated by emission appearing during energy production, especially for production of paper (almost three-fourth of total), but also from energy consumption at the model printing company (about one-fourth of total). Nutrient enrichment and acidification contribute less but significantly and are, as global warming, related to energy production. The impact category photochemical ozone formation is dominated by contributions from printing (e.g. emissions of isopropyl alcohol), paper production (e.g. energy-related VOC emissions) and cleaning at the printing house (e.g. emissions of hexane).

If the avoided impacts from incineration of paper (i.e. avoided fossil fuel consumption; "incineration" in Fig. 3) and the avoided impacts from recycling paper (i.e. avoided production of virgin paper; "recovery" in Fig. 3) are allocated to paper production, the contribution from paper to the total impact profile is reduced significantly.

Even though recycling is included in this study (Fig. 3; "recovery"), there is no special focus on the additives/impurities in the recycled paper. However, as described above, the study shows that potential toxic impacts from the production and use of chemicals like pigments, solvents, metals and biocides may play a very significant role in the impact profile of printed matter. Focusing on chemicals, the overall results for the printed matter impact profile, with avoided impacts from incineration and recycling allocated to paper production, are described below (in brackets: percentage contribution to the total normalised and weighted impact potential):

- Emissions of ink residues like tetradecane and emissions of cleaning agents like hexan and tetradecane, all during the printing process and cleaning (35%)
- Emissions of dichlorobenzidine, chloroaniline, cuprous chloride and more during pigment production (17–20%)
- Emissions of heavy metals and AOX (as dichlorobenzene) during paper production (>3%)
- Emissions of fountain chemicals (i.e. isopropyl alcohol) during the printing process (6%)
- Emissions of biocides and hydroquinone from the repro- and plate-making process (3%)

4 Discussion

The case study described here shows that emissions of chemicals, including substances that might be considered as additives in the printed matter life cycle, may contribute significantly to the LCA impact profile. In order to increase the reliability of this result, confirmation, by use of newer and improved LCIA methodology and updated LCI data for the background processes, are desirable. Newer LCIA methodology has actually been used in other LCA studies on printed matter, but in all cases, the inclusion of chemical emissions and (eco)toxicity is weak. Even a most recent Finnish LCA case study on different printing technologies focuses on energy (and material) consumption and only includes toxicity-related impact categories (human toxicity, terrestrial ecotoxicity and freshwater ecotoxicity) for the case study on a photobook, i.e. electrophotography/digital printing [21]. The LCIA method used is one of the newest, i.e. ReCiPe (www.lcia-recipe.net (version November 2009)), but the study only includes cradle to consumer (no "end of life" or recycling included). The resulting LCA impact profiles in this Finnish case study shows dominance of the paper production together with the packaging material (plastic) for the photobook and transport to the consumer. Regarding the toxicity-related impact categories, only the normalised impact potential for "freshwater ecotoxicity" is significant and mainly related to metal emissions from plastic production. No other contribution from emissions of chemicals used (e.g. additives) is mentioned in the study.

4.1 Coverage of Chemical Emissions

In the case study described in this chapter, a better coverage of the chemical-related impact categories than in former has been aimed at by including characterisation factors from recent work in other industry sectors and by calculating new ones for chemical emissions expected to contribute significantly. Despite the fact that the inventory of the production stage is much more detailed than that of the other stages, even the composition of the raw materials used during the production stage is based on simplifying assumptions, and some minor components have been excluded due to lack of data.

The total number of chemical emissions to air included is about 100. Among these, 33% are covered by characterisation factors for human toxicity and 26% are covered by characterisation factors for ecotoxicity. The emissions from the material stage and the disposal stage (mainly the former) include unspecific categories like VOC, NMVOC and unspecified dust for which more specific information of actual content is not available. In total, 48% of the emitted quantity (kg) is covered by characterisation factors for human toxicity and 21% for the ecotoxicity part. If we exclude the amount coming from some of the highest contributing emissions (SO_2, NO_x, unspecified dust, calcium, Cl^- and suspended solids), for which at least the main part typically does not contribute significantly to the potential ecotoxicity impact, the coverage becomes 64% for the ecotoxicity impact category.

Regarding the total number of emissions to water, around 120 are included. About 25% of the waterborne emissions are covered by characterisation factors for human toxicity, and for ecotoxicity, the corresponding figure is 37% of the total number. The waterborne emissions from the material and disposal stage also include unspecific types like COD, TOC, VOC and suspended matter, for which information of the actual content is not available. Only 3.1% of the total emitted quantity (by weight) is covered by characterisation factors for human toxicity, and only 3.4% is covered for ecotoxicity. If we exclude the amount coming from the highest contributing emissions (SO_4^-, Tot-P, Na^+, COD, calcium, Cl^- and suspended solids), for which at least the main part typically does not contribute significantly to the toxicity impact categories, the coverage becomes 48% for human toxicity and 53% for the ecotoxicity part.

The main part of the specifically known individual emissions to water, which are not included (i.e. characterisation factors lacking), consists of inorganic salts (e.g. disodium silicate, sulphates), polymers (e.g. acrylates, modified phenol resin) and acids/bases (e.g. NaOH, HCl). In general, these substances/mixtures have a low toxicity and are not expected to contribute significantly to the toxicity impact categories, if not emitted in high quantities. In the latter case they will typically contribute only to acute ecotoxicity (e.g. reactive monomers from binders, acids or bases causing low or high pH), and only if not treated in a wastewater treatment plant (WWTP) before emission to the water recipient. Most of them have been assessed in Larsen et al. [22–25] and Nielsen et al. [26], on the basis of hazard assessments and/or generic risk assessments, regarding the potential effects if emitted to a WWTP or directly to a water recipient.

Known emissions from the production stage, which are not covered by characterisation factors and which may contribute significantly to the toxicity impact categories, include emissions of components occurring in small quantities in the raw materials (typically well below 5%) like siccatives (organic metal compounds), softeners (phthalates), antioxidants (aromatics) and “wetteners” (surfactants). Due to lack of readily available knowledge of their exact identity and/or lack of readily available data on their inherent environmental properties, it has not been possible to include them in the case study.

4.2 Potential Contributing Additives

As described in the chapter “Case Study on Printed Matter in Denmark” in Volume I of “Global Risk-Based Management of Chemical Additives” [11], a substitution project within the Danish printing industry was started up in 2006. A major part of the work was to map the presence of chemicals which are potential candidates for substitution (e.g. PBT, CMR, vPvB, EDS), especially related to the REACH regulation [27]. The mapping comprised a combination of a literature study and an investigation of the actual (2007) presence of candidate substances at 15 Danish printing houses including the examination of almost 900 MSDSs (i.e. products). Furthermore, a focused search in the Danish Product Register (http://arbejdstilsynet.dk/en/engelsk/produktregistret.aspx) was included. About 30 of the substances, actually found in the Danish printing industry, fulfil one or more of the criteria (e.g. CMR, EDS) for the REACH Annex XIV candidate list [28], i.e. the candidate list for the Authorisation list [29]. Eighteen of those substances appear as components of printing inks and/or glues and therefore, in varying degrees, become part of the printed matter when produced. When recycled, these substances may therefore occur in the recycled paper as impurities.

Table 1 Substances appearing as components of inks or glues and found in the Danish printing industry. All substances meet one or more of the criteria (e.g. CMR, EDS) for the REACH Annex XIV candidate list

Name	CAS No.	Annex XIV criteria	REACH status (June 2012)
Pigment yellow 34 (lead-chromate)	1344-37-2	Carc 1B, Rep 1A	Authorisation list
Pigment red 104 (lead-chromate)	12656-85-8	Carc 1B, Rep 1A	Authorisation list
Di(2-ethylhexyl)phthalate, DEHP	117-81-7	Rep 1B, EDS list (Cat 1)	Authorisation list
Dibutyl phthalate, DBP	84-74-2	Rep 1B, EDS list (Cat 1)	Authorisation list
Benzyl butyl phthalate, BBP	85-68-7	Rep 1B, EDS list (Cat 1)	Authorisation list
Trichloroethylene	79-01-6	Carc 1B	Candidate list
Cobalt siccatives[a]	(10124-43-3)	(Carc 1B, Rep 1B)	Candidate list
Benzene	71-43-2	Carc 1A, Mut 1B	Not listed[b]
2-Methylaziridine	75-55-8	Carc 1B	Not listed[b]
Aziridine	151-56-4	Carc 1B, Mut 1B	Not listed[b]
Propylene oxide	75-56-9	Carc 1B, Mut 1B	Not listed[b]
2-Methoxy propylacetate	70657-70-4	Rep 1B	Not listed[b]
Alkylphenol ethoxylates	(25154-52-3)	EDS list (Cat 1)	Not listed[b]
Octamethylcyclotetrasiloxane (polydimethylsiloxane)	556-67-2 (9016-00-6)	EDS list (Cat 1), possible PBT/vPvB substance	Not listed[b]
Bisphenol A	80-05-7	EDS list (Cat 1)	Not listed[b]
Resorcinol	108-46-3	EDS list (Cat 1)	Not listed[b]
Styrene	100-42-5	EDS list (Cat 1)	Not listed[b]
Decamethylcyclopentasiloxane	541-02-6	Possible PBT/vPvB substance	Not listed[b]

[a] Possible content of soluble cobalt(II) salts. Cobalt(II) sulphate, cobalt dichloride, cobalt(II) carbonate, cobalt(II) dinitrate and cobalt(II) diacetate all appear on the recently updated REACH Annex XIV candidate list [28]. IARC classifies all soluble cobalt(II) salts as possible carcinogenic, i.e. group 2B (http://monographs.iarc.fr/ENG/Monographs/vol86/mono86.pdf)

[b] Meaning not listed on the Authorisation list nor on its candidate list

The 18 substances are shown in Table 1. Five of these substances are now (June 2012) included in Annex XIV (Authorisation list) [29]. These substances are the lead-chromate pigments, pigment yellow 34 and pigment red 104, and the phthalates DEHP, DBP and BBP, which all are used as components/additives in some printing inks. As evident from Table 1, cobalt(II) salts and trichloroethylene appear on the Annex XIV candidate list [28], and they are also used as additives in some printing inks. ECHA has recommended in its third recommendation [30] to put these two substances on the Authorisation list [29]. Besides these seven substances of very high concern (SVHC substances) appearing on either the Authorisation list or its candidate list, 11 other substances that meet one or more of the criteria for the candidate list are shown in Table 1. These substances are also highly problematic and have the potential to follow the substrate, i.e. paper, when recycled. Furthermore, it may be relevant, here, to mention that 26 hydrocarbon mixtures, most probably containing hazardous single substances (e.g. hexane, heptane, naphthalene) were also found in the Danish printing industry. Many of these are used as components in printing inks (and cleaning agents) and therefore may follow the printed substrate when recycled.

Actually, according to newer German investigations [31], dibutyl phthalate and mineral oil components have been found in recycled paper used for food packaging, giving rise to serious concern about potential human exposure. Also bisphenol A, DEHP and alkylphenol ethoxylates have recently been found in recycled paper-based food packaging on the Italian market [32].

5 Research Needs

In order to improve the comprehensiveness of the basis for the assessment, including the coverage of chemical emissions, future LCA case studies on printed matter need to include at least the following issues:

- Ink component (and their precursors) production: siccatives, antioxidants, pigments, dyes, etc.
- Water emissions from paper production: softeners (BPA), other phenolic compounds (NPE, APE), other surfactants (LAS), biocides (benzothiazoler, dibromo compounds), wood extractions (terpenoids, resin acids) and more
- Recycling of paper: fate of paper chemicals, ink chemicals, glue chemicals, etc.
- Treatment of chemical waste: fate of (hazardous) waste from printing (ink waste, used cleaning agents, used rinsing water, etc.) and from recycling of paper (sludge from repulping)

The case study described here, though being the far most comprehensive on chemical emissions and focus on toxicity-related impact categories, is a relatively old study, and LCIA methodology has been extended and improved since it was performed. Furthermore, it is always good to test the robustness of LCA results by including different LCIA methods and different weighting principles. Therefore, with the aim of trying to confirm the overall case study results and increase its reliability, an updated LCA with especially improved background inventory data and use of improved and different LCIA methodology is recommended. Actually, in the ongoing (2012) EU FP7 research project LC-Impact (www.lc-impact.eu), an improved and updated version, of the database used for the LCA case study shown in this chapter, is going to be the basis for a new printed matter case study including the involvement of ILCD-recommended LCIA methodology like USEtox [33] for the toxicity-related impact categories.

6 Conclusion

The case study presented here shows that chemical emissions may play a significant role in the LCA impact profile of printed matter. Some of the chemicals related to these emissions, like pigments and certain solvents, may be considered as additives in the life cycle of printed matter. A survey in the Danish printing industry shows occurrence of SVHC, and many of these, e.g. lead-chromate-based pigments and a number of phthalates, are components of printing inks or glues that remain on the paper when the printed matter is produced. They therefore have the potential of becoming part of the recycled paper. Actually, some of these substances have been found in food packaging based on recycled paper in recent German and Italian studies. It might be that these additives/impurities contribute significantly to the printed matter/paper LCA impact profile due to direct human exposure during the use stage or emissions to the environment during the processing of the recycled paper. However, this issue still needs to be investigated.

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LCA Case Study Cushion Vinyl Floor Covering and DEHP

Environmental Impacts of Use and Recycling of Additives (DEHP) in Products

Lauran van Oers and Ester van der Voet

Abstract To illustrate the LCA method and its relevance for risk-based management of additives, an example is elaborated for a phthalate plasticizer, di (2-ethylhexyl) phthalate (DEHP), as used in the application in cushion vinyl floor covering. In LCA environmental impacts are estimated for the total of emissions, not restricted to toxic effects and/or one substance (like DEHP). Furthermore emissions relate to the cradle-to-grave chain of the additive application in cushion vinyl floor covering. For the waste disposal of the EoL cushion vinyl floor covering four different scenarios are elaborated: incineration; controlled landfill; uncontrolled land fill, assuming DEHP emission; and material recycling. Emissions of DEHP are missing in the LC Inventory database. Therefore, additional estimates for the emission of DEHP during production, use and waste disposal are based on several MFA studies. The discussion mentions several limitations of the study. Given these limitations, the scenario in which the EoL PVC waste is incinerated is the environmentally worst option. The total weighted impacts for the other scenarios are not far apart. However, the impact of incineration, with energy recovery, is overestimated because burdens of waste incineration are completely attributed to the cushion vinyl floor covering. The impact of uncontrolled landfill is underestimated because the time horizon of DEHP leakage from the site is defined rather short. The contribution of phthalates emissions to the impact score appears to be small. An exception is the scenario in which the EoL waste is dumped on an uncontrolled land fill site. In this case the fresh water ecotoxicity score becomes substantial and is dominated by the emission of phthalate from the landfill site. This will become even more apparent if a larger time horizon for DEHP leakage from the landfill site is assumed.

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Keywords Additive, Cushion Vinyl Floor Covering, DEHP, Life Cycle Analysis, LCA, Plastic, Waste Treatment

Contents

1 Introduction

To illustrate the LCA method [1] and its relevance for risk-based management of additives, an example is elaborated for a phthalate plasticizer, di (2-ethylhexyl) phthalate (DEHP), as used in the application in cushion vinyl floor covering.

This study deals with life cycle assessment of emissions related to the use of additives in a plastic application. This means that environmental impacts are estimated for the total of emissions, not restricted to toxic effects and/or one substance (like DEHP). Furthermore emissions relate to the cradle-to-grave chain of the additive application in cushion vinyl floor covering.

2 Inventory Analysis

2.1 System Description and Flow Chart

In this study the environmental impacts are calculated for the use of 1 m^2 cushion vinyl floor covering, with a lifetime of 15 years (in LCA terms called the functional unit). Figure 1 shows the process flowchart for the production, use and waste disposal of a cushion vinyl floor covering. Cushioned flooring is produced by spread coating. The glass fibre is used as a substrate. Several layers, each with its

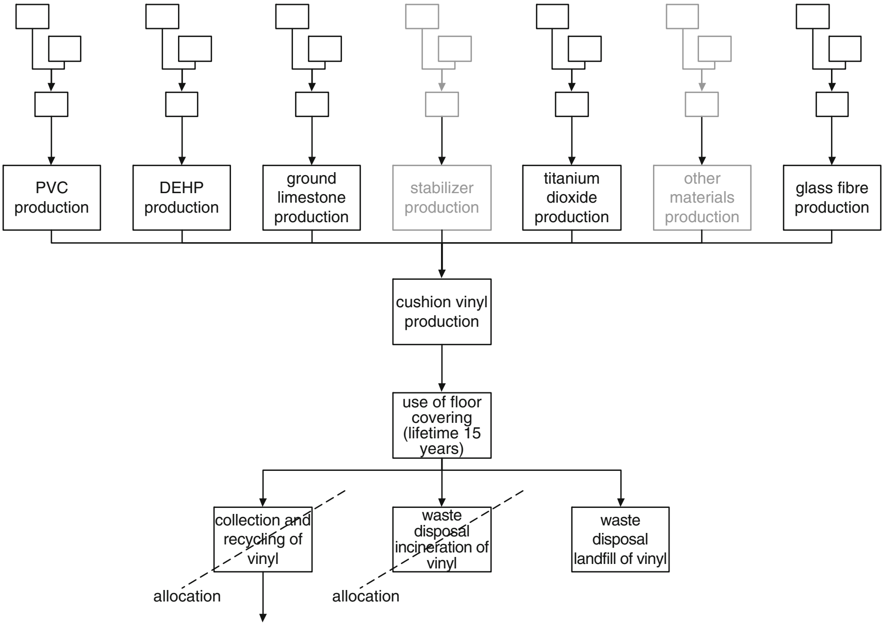

Fig. 1 Flow chart of the production, use and waste disposal of cushion vinyl floor covering

Table 1 Composition of 1 m^2 cushion vinyl floor covering [3]

Cushion vinyl floor covering	kg	%
PVC	0.84	48.4
DEHP	0.51	29.1
Limestone	0.25	14.4
Stabilizer	0.050	2.9
Pigment	0.0050	0.3
Other materials	0.030	1.7
Glass fibre	0.055	3.2
Cushion vinyl floor covering	1.74	100

own function, are applied to the glass fibre. The product is so-called “cushion flooring” since it typically involves at least one foam layer. The foamed layers are mixtures of polyvinyl chloride, plasticizer, limestone, stabilizers, pigments and some other additives [2–4].

The process description for the production of cushion vinyl floor covering is to a large extent based on Potting and Blok [3]. In Table 1 the composition of 1 m^2 cushion vinyl floor covering is given. In the plastic and additive market DEHP is called a plastic additive, despite the large mass volume of DEHP used in CVFC. An additional process for the production of DEHP is defined based on Potting and Blok [3] and processes from the Ecoinvent database. Process descriptions of the background processes are based on the Ecoinvent database, version 2.2 [5]. Process descriptions for the production of stabilizers and other materials are missing

Table 2 DEHP emission factors to air and water based on MFA studies

	Air	Water	Unit	Reference
DEHP production	1.80E-06	4.50E-06	kg/kg	[5]
DEHP industrial use	2.00E-04	6.00E-05	kg/kg	[6]
End use floor covering	5.00E-04	0	kg/kg year	[6]
Waste incineration	0	0	kg/kg	[2, 6]
Waste landfill	0	0	kg/kg year	[2, 6]

(marked grey in Fig. 1). In this study these materials are not further elaborated (see Sect. 5). In the Ecoinvent database also emissions of DEHP are lacking. Therefore, additional estimates (Table 2) for the emission of DEHP during production, use and waste disposal are based on several Material Flow Accounting (MFA) studies [2, 6–8].

The lifetime of the cushion vinyl floor covering is assumed to be 15 years. Indoor emissions of DEHP during these 15 years are taken into account. The maintenance of the floor is not taken into account.

For the waste disposal four different scenarios are elaborated:

- Incineration of the cushion vinyl floor covering
- Landfill of the cushion vinyl floor covering
- Landfill of the cushion vinyl floor covering, assuming additional DEHP emission
- Material recycling of the cushion vinyl floor covering

2.2 *Process Data for Incineration and Landfill*

Emissions from incineration and landfill are based on material-specific inventories for PVC sealing sheet, containing PVC, plasticizer, limestone and glass fibre. The technologies described in the Ecoinvent database for incineration and landfill of PVC should be considered as representative for a "high tech" society. For example, the landfill represents a controlled site in which precaution measures are taken to prevent direct leakage of toxic substances to surface and ground water. Furthermore, in a controlled landfill site the effluent from the site will be processed in a sewage treatment plant and the sewage sludge will be incinerated. The process data for landfill of PVC floor covering in the Ecoinvent database are inclusive the burdens from the landfill, the waste water treatment of the effluent and the incineration of the sludge [9].

The material-specific burdens for the waste treatment are calculated by a supporting spreadsheet of Ecoinvent. Necessary data for the calculation of the burden are, e.g. element composition, water content, energy content, degradability in landfill, etc. Note that the Ecoinvent waste management model estimates emissions based on the element composition and some general characteristics of the materials (like degradability). Detailed characteristics, like the mobility of

DEHP from PVC, are not taken into account. Therefore, additional assumptions are made for the emission of DEHP from landfill of PVC.

In the MFA studies no direct emission of DEHP from waste incineration or landfill to air or surface water are reported. For incineration it is assumed that DEHP is decomposed into CO_2 and H_2O. For landfill it is assumed that DEHP is degraded into CO_2 and CH_4 [10] or waste water (incl. DEHP) is treated in the WWTP [2, 6].

The above described landfill refers to a highly controlled landfill site with emission precaution measures. However, in less controlled conditions DEHP emissions might occur. Therefore, an additional assumption is made for emissions of DEHP from uncontrolled landfill. The same yearly emission factor is used as for the use phase of the floor covering, assuming a time period of 30 years instead of 15 years.

2.3 *Process Data for Recycling, Mechanical Recycling of PVC and Allocation*

There are several options for the recycling of plastics (Delgado and Stenmark [11]):

- Mechanical recycling of materials (plastics)
- Chemical recycling of raw materials (monomers, etc.)
- Incineration, with energy recovery

Mechanical recycling is the preferred route for homogeneous and relatively clean plastics waste streams. It is assumed that the cushion vinyl floor covering will be mechanically recycled [11].[1]

In LCI databases no process data are found for the process of mechanical recycling of PVC. Therefore, some rough assumptions have been made for the definition of the process, like energy use, auxiliary material use and emissions (including phthalate emissions).

The energy use and emissions are similar as in the process “production of cushion vinyl floor covering”, but discarded cushion vinyl floor covering (waste) is the economic inflow and the different materials (goods), like PVC, limestone, glass fibre, etc., are the economic outflows.

The recycling of cushion vinyl floor covering is a multi-functional process with the functions “treatment of waste” and “production of (several) materials”. The “treatment of waste” is considered to be part of the primary system “cushion vinyl floor covering”. The production of the materials is considered to be part of the

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[1] The building and construction plastics account only for 3% of overall collectable plastic waste in Western Europe in 2002, of which about 8% is mechanically recycled within Europe on a regular basis. However, the building and construction sector is an important end market for recycled plastics from many sectors. Some 30% of overall recycled plastics are used in applications such as insulation, fences and flooring.

secondary system. This might be the secondary use of the materials for the production of secondary cushion vinyl floor covering. The system boundary between the primary and secondary system is situated within the recycling process. As a proxy it is assumed that half of the process is allocated to the primary system and half is allocated to the secondary system.

3 Impact Assessment

The aim of the Life Cycle Impact Assessment (LCIA) is to facilitate the interpretation of the results of the inventory analysis. The result of the inventory analysis is an emission profile for each alternative system. In this study the emission profile is the total of all emissions to air, water and soil from the grave-to-cradle chain for the use of cushion vinyl floor covering, including the up chain processes, like electricity production and the down chain processes, like the incineration and landfill of the waste. Such an emission profile may consist of hundreds of emissions and extractions. In LCA impact assessment the total of interventions (emissions, extractions) of a process chain is evaluated in terms of environmental problems (impact categories).

Basically the impact assessment involves the following steps:

- Characterization
- Normalization
- Weighting

Table 3 gives an overview of the environmental impact categories that are taken into account in the environmental impact assessment according to the baseline method that is recommended in the Dutch LCA Handbook [1]. The characterization for toxicity is based on factors derived by the Usetox model [12]. The impact categories “depletion of water” and “ionizing radiation” are not taken into account because reliable characterization factors are not available.

ISO 14042 defines normalization as “calculation of the magnitude of indicator results relative to reference information”. The main aim of normalizing the category indicator results is to better understand the relative importance and magnitude of these results for each product system under study. For the purpose of normalization in LCA, Wegener Sleeswijk et al. [13] have made a comprehensive inventory of extractions and emissions of substances for the world level in the year 2000. The normalization in this project is based on these reference emissions and extractions. As a result the normalized score of an impact category for the cushion vinyl floor covering case is expressed as a fraction of the world problem.

Weighting is an optional step of impact assessment, in which the (normalized) indicator results for each impact category assessed are assigned numerical factors according to their relative importance, multiplied by these factors and possibly aggregated. Weighting is based on value choices (e.g. monetary values, standards, expert panel). A convenient name for the result of the weighting step is “weighting

Table 3 Impact categories, characterization and weighting factors

Impact category	Baseline characterization factor	Weighting factor (%)
Climate change (global warming)	GWP_{100}	28
Stratospheric ozone depletion	ODP_{∞}	5
Photo-oxidant formation (photochemical oxidation)	POCP	6
Human toxicity	HTP_{∞}	21
Fresh water aquatic ecotoxicity	$FAETP_{\infty}$	19
Acidification	AP	5
Eutrophication	EP	8
Depletion of abiotic resources	ADP	8
Total		100

result", of which there is generally one for each alternative product system analysed. Table 3 shows the weighting set that is used in this study to relatively weight the environmental problems (impact categories) from the problem-oriented approach. The weighting set is loosely based on the weighting sets for midpoint impact categories as reported by Huppes and van Oers [14], a study funded by the EC in which weighting sets are proposed to assess the overall EU27 impact based on decoupling indicators.

4 Results, Environmental Impact Scores for the Use of Cushion Vinyl Floor Covering

The environmental impact scores are calculated for four different sets of data. The data sets differ in the type of waste treatment that is assumed for the end-of-life waste:

- Use of cushion vinyl floor covering with incineration
- Use of cushion vinyl floor covering with landfill
- Use of cushion vinyl floor covering with landfill, incl. assumed DEHP emissions
- Use of cushion vinyl floor covering with recycling

Two versions for the waste treatment by landfill are elaborated. In one version there are no emissions of DEHP from landfill sites. This assumption can be considered as representative for a highly *controlled* landfill site. In a second version of the waste treatment at an *uncontrolled* landfill site a DEHP emission is assumed.

4.1 Weighted Results

Figure 2 shows the weighted impact scores of the use of 1 m^2 cushion vinyl floor covering, broken down into environmental impact categories and Life Cycle stages.

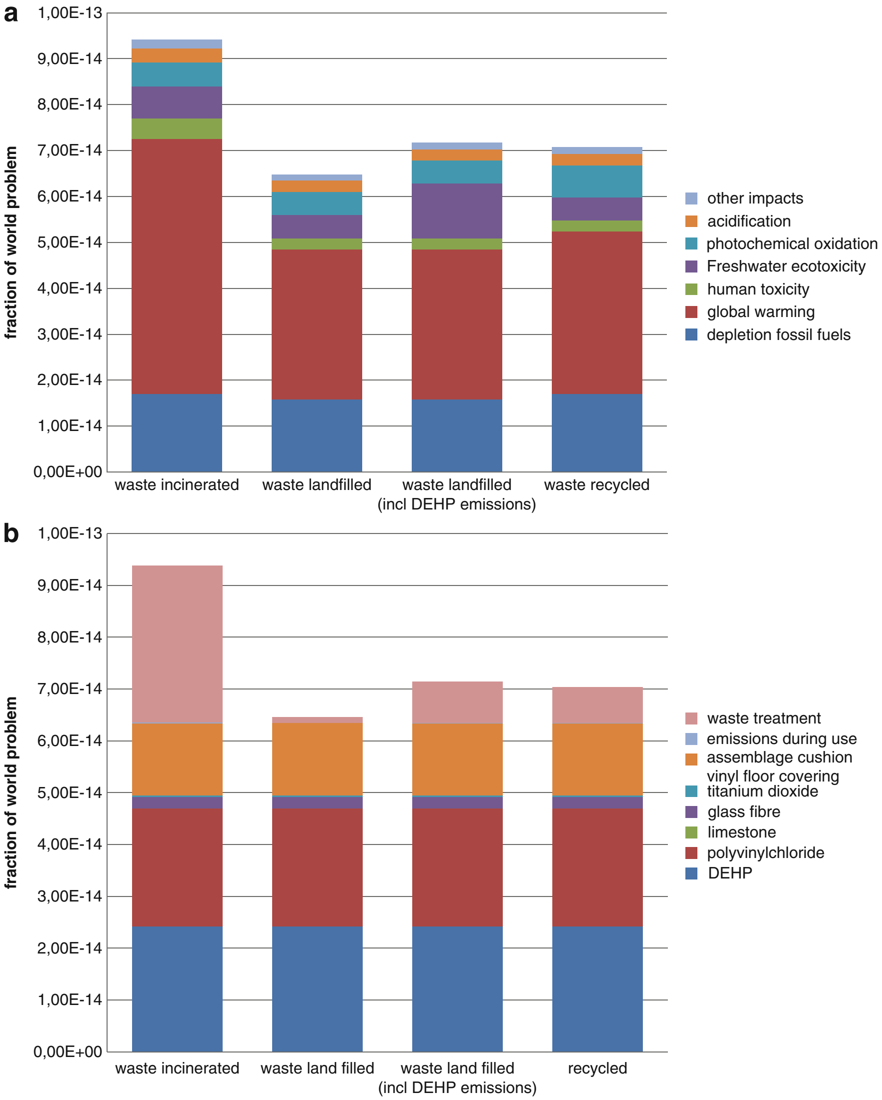

Fig. 2 Weighted impact scores of the use of 1 m^2 cushion vinyl floor covering, broken down into impacts (**a**) and Life Cycle stages (**b**)

Results are given for four different scenarios of waste treatment. Note that the scores are the results of a weighting across different impacts categories.

According to these results, landfill of the waste, assuming no DEHP emissions, is the most environmental friendly option, closely followed by the scenario assuming material recycling of the end of life PVC waste. The worst option from an environmental point of view is the incineration of the EoL PVC waste.

Figure 2a shows that for all scenarios the impact categories "global warming" and depletion of fossil fuels contribute most to the total weighted score, respectively, about 50% and 20–25%. The contribution of "global warming" for the scenario with waste incineration is substantially higher, about 60% instead of 50%. In the waste treatment scenario "landfill with DEHP emission" also the impact category "fresh water aquatic ecotoxicity" has a substantial contribution to the total weighted impact score, about 15%. To a large extent this can be attributed to the assumed emission of DEHP to water.

Figure 2b shows the contribution of the different Life Cycle stages of the use of cushion vinyl floor covering to the weighted impact score. Most important processes contributing to the weighted score are the production of DEHP and PVC, about 30–35%. In the case of waste incineration also the waste treatment has a substantial contribution, about 30%. Finally, the assemblage of cushion vinyl floor covering has a contribution of about 20%. The emission of DEHP from the cushion vinyl floor covering during use appears to have a negligible contribution.

According to these results, the production of the additive DEHP contributes to a large extent to the total environmental impact score of the use of cushion vinyl floor covering. Note that these impacts may be caused by substances other than DEHP!

Now the question is to which substances can the contributions be attributed? Table 4 shows the contribution of the emitted substances from processes for the weighted impact score. The emission of CO_2 during incineration of EoL PVC and other processes appears to have a large contribution. Also the ecotoxicity effect of the emission of phthalate to water during landfill of EoL PVC appears to have a substantial contribution.

4.2 Normalized Results

In the previous paragraph results are presented for the weighted impact score based on all impact categories that are mentioned in Table 3. In this paragraph the focus is on a selection of the impact categories. From a riskcycle perspective the toxicity impacts are most relevant. Next to toxicity also global warming is presented because it generally is considered an important problem. The results presented in this paragraph are based on the normalized scores without a "value choice" weighting between impact categories. Figure 3 shows the normalized scores for the use of 1 m^2 cushion vinyl floor covering for the impact categories "global warming", "human toxicity" and "aquatic ecotoxicity".

Figure 3 shows that compared to "global warming" the cushion vinyl floor covering has a relative low score for "human toxicity" and "aquatic ecotoxicity".

In Figs. 4, 5 and 6 the normalized results are broken down into Life Cycle stages. Tables 5 and 6 give the contribution of the emitted substances from processes for the normalized impact scores for "human toxicity" and "aquatic ecotoxicity".

The differences between the scenarios are completely explained by the differences between the waste treatment options.

Table 4 Contribution of substance emissions to the weighted score for 1 m^2 cushion vinyl floor covering (contributions <1% suppressed)

			Contribution (%)			
Process	Elementary flow	Category	Incineration	Landfill	Landfill with DEHP emissions	Recycling
PVC flooring waste incineration	Carbon dioxide [air]	Global warming	21			
Heat production from natural gas	Carbon dioxide [air]	Global warming	11	16	14	18
Polyvinylchloride production	Carbon dioxide [air]	Global warming	9	13	12	12
Cushion vinyl floor covering, to landfill	Phthalate, dioctyl-[water]	Freshwater ecotoxicity			9	
Cushion vinyl production	Ethene [air]	Photochemical oxidation	4	6	5	5
Natural gas extraction	Natural gas [resource]	Resource depletion	2	6	5	6
Polyvinylchloride production	Natural gas [resource]	Resource depletion	2	4	3	3
Polyvinylchloride production	Crude oil [resource]	Resource depletion	2	3	3	3
Polyvinylchloride production	Carbon dioxide [air]	Global warming	2	3	2	2
Polyvinylchloride production	Mercury [air]	Human toxicity		1	1	1
Ethylene production	Crude oil [resource]	Resource depletion	1	2	2	2
Ethylene production	Carbon dioxide [air]	Global warming	2	2	2	2
Ethylene production	Natural gas [resource]	Resource depletion		1		
Incineration residue, landfill	Chromium VI [water]	Freshwater ecotoxicity	2	2	2	2
Xylene production	Carbon dioxide [air]	Global warming	2	2	2	2
Xylene production	Crude oil [resource]	Resource depletion		1	1	1
Xylene production	Natural gas [resource]	Resource depletion		1		
Heat production from heavy fuel oil	Vanadium [air]	Freshwater ecotoxicity		1	1	1
Recycling of cushion vinyl floor covering	Ethene [air]	Photochemical oxidation				3
Total	Total	Total	59	65	66	66

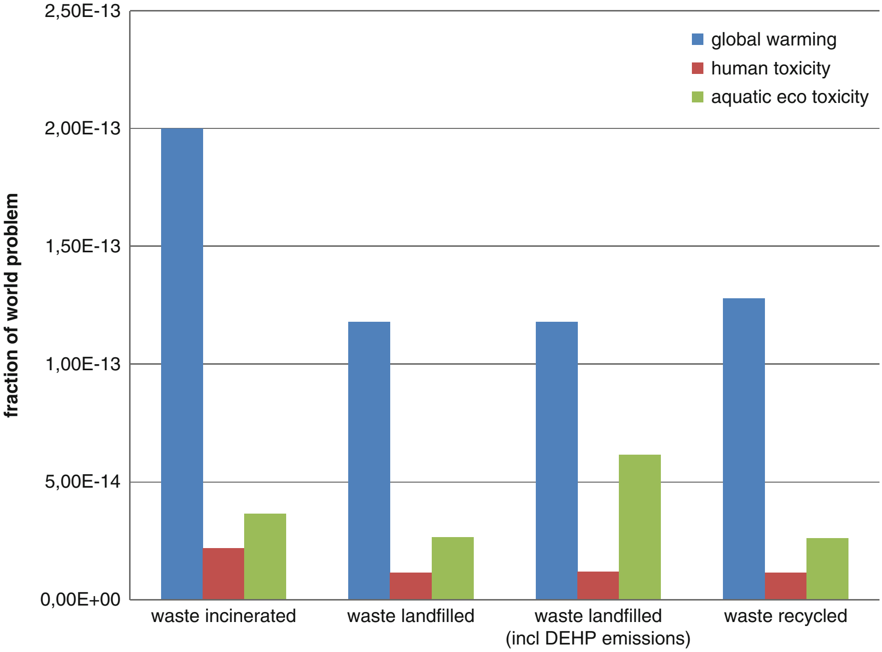

Fig. 3 Normalized scores for the use of 1 m^2 cushion vinyl floor covering for the impact categories “global warming”, “human toxicity” and “aquatic ecotoxicity”

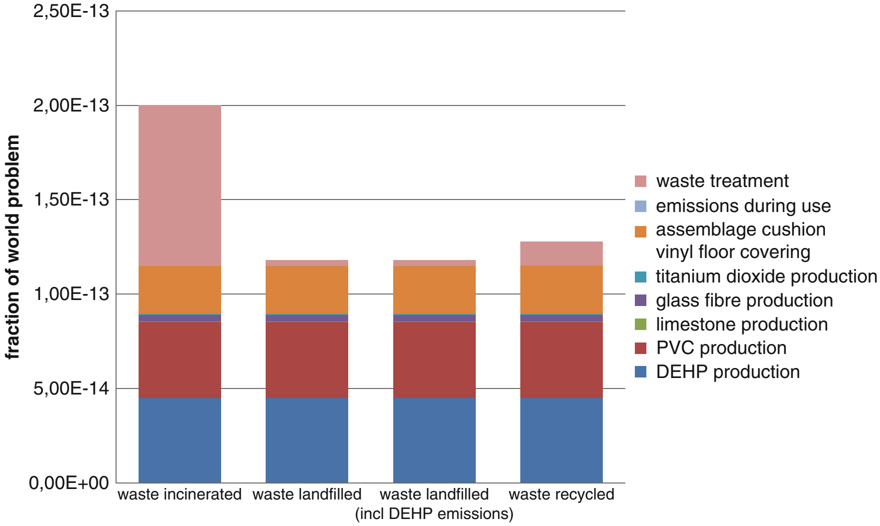

Fig. 4 Normalized global warming impact scores of the use of 1 m^2 cushion vinyl floor covering, broken down into Life Cycle stages

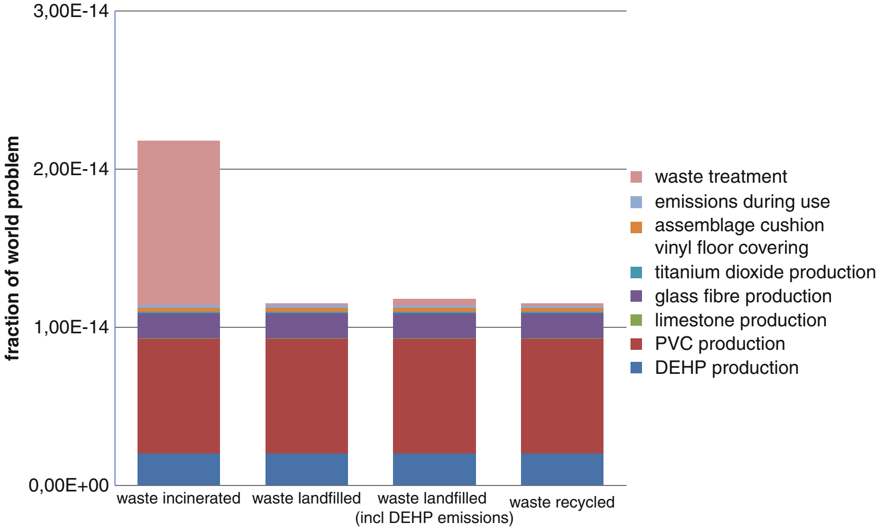

Fig. 5 Normalized human toxicity impact scores of the use of 1 m^2 cushion vinyl floor covering, broken down into Life Cycle stages

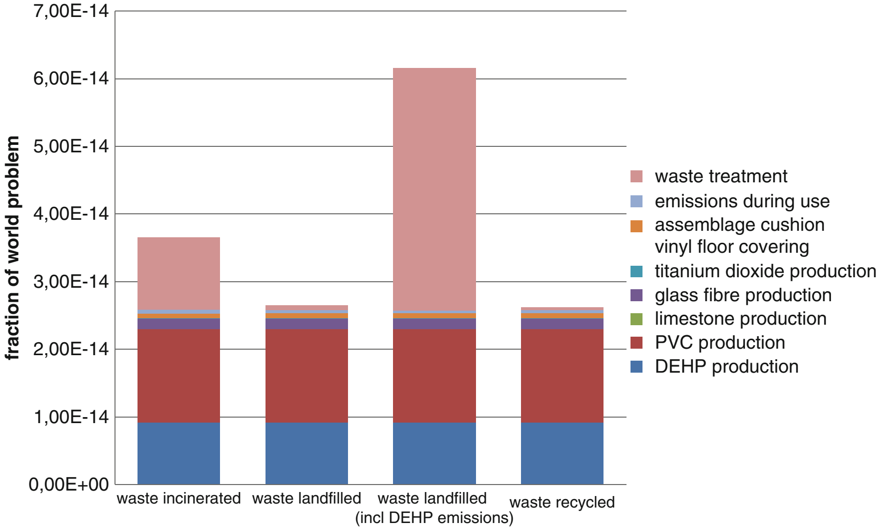

Fig. 6 Normalized aquatic ecotoxicity impact scores of the use of 1 m^2 cushion vinyl floor covering, broken down into Life Cycle stages

The waste treatment scenario with incineration has by far to the highest score for global warming, followed by the scenario considering recycling. The impact scores for the landfill scenarios are the lowest and, expectedly, the same for both scenarios. The combustion of the EoL plastic will lead to large CO_2 emissions. About 40% of

Table 5 Human toxicity, contribution of substance emissions to the normalized score for 1 m^2 cushion vinyl floor covering (contributions <1% suppressed)

		Contribution (%)			
Process	Elementary flow	Incineration	Landfill	Landfill with DEHP emissions	Recycling
Polyvinylchloride production	Mercury [air]	26	48	47	47
Mercury production	Mercury [air]	15			
Sodium hydroxide production	Mercury [air]	15			
Steel production, electric	Mercury [air]	2			
Steel production, electric	Mercury [air]		2	2	2
Incineration residue, landfill	Chromium VI [water]	4	8	8	8
PVC flooring waste incineration	Chromium VI [water]	2			
Glass fibre production	Arsenic [air]	3	6	6	6
Incineration residue, landfill	Arsenic, ion [water]		3	3	3
PVC flooring waste incineration	Arsenic, ion [water]	3			
Hard coal ash, landfill	Arsenic, ion [water]		1	1	1
Hard coal ash, landfill	Arsenic, ion [water]	1			
Incineration residue, landfill	Arsenic, ion [water]	2			
Glass fibre production	Cadmium [air]	3	5	5	5
PVC flooring waste incineration	Lead [air]	1			
Cushion vinyl floor covering, to landfill (incl. DEHP emissions)	Phthalate, dioctyl-[air]			1	
Use of floor covering (15 years)	Phthalate, dioctyl-[air]		1	1	1
Cushion vinyl floor covering, to landfill (incl. DEHP emissions)	Phthalate, dioctyl-[water]			1	
Zinc production, primary	Zinc [air]	1	1	1	1
Total	Total	78	76	77	76

the global warming impact score can be attributed to the incineration of EoL PVC. While emissions of greenhouse gases (GHG) in case of landfill of plastic will be small because of the low degradability of the plastics. Emissions of GHG during recycling are related to the energy consumption. About 10% of the global warming impact score is caused by the energy consumed by the recycling process.

Table 6 Aquatic eco toxicity, contribution of substance emissions to the normalized score for 1 m^2 cushion vinyl floor covering (contributions <1% suppressed)

		Contribution (%)			
Process	Elementary flow	Incineration	Landfill	Landfill with DEHP emissions	Recycling
Cushion vinyl floor covering, to landfill (incl. DEHP emissions)	Phthalate, dioctyl- [water]			56	
Cushion vinyl production	Phthalate, dioctyl- [water]		1		1
Incineration residue, landfill	Chromium VI [water]	21	29	12	29
Heat production from heavy fuel oil	Vanadium [air]	11	14	6	15
Polyvinylchloride production	Zinc, ion [water]	9	12	5	13
PVC flooring waste incineration	Chromium VI [water]	10			
Slag, unalloyed electr. steel, to landfill	Chromium VI [water]	4	3	1	4
Polyvinylchloride production	Copper, ion [water]	3	5	2	5
Incineration residue, landfill	Arsenic, ion [water]	1	2		2
PVC flooring waste incineration	Arsenic, ion [water]	3			
Glass fibre production	Arsenic [air]	2	2		2
Use of floor covering (15 years)	Phthalate, dioctyl-[air]	1	2		2
Polyvinylchloride sealing, to sanitary landfill [CH]	Vanadium, ion [water]		2		
PVC flooring waste incineration	Vanadium, ion [water]	2			
Polyethylene waste incineration	Antimony [water]	1			
Xylene production	Nickel [air]		1		1
Total	Total	67	73	83	72

Again, the waste treatment scenario with incineration has by far to the highest score for human toxicity. The scores for the other scenarios are more or less the same. The incineration of EoL PVC will lead to toxic emissions of metals (arsenic, lead, chromium, see Table 5) causing human health effects. However, the most important contribution to the human health effect is caused by the emission of mercury in the upchain processes of the production of mercury and sodium hydroxide. Sodium hydroxide is an auxiliary material in the waste incineration process. Mercury cells are used for the electrolysis of NaCl into chlorine and sodium hydroxide. Toxic emissions for human health in the other waste treatment processes seems to be limited. Also for PVC production mercury appears to be the most dominant emission. Again this is caused by the use of mercury cells for the production of chlorine which is used in PVC production. Finally, there are substantial contributions related to the production of additives DEHP and glass fibre to the human toxicity score. Note that these impacts may be caused by substances other than DEHP or glass fibre! In fact Table 5 shows that DEHP emission of the production of DEHP has a negligible contribution to the human toxicity score (contribution $<1\%$). Of minor importance are emissions of DEHP during use and landfill of the PVC (1–3%).

The comparison of aquatic ecotoxicity scores between the scenarios is completely dominated by the assumed emission of DEHP from the (uncontrolled) landfill site. If an emission is assumed the score for aquatic ecotoxicity will increase substantially (a factor 2).

5 Discussion

5.1 *Process Data*

5.1.1 Lacking Process Data

Process data for the production of stabilizer and other materials are lacking. Also possible emissions of these additives during use and waste disposal are missing. According to Tukker et al. [2] and Jönsson et al. [4] possible other materials might be:

- Stabilizer: Ba/Zn stabilizer, Ca/Zn stabilizer, SnS stabilizer, organotin (small market)
- Other additives like flame retardants (BBP), etc.
- Other materials: PUR

5.1.2 Estimated Process Data on Waste Treatment

To estimate material-specific emissions from the waste treatment processes, landfill and incineration, of EoL cushion vinyl floor covering a supporting spreadsheet of Ecoinvent is used. The results will depend on the assumptions that are made in these models. In this project these assumptions are not studied in detail. Necessary data for the calculation of the burden are, e.g. element composition, water content, energy content, degradability in landfill, etc. Note that the Ecoinvent waste management model estimates emissions based on the element composition and some general characteristics of the materials (like degradability). Detailed characteristics, like the mobility of DEHP from PVC are not taken into account. Therefore, additional assumptions are made for the emission of DEHP from landfill of PVC. Such additional assumptions might also be necessary for other substance emissions, e.g. emission of methane from landfill sites, etc. For a detailed comparison of the waste treatment processes a more detailed analysis of the processes, the characteristics of the disposed materials and the underlying models, is necessary.

Waste incineration with energy recovery is a common technique in Europe. The process of waste incineration in the Ecoinvent database is also described as a multifunctional process which delivers the function "waste treatment", "electricity production" and "heat production". However, a more detailed study of the background report of the incineration processes shows that all the burdens are allocated to the "waste treatment" function. So the production of electricity and heat are without any burdens. This partly explains the high contribution of waste incineration to the total weighted impact score. If part of the burdens will be allocated to the energy services, e.g. by using partitioning based on revenues (economic allocation), the impact of the waste service which is attributed to the cushion vinyl floor covering will decrease. As a result the total weighted impact score for the incineration scenario will decrease. For example, if economic allocation is used for partitioning over the two different functions, assuming equal revenues for waste treatment and energy production, the impacts related to the incineration of the EoL plastic waste will be halved.

In the scenario for the controlled landfill site the treatment of effluent from the site by sewage treatment and the incineration of the sludge are taken into account. An additional scenario is made for an uncontrolled landfill site, assuming DEHP emissions. However, in an uncontrolled landfill site not only DEHP will emit from the site but also other toxic releases like heavy metals. So the results presented for the uncontrolled landfill site are an underestimation. For a more realistic assessment of impacts related to the uncontrolled landfill of PVC, additional estimates are necessary for the emissions of (toxic) releases. As a consequence, the impact assessment score for human and aquatic ecotoxicity for the uncontrolled landfill site will increase. The relative contribution of DEHP to these scores will decrease because also other emissions which are in the present assumptions are now lacking, like heavy metals, will contribute to the score.

Furthermore, the emission of DEHP from the uncontrolled landfill site most likely is underestimated. The estimate is based on the yearly emission factor that is used for the indoor emission during the use of the floor covering. The time period of the DEHP leakage from cushion vinyl floor covering at the landfill site is quite arbitrarily set at 30 years. The emission from landfill site attributed to the functional unit of the use of 1 m^2 cushion vinyl floor covering will increase if the estimate is based on a larger time period, e.g. 100 years. Therefore, given the fact that landfilled waste will remain on the site for a long period of time the impacts of toxic emissions from the uncontrolled landfill site most likely are underestimated.

5.1.3 Outdated Process Data

In the results the emissions of mercury appear to have a very substantial contribution for the human toxicity impact score. These emissions are caused by the coproduction of chlorine and sodium hydroxide by electrolysis using a mercury cell. However, this technique is phased out. Therefore, the process descriptions in the Ecoinvent database do not represent up to date technology. In the Ecoinvent database the process for PVC production, in which chlorine is used as one of the compounds, is an aggregated processes based on, seemingly outdated, data from PlasticsEurope. These outdated data also influence the impacts related to waste treatment by incineration because sodium hydroxide is necessary for the waste incineration process.

5.2 Impact Assessment

5.2.1 Dominance of Heavy Metals

In the LCIA community there is much discussion on the characterization of heavy metals for toxicity. Due to large residence times in the environment, the characterization factors for heavy metals tend to dominate the impact scores for toxicity impact categories. This might suppress the impacts of other relevant toxic substances, like DEHP. For this reason the results are calculated using the characterization factors derived by the Usetox model instead of the Uses model. Uses model is the original baseline characterization model that is recommended in the Dutch LCA Handbook [1].

5.2.2 Missing Pathways Human Toxicity

In Franco et al. [15] it is concluded that the characterization models, like EUSES and ACC-human, underestimate human exposure to phthalate esters because they consider only a few key pathways. It is not known whether the more relevant pathways for phthalate esters are taken into account in the Usetox model?

5.2.3 Missing Pathways for Indoor Emissions During Use Phase

Emissions of DEHP during use of the cushion vinyl floor covering appear to have a negligible contribution in the total weighted score. However, the assessment of the impact of the DEHP emission on human health is based on a characterization model that is developed for outdoor emissions, Usetox. The emission of DEHP during the use phase of the floor covering is indoors and therefore fate and the human exposure will be different compared to an outdoor emission. It is very likely that indoor emissions of DEHP will have a larger impact on human health effects than outdoor emissions. In most LCAs effect on human health due to indoor emissions are not considered in the total weighted impact score.

So the indoor emissions need a specific fate and exposure modelling. In Meijer et al. [16, 17] a characterization model and characterization factors for indoor emissions are presented. In the articles also indoor emissions of some building materials are estimated and their effects are calculated. It is concluded that damage effects of indoor emissions cannot be neglected.

However, although a characterization model is available for indoor emissions it is still difficult to take into account these indoor emissions because for the interpretation of the impact assessment also normalization data are desirable. For this a world covering estimate of the indoor emissions of toxic substances is necessary.

5.3 Weighting Across Impact Categories

The contribution of different impact categories to the total weighted score by definition depends on the weighting set that is used to weight across impact categories. In the weighting set that is applied in this project (Table 3) relative high weighting factors are given for the impact categories “global warming” (28) and “human toxicity” (21). The weighting across impact categories are based on subjective choices and therefore by definition a topic of discussion. Nevertheless, in this project weighted impact scores are used to get an overall picture of the environmental impacts for the different scenarios. Subsequently the focus is put on the separate impact categories “human toxicity”, “aquatic ecotoxicity” and “global warming”, avoiding the weighting.

6 Conclusion

6.1 General Conclusions Based on the Weighted Impact Scores

Given the system assumptions and characterization models that are used in this project the scenario in which the EoL PVC waste is incinerated is the environmentally worst option. The total weighted impacts for the other scenarios are not far apart.

However, the assumptions of the present system have some important draw backs. The impact of incineration, with energy recovery, is overestimated because burdens of incineration are completely attributed to the waste treatment of cushion vinyl floor covering while none is attributed to the production of energy, which is a co-function of the waste incineration.

Furthermore, the impacts on toxicity scores for the uncontrolled landfill site are most likely underestimated. The time period of DEHP leakage from the landfill site is assumed to be rather short (set at 30 years whilst a larger period, e.g. 100 years, seems more appropriate).

The impact to the total weighted score of the emission of DEHP during use of the cushion vinyl floor covering is negligible.

The impact category "global warming" contributes most to the total environmental impact score (60–50%).

The impact category "human toxicity" (based on USESTOX characterization factors) has a small contribution to the total environmental impact score (about 5%).

Also the impact category "aquatic ecotoxicity" has a small contribution to the total environmental impact score (about 8%), with an exception for the landfill scenario with DEHP emission (about 17%). Emission of DEHP from an uncontrolled landfill site, the landfill scenario with DEHP emission, appears to have a substantial contribution to the total weighted impact score.

6.2 Conclusions Based on the Normalized Toxicity Scores

The impact score for human toxicity appears to be relatively low compared to the other environmental impacts. The contribution of phthalates to this impact score is small. If incineration is assumed this contribution is less than 1%. The other extreme, if landfill with DEHP emission is assumed, this contribution is 3%.

The impact score for fresh water ecotoxicity is relatively low compared to the other environmental impacts for the cases incineration, landfill without DEHP emissions and recycling.

Only in the case of landfill with DEHP emissions the contribution of phthalate emissions to the freshwater ecotoxicity becomes dominant. In this case also the fresh water ecotoxicity score is substantial compared to the other environmental impact scores.

6.3 Conclusions for the Additive DEHP

For aquatic toxicity the landfill without leaching prevention is by far the worst option, while the controlled landfill site is the best one, together with recycling. The waste phase therefore is a crucial issue, and can be influenced to a large extent. Secondly, DEHP is important in the life cycle of PVC flooring, both in the production and the waste management phase. In the third place, emissions during use, although included in the analysis, do not seem to be important in the life cycle.

For global warming the DEHP production contributes significantly to GHG emissions. Also the waste phase seems to be important and can be influenced. Incineration seems the worst option for waste treatment due to CO_2 emissions from incinerated plastic. The two landfill options appear to be the best ones – in this case, the least energy-intensive.

So from the point of view of additives, it seems that they may indeed contribute significantly to life cycle impacts. The case study of PVC flooring shows that additives contribute significantly, not just to toxicity impact due to DEHP emissions but also to global warming due to GHG emissions along the Cradle-to-Grave chain of the compound DEHP.

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Chemicals in Leather: International Trends on Risk-Based Control and Management

Stefan Rydin

Abstract The leather sector is a traditional industry. This chapter will give an overview of the use of chemicals in the leather sector and identify different types and amounts of chemicals used in the different processes.

During recent years, there has been an increased focus on chemical substances including additives in many different articles such as shoes and gloves. In particular articles that come into contact with humans have been in focus. The concern being that humans and the environment will be exposed to hazardous substances from articles.

This chapter will give an overview of recent international trends and initiatives regarding chemicals in leather and articles containing leather. That includes the identification of chemicals in the produced leather that are common on restricted substance lists and present ongoing recent initiatives to control the impact from these chemicals including both legislative measures and initiatives from customers such as international brands or purchasing sectors and different eco-labels.

Keywords Additives, Chemicals, Eco-label, Leather, Restricted substances, Tanning

Contents

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Abbreviations

AOX	Adsorbable organic halogen
APE	Alkylphenol ethoxylates
BAT	Best available techniques
BBP	Benzyl butyl phthalate
BREF	BAT reference document
COD	Chemical oxygen demand
DBP	Dibutyl phthalate
DEHP	Bis(2-ethylhexyl) phthalate
DMF	Dimethyl fumarate
EPA	Environmental Protection Agency
EU	European Union
GADSL	Global automotive declarable substance list
IED	Industrial Emissions Directive
LWG	Leather Working Group
NGO	Non-governmental organisation
NP	Nonylphenol
NPE	Nonylphenol ethoxylates
PCP	Pentachlorophenol
PFOS	Perfluorooctane sulfonates
POP	Persistent organic chemicals
REACH	Registration Evaluation, Authorisation and Restriction of Chemical Substances (European Community Regulation on chemicals and their safe use)
RSL	Restricted substance lists
SCCP	Short-chain chlorinated paraffins
SSEI	Swedish Shoe Environmental Initiative
STWI	Sweden Textile Water Initiative
SVHC	Substance of very high concern
TCP	Trichlorophenol
VOCs	Volatile organic compounds

1 Background

The leather industry is a traditional industrial sector. The industry uses both a high variety and high amount of chemicals during the production of leather from raw hides and skins.

Tanneries use around 2–3 kg of chemicals for every kilogram of leather that is produced. It is not uncommon that a medium-sized tannery uses around 300–400 different chemicals in the production, and recent published data from a tannery showed they were using around 350 different chemicals in the production [1]. It should also be noted that less than 20% of the weight of the hides that will be processed will actually end up as leather. The remaining part will become waste or by-products. A typical mass balance from a tannery producing leather from bovine hides is given in Fig. 1.

The production of raw hides and skins depends on the availability of raw materials, which is regulated by animal population, offtake ratio and the weight per hide and skin recovered. The availability of raw material depends therefore on the meat consumption in the world. The main centres for raw hide/skin production do not necessarily coincide with the major leather production centres. There is a worldwide transport of salted hides/skins from areas with raw hide production to areas with a tanning industry. Between the early 1980s and mid 1990s, a major part of the world production was moved to the developing countries from the developed countries. The developing countries produce around 64% of the number of hides, and with respect to the sheepskins, developing countries account for about 65% of the global number of skins produced. In particular, the tanning industry has increased in size in the Far East and Latin America. The main producing country of leather today is China followed by Italy, India and Brazil.

Europe is still the main market for leather products and leather produced in the developing countries, e.g. Southeast Asia, may therefore end up on the European market and to European consumers. Chemicals that are added during the production, and which stay on/in the product, will hence be transported by the product to the final markets, and there will be a chemical flow around the world through the transport of leather and leather products containing chemicals. Since the tanning industry is a chemically intensive industry, an efficient chemical management in tanneries is necessary in order to minimise the overall use of chemicals and in particular also to reduce the amount of hazardous chemicals used in order to minimise eventual health effects on the consumer.

There are several initiatives and actions in order to control and stimulate a more efficient chemical management in the tanning sector. The main incentives are environmental legislations and customer requirements. The customer requirement can be expressed as either eco-labels or restriction substance lists (RSL) of chemicals in the products developed by major brands or several industrial groups.

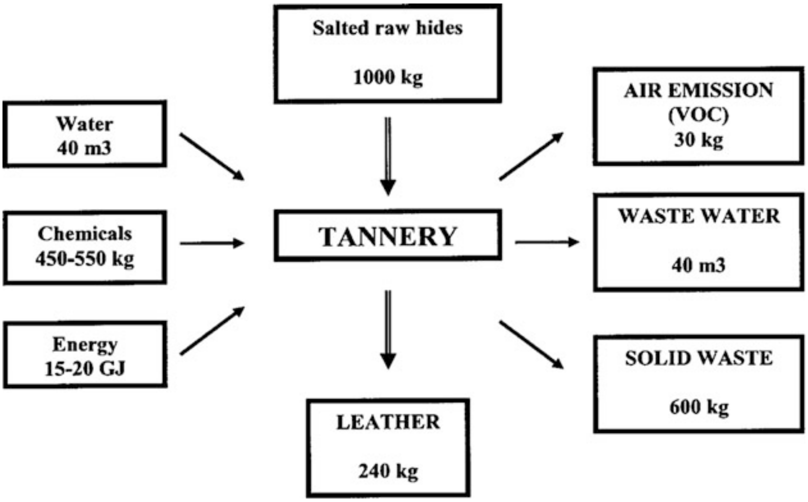

Fig. 1 Mass balance during leather production

2 Use of Chemicals in the Leather Sector

The amount of chemicals used varies significantly with the specification of the final product, the types of hides and skins that are treated and the process chosen. Figures for the consumption of chemicals can therefore only be given within a broad range. The water content must also be taken into account when comparing consumption figures. An example of a brief overview of the chemical consumption is given in Table 1 [2].

The major parts of the chemicals that are use are inorganic bulk chemicals. Around 20–50% of the chemicals that are added are inorganic standard chemicals. The inorganic chemicals generally used are calcium hydroxide, sodium chloride, sodium sulphide, acids, carbonates and sulphates. Besides the inorganic standard chemicals, chromium sulphate is also widely used as a tanning agent, and the consumption of chrome tanning agents is often around 80 kg/ton salted hides (corresponding to around 15 kg chromium/ton salted raw hide).

Around 10–40% of the chemical consumption in a tannery is organic chemicals. Examples of standard organic chemicals used are organic acids and their salts.

Besides the main process chemicals, a great variety of chemicals are used for auxiliary process purposes. These auxiliary agents may demand special attention because of the problem of reactivity, toxicity, persistence, bioaccumulation, mobility and the generation of problematic metabolites. It is, therefore, important to know the quantities used and their characteristics.

Globally, approximately 6.0 million tonnes of raw hides (on a wet salted basis) is processed to leather [3]. In addition, around 650,000 tonnes of goat- and sheepskins is processed to leather [3]. This indicates that globally around 3 million tonnes of chemicals is used to produce leather. It is hence of importance that the chemical

Table 1 Use of chemicals in the leather sector

Chemical	Kg/ton salted raw hide
Standard chemicals, inorganic	215
Standard chemicals, organic	35
Enzyme preparations	7
Detergents	8
Biocides	1
Chrome tanning agents	80
Vegetable and synthetic tanning agents	40
Resins and dye assistants	10
Dyes	9
Fatliquoring agents	40
Waterproofing agents	2
Pigments	4
Finish chemicals	46
Organic solvents	24
Total	521

consumption is reduced as much as possible and that the use of hazardous chemicals is avoided. The substitution of hazardous chemicals to less toxic chemicals should have a high priority for the leather sector.

A practical problem faced by tanneries is that many chemical products are proprietary products. Many suppliers do not specify the chemical composition of the products, so tanneries may have to seek additional information from the chemical suppliers in order to determine the environmental impact of the products they use. Sometimes it is also difficult for tanneries to receive accurate information also from the suppliers of the chemicals. Material safety data sheets generally provide some data on the toxicity of the products to humans and environment, and many tanneries use these as the sole source of information to determine the environmental impact of a certain substance. It can be expected in the EU in the future that tanneries will receive more detailed information about the substances used because of the REACH legislation.

3 Drivers for Chemical Management in Tanneries

The chemicals that are used in the tanning sector will end up either in the leather product, in the waste or will be discharged either to water, air or soil. There is different legislation depending on if the chemical will end up in the product or if it will end up in the environment. This chapter focuses on the drivers for avoiding or restricting certain chemicals in the products.

There are basically two stakeholder groups involved in the development of criteria for leather products or development of restricted substance lists. These stakeholder groups are legislators (national regulations and laws and international agreements and regulations) and manufacturers/brands and eco-labels (global brands, industrial sectors and several different types of eco-labels for consumer items).

3.1 National Regulations and Laws

The relevant legislation for tanneries regarding the use of chemicals can be found both in legislation regarding environmental permits for the industrial installations which in some cases addresses substitution of chemicals. One example of this is the EU Industrial Emissions Directive [4] which regulates emissions from industrial installation within the EU. One key aspect in this directive is how problematic chemicals should be substituted to more environmentally friendly alternatives by tanneries.

The other type of legislation regulates the use of chemicals and also regulates the content of some specific chemicals in the final products. As example, the European chemical legislation REACH can be mentioned [5]. Annex XVII sets out the list of restrictions on the manufacture, placing on the market and use of certain dangerous chemical substances, mixtures and articles.

The different types of legislation are presented below.

3.1.1 Industrial Emissions Directive

The EU Directive on industrial emissions [4] which often is called IED was adopted on 24 November 2010 (it was a result of merging seven different EU Directives including the IPPC Directive into one directive). The directive regulates emissions from large industrial installations within the EU. The directive was put into force on 6 January 2011 and should be implemented by all the 27 member states in the EU by 7 January 2013.

The directive sets out the main principles for the permitting and control of industrial installations based on an integrated approach and the application of best available techniques (BAT) which are the most effective techniques to achieve a high level of environmental protection, taking into account the costs and benefits.

In order to have a common understanding of BAT within Europe, BAT reference documents (BREF) are developed by the European Commission. These documents describe what is considered to be the BAT at the different process stages. Under the direction of the IPPC office in Seville, BREF documents are produced within technical working groups (TWG) with the participation of industry, EU member states and relevant organisations. The work on a BREF frequently takes several years and results in a comprehensive document with detailed descriptions of technical benchmarks for all parts of an industrial process. A BREF is revised roughly every eighth year. There exist currently (2012) 35 BREF, and one of these BREFs is one developed for the tanning industry (TAN BREF).

The TAN BREF document is at the moment revised, but a new version is expected to be adopted by the end of November 2012. The document contains information about the leather industry in general, the leather industry in EU, conventional technologies used, BAT and also emission levels which are possible to be achieved by the use of BAT. The document includes information of substitution of chemicals in the industry. However, the document does not specifically address human health risks due to chemicals in the products since that subject is covered by other legislation within the EU. However, the document gives guidance on use of alternative chemicals as an alternative to the use of several problematic chemicals.

The TAN BREF document can be found on the homepage of the European IPPC Bureau [3].

3.1.2 Legislation Concerning Chemicals

Each country has its own regulation and laws regarding chemicals. There are major differences between different countries, and some countries have considerably more regulations than other countries.

The chemical legislation in the European Union has been put together into one EU Regulation which is the EU Regulation called REACH [5]. Since the legislation is in the form of a regulation, it is mandatory for all 27 member states in the European Union. It deals with the registration, evaluation, authorisation and restriction of chemical substances. The law entered into force on 1 June 2007. The main objective of REACH is to improve the protection of human health and the environment through the better and earlier identification of intrinsic hazardous properties of chemical substances. One of the main reasons for developing and adopting the REACH Regulation was that a large number of substances have been manufactured and placed on the market in Europe for many years, sometimes in very high amounts, and yet there is insufficient information on the hazards that they pose to human health and the environment.

Furthermore, the EU regularly produces and regularly updates the list of substances of high concern, i.e. the SVHC list. The identification of a substance as a SVHC and its inclusion in the candidate list is the first step of the authorization procedure. The European Chemical Agency in Helsinki identifies from the candidate list priority substances to be included in Annex XIV of REACH (the authorisation list). The substances on the candidate list will most probably be liable to stricter regulation in the future (authorisation/banning) which will stimulate the substitution of these chemicals. Currently in June 2012, there are 84 substances included in the candidate list. Examples of chemicals on the candidate list which may be relevant for the leather industry are phenolphthalein, boric acid, cobalt dichloride, dichromate (although not used by leather industry), phthalates (DEHP, DBP and BBP), acrylamide and short-chain chlorinated paraffins.

Companies may have immediate legal obligations following such inclusion which are linked to the listed substances on its own, in preparations and articles.

Furthermore, many restriction lists and eco-labels will include chemicals on the SVHC list in their restriction lists and criteria for eco-labels.

The restriction of chemicals has been included in Annex XVII of REACH. The annex deals with the restriction of manufacture, placing on market and use of certain dangerous substances, preparations and articles.

The EU Regulation restricts either

- The sale or manufacture within the EU of product formulations containing more than certain amounts of chemical substances
- The presence of certain chemical substances in consumer goods

Other countries besides the EU also have introduced legislation regarding chemicals in products although the EU is a key driver regarding environmental legislation. For example, the Federal Agencies, EPA (Environmental Protection Agency) and CPSC (Consumer Product Safety Commission), which control regulations and guidelines at a national level in the USA, may be mentioned. In addition, the individual states have their own regulations (e.g. California).

Japan has regulations for harmful substances, and the most relevant for the leather industry is the Law 112 restricting harmful substances (e.g. formaldehyde) in household products.

Furthermore, China has recently implemented a chemical legislation similar to EU REACH, and the legislation is sometimes called the China REACH. The China REACH came into force in 15 October 2010.

3.2 International Agreements and Regulations

There are several international treaties and agreements administrated by the United Nations which limit specific chemicals.

One of the most known is the “Stockholm Convention of Persistent Organic Pollutants (POPs)” which is signed by 151 countries [6]. The Stockholm Convention, which was adopted in 2001 and entered into force in year 2004, requires all parties to take measures to eliminate or reduce the release of POPs into the environment.

POPs are organic chemical substances that resist biodegradation, are toxic to both humans and wildlife and furthermore tend to accumulate in living tissues.

The convention includes currently 21 POP substances such as chlorinated organic pesticides, brominated organic flame retardants and perfluorooctane sulfonates (PFOS).

3.3 Eco-labels for Consumer Items

An eco-label is a logo that identifies a product that has met an environmentally preferable standard. It is not always obvious what an eco-label means, and there are a high number of eco-labels available for leather. In many cases, the eco-labels have been developed by a test institute or a group of test institutes who are responsible for monitoring the compliance of these eco-labels. Typically, a company applies to an eco-labelling organisation for the right to use its label on their products, and in order to gain certification, the company and product must continually conform to the required standards of the organisation. Some eco-labels consider only the product (avoid toxic chemicals in the product), while others also take the environmental impact during the production into consideration as well as the quality and durability of the product.

It is sometimes difficult for a tannery to decide which eco-label is suitable due to the high number of different schemes that exist on the market. In order for an eco-label to be successful, it has to be recognised and used for consumer items. It should also be noted that many of the eco-labels for leather are strongly textile oriented and the criteria are sometimes more relevant for the textile sector.

The most relevant eco-labels for the leather industry are presented below.

3.3.1 Blue Angel (Der Blaue Angel)

The Blue Angel is a German eco-label for products and services [7]. The eco-label was introduced in 1978 and was one of the first worldwide environmental labels. The Blue Angel is an official label since it is owned by the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety in Germany. The award criteria are established by the Federal Environmental Agency in Germany with the support of scientific institutes and the industry.

Currently in 2012, the Blue Angel has around 80 product categories, and more than 10,000 products have been awarded the Blue Angel. The Blue Angel has developed two product categories that are relevant for the leather sector. These are low-emission upholstery leather and footwear.

The Blue Angel eco-labels for leather may be awarded to the product “leather” which has been manufactured in an environmentally friendly way, from the health point of view does not have an adverse impact on the living environment and does not contain any hazardous substances that would significantly impede recycling.

The criteria for the Blue Angel eco-labels go beyond legal provisions. The Blue Angel eco-label includes a number of different criteria for leather which are related to the following:

- Dangerous substances in the final product
- Water use during production
- Emissions from the production (COD, chromium, sulphide, AOX and toxicity)
- Durability of product
- Emissions of volatile organic compounds (VOCs)
- Consumer information

3.3.2 EU Eco-label for Footwear (Previously Called the EU Flower)

The EU eco-label [8] was launched in 1992 when the European Community decided to develop a Europe-wide voluntary environmental scheme that consumers could trust. The EU eco-label covers a huge number of products and services. The criteria are developed by key experts in consultation with main stakeholders in order to decrease the environmental impacts over the entire life cycle of a product. The criteria are revised every 4 years in order to take new developments and knowledge into consideration.

The EU eco-label that is relevant for the leather industry is the eco-label for footwear. The EU eco-label is given to consumer products. Leather is not in itself a consumer product, but criteria for leather are included in the criteria for footwear. The criteria can be found in Commission Decision of 9 July 2009 establishing the ecological criteria for the award of the Community eco-label for footwear (2009/563/EC).

The European eco-label for footwear includes a number of different criteria for leather which are related to the following:

- Dangerous substances in the final product (chromium VI, arsenic, cadmium and lead and free formaldehyde)
- Reduction of water consumption during production
- Emissions from the production (COD and chromium)
- Use of hazardous substances (PCP, TCP, forbidden azo dyes, SCCP and APE)
- Energy consumption (to be declared)
- Durability of product

3.3.3 The Nordic Eco-label Svanen

The Nordic eco-label is the official eco-label for the Nordic countries [9]. It was founded in 1989 and the aim is to provide customers with a tool (the Nordic eco-label logo) to help them choose among the best, environmental performing products on the market. The criteria are developed by using a life-cycle perspective. The Nordic eco-label has in total 63 product groups.

The Nordic eco-label has developed criteria for leather based on environmental, health and quality requirements. The requirements are imposed on the production process, from the production of skins to the final leather products. The Nordic eco-label is to some extent coordinated with the European eco-label. The criteria for the Nordic eco-label for leather are currently in 2012 being revised. At the moment the Nordic eco-label for leather includes the following criteria regarding:

- Dangerous substances in final product (e.g. chromium VI, lead, cadmium, formaldehyde and many other chemicals)
- Discharge to wastewater (COD and chromium)
- Use of hazardous chemicals (nonylphenol ethoxylates (NPE), PCP and many other chemicals)

3.3.4 Oeko-Tex 100

The Oeko-Tex Standard 100 [10] was introduced in the beginning of the 1990s. It was developed by the Austrian Textile Research Institute (ÖTI) and the German Research Institute Hohenstein and is a product label based on test for harmful substances in leather (or textiles), and the primary target group is the textile and clothing industry.

A tested product is allocated into one of four product classes based on its intended use. The more intensively a product comes into contact with the skin, the stricter the human toxicity requirement must be fulfilled by the product. A certificate is issued and will be valid for 1 year and can be renewed.

The Oeko-Tex label tests for and restricts a high number of chemicals in the product. It should be noted that chrome-tanned leather cannot receive the Oeko-Tex Standard 100 certificate due to stringent demands on chromium. Since around 85–90% of all leather in the world is tanned with chromium, the certificate is only valid for a minor part of the leather production.

3.3.5 SG Label

TÜV Rheinland in Germany was founded in 1872 and developed from a regional testing agency to an international provider of services. TÜV Rheinland has developed the SG Mark [11] which is a certification related to harmful substances developed by TÜV Rheinland. This certificate only relates to chemicals in the product.

The objective with the certification is to ensure that the certified products present no danger to human health to the best current knowledge. Furthermore, the product undergoes testing and will continue to undergo random tests after the mark is issued.

The testing includes test for prohibited azo dyes, pentachlorophenol (PCP), formaldehyde and heavy metals.

3.4 Manufacturers and Brands

There are several international brands that publish their own lists of restricted substances. Examples of brands are Adidas, H&M, IKEA, GANT and many more. In many cases the lists from the brands are quite identical since they very often are based on legislative demands from for instance the REACH legislation. Also very often chemicals on the SVHC list will be included in the list of restricted substances from the brands.

One sector which traditionally has been a driver regarding restriction lists for a long time is the automotive industry. In particular, the automotive industry present detailed specifications on many different chemicals and substrates. In the past, most of the different automotive industries had their own specifications and different demands from different customers. However recently, the automotive industry has started to cooperate regarding which chemicals that should be restricted and declared. The European automotive industry has to comply with the End of Life Vehicle Directive requirements and has set up a database to record each component used in cars. To ensure that information on restricted substances is collected worldwide, the global automotive declarable substance list (GADSL) has been established and requires those in the supply chain to provide information for the listed substance. The list contains 2,732 substances in 2011 and the GADSL list is normally updated each year [1].

Also the automotive industry in other countries has started to produce restriction lists. The Japanese automotive industry (JAMA) introduced in 2005 voluntary air quality standards which limits the emissions inside cars.

Another initiative is the Leather Working Group (LWG) which is an initiative with stakeholders in the leather industry including brands, manufacturers, suppliers, NGOs and other end users. The LWG was formed in 2005. The group has developed an environmental protocol for the leather manufacturing industry. The group endeavours to promote improvement in the tanning industry by bringing visibility to best practices and providing guidelines for continual improvement. The LWG has developed an environmental assessment tool. The protocol provides a framework of scoring structures that reward good environmental practice. The scoring system enables those that perform better to achieve higher awards, and tanneries can achieve gold, silver or bronze ratings. Some brands and end users use this list as a sourcing tool to select preferred suppliers from the rated tanneries.

Furthermore, some recent initiatives from groups of companies in the Nordic countries should be mentioned. Sweden Textile Water Initiative (STWI) started in 2010 as a joint project between textile and leather retail companies in Sweden. As of November 2011, 32 companies have joined STWI. The aim of the STWI is to produce guidelines for sustainable water management both for the textile sector and the leather sector.

The STWI has produced guidelines for leather and textile production, and these guidelines cover three areas which are water efficiency, water pollution prevention and wastewater. The purpose of the water efficiency part is to ensure that only the necessary amount of water is used in the factory reducing the size of wastewater treatment plants as well as reducing energy and water costs. The areas of water pollution prevention and wastewater aim to reduce negative health and environmental impacts from chemicals used in the production processes. The guidelines have divided companies into three categories which are level 1 (minimum level), level 2 (improver) and level 3 (achiever). The purpose of the three-level structures is to facilitate continuous improvements and to enable factories at all levels of performance to use the guidelines. The first version of the guidelines was finalised and released in May 2012.

Another recent initiative in Sweden is the formation of Swedish Shoe Environmental Initiative (SSEI) which is an initiative from the Swedish shoe industry. The objective is to develop a sustainability index to be used primarily for development and purchase. The initiative started in 2012 and has so far gathered more than 20 Swedish companies in the shoe sector. The development of a sustainability index is expected to take around 3 years.

4 Restricted Chemicals with Relevance for the Leather Sector

There are, as mentioned in the previous section, a number of eco-labels and product labels available on the market. Many of the requirements from different eco-labels and RSL are similar, and some of the restricted chemicals are the same in the different initiatives. A number of chemicals that very often are included in product labels and list of harmful substances are presented below. This section only describes some examples of chemicals that frequently are included in RSL, but other chemicals will also be briefly included.

4.1 Aromatic Amines from Azo Dyes

Around 90% of all leather and textile dyes used are azo dyes. The azo dyes break down during reductive conditions to form aromatic amines. Twenty two (22) aromatic amines are forbidden in the EU Regulation 1907/2006 [5] since these 22 amines are known to be carcinogens or potential carcinogens. The focus on these aromatic amines started in Germany, and in 1994 it became forbidden according to the German Consumer Goods Ordinance to produce, import and sell garments and fabric dyes with certain azo colourants (those azo dyes which can break down under reductive conditions to release any of the 22 aromatic amines). Since the German leather market is the most important market in Europe, all major chemical suppliers of dyes very quickly substituted dyes containing prohibited azo colourants.

In 2002, the European Commission also prohibited the use of azo dyes which by reductive cleavage of one or more azo groups may release one or more of the 22 amines. The dyes were prohibited according to the EU Directive 2002/61/EC from July 2002 amending for the 19th time the Council Directive 76/769/EEC. This directive was later replaced by Regulation EC 1907/2006 (REACH) according to an EU Regulation from 2009.

Most of the commercially available azo dyes do not break down to produce these forbidden amines. The European legislation which states that leather articles that come into contact with human skin should not contain any of the 22 aromatic amines in concentrations above 30 ppm can be found in Annex XVII [12] of REACH. Furthermore, most eco-labels and RSL have the same criteria.

4.2 Pentachlorophenol

PCP was widely applied by the leather industry before the 1990s for improving the biocidal activity of raw hides and skins. Due to the risk of transformation into dioxin during burning, the use of PCP and its salts and esters in leather manufacturing is not allowed in the EU according to EU Regulation 1997/2006 (Annex XVII) [12].

Some member states in the EU like Germany, Austria and Denmark have in addition implemented stricter legislation than EU and restrict the marketing of leather products containing PCP and its salt and esters.

Furthermore, most eco-labels and restriction lists include PCP. PCP is also discussed in connection with the Stockholm Convention on POPs and may be restricted or forbidden worldwide through the Stockholm Convention in the future.

4.3 Chlorinated Paraffins (SCCP, Short Chain)

Chlorinated paraffins are very complex mixtures and are often divided into several groups depending on the chain, length of the starting material and the amount of chlorine in the final product. Three major groups are short-, medium- and long-chained chlorinated paraffins (SCCPs, MCCPs and LCCPs).

Short-chained chlorinated paraffins (SCCP) are those with a chain length of C10–C13. EU Regulation 1907/2006 [12] restricts the marketing and sale of SCCP in preparations to a maximum of 1%. SCCP were mainly in the past used as fatliquors, but other alternatives are available in the market. The use of SCCP is also restricted by many eco-labels and RSL.

SCCP are just like PCP currently discussed in connection with the Stockholm Convention on POPs and may be restricted or forbidden worldwide through the Stockholm Convention in the future.

4.4 Chromium (VI)

Hexavalent chromium in leather products has become in focus during the last 10 years although the chemical is not used by the leather industry. Chromium (VI) is known to cause severe allergic contact dermatitis in humans, is able to elicit dermatitis at very low concentrations and is strongly suspected to be carcinogenic, mutagenic and reprotoxic. Chromium (VI) is not used intentionally in the production of leather but may be formed within the leather by oxidation of chromium (III) used for the tanning of the leather. The mechanisms of the formation of chromium (VI) in the leather are today well known, and measures for prevention of the formation of chromium (VI) in measurable concentrations have been developed and implemented in most tanneries in the EU. The first survey of leather products was made in Denmark in 2002 and revealed that around 30% of the tested leather articles contained hexavalent chromium [13]. Recent surveys of chromium (VI) in articles of leather in Germany and Denmark in 2007–2008 have demonstrated that still more than 30% of the tested articles contained chromium (VI) in concentrations above 3 mg/kg.

Denmark has in 2012 proposed that articles of leather, coming into direct and prolonged contact with the skin, shall not be allowed to be placed on the European market if leather contains chromium (VI) in detectable concentrations as measured by ISO EN 17075:2007, with a detection limit of 3 ppm.

The Danish proposal for a European legislation is currently in 2012 on a public consultation which ended on 16 September 2012. Two committees will present opinions on the proposal which will be available by 16 March 2013. The committees are for risk assessment (RAC) and socio-economic analyses (SEAC). After this, the Commission will make a final decision regarding the proposal from Denmark [14].

4.5 Dimethyl Fumarate

Dimethyl fumarate (DMF) is used by producers as a biocide to kill moulds that may cause furniture or shoe leather to deteriorate during storage and transportation in a humid climate. Placed in sachets, which are fixed inside the furniture or added to the footwear boxes, DMF evaporates and impregnates the leather, protecting it from moulds. However, it has been found to seriously affect consumers who were in contact with the products. DMF penetrated through the clothes onto the skin of many consumers. Cases of severe health problems have been reported in UK, Finland, France and Poland. Although it is normally not used by tanneries, there are examples where tanneries have used DMF.

The use of DMF in biocidal products was prohibited in the EU according to EU Directive 98/8/EC [15]. However, the directive did not restrict the import of articles treated with DMF into the EU. As a consequence, the European Union made a temporary restriction to place products containing DMF on the market in 2009 (Decision 2009/251/EC). The restriction was on 15 May 2012 made permanent by the EC Regulation 412/2012 amending Annex XVII to EC Regulation 1907/2006 (REACH) [12]. The text in REACH states that articles or any parts thereof in concentrations greater than 0.1 mg/kg shall not be placed on the market.

4.6 Nonylphenol Ethoxylate/Nonylphenol

Nonylphenol (NP) has high aquatic toxicity and low biodegradability. Furthermore, an extensive risk assessment showed that nonylphenol displays endocrine-disrupting properties, i.e. hormone disrupting showing oestrogenicity. The use of products and product formulations that contain more than 0.1% of NP or NPE was forbidden from January 2005 in the EU, and the ban is now incorporated in the REACH legislation [12]. The only exception is in case of closed applications systems where no release to wastewaters occurs.

NPE was previously used extensively as nonionic surfactants and emulsifiers in both the textile and the leather industry but has now been replaced by alternative surfactants in Europe. The main alternatives in the leather industry are linear alcohol ethoxylates with different chain lengths and ethoxylation degrees. These compounds are much easier than NPE degraded to non-toxic compounds. The efficiency of linear alcohol ethoxylates as degreasing agents is comparable to that of NPE.

The use of NPE is highly restricted in the EU but can still be found in leather products imported from outside the EU. However, most eco-labels and restricted substance lists restrict the use of NPE in the leather production.

4.7 Other Chemicals

Several other chemicals are often included in different RSL or eco-labels. Examples of metals often included are lead, cadmium and arsenic. Lead and cadmium may still be used as metal complex dyes but have in most cases been substituted. Metal complex dyes are often used to increase the fastness properties of leather, but metal complex dyes with lead and cadmium should be avoided.

Other chemicals that are common in different RSL are phthalates. Phthalates are usually used as softening agents in plastics to obtain the required flexibility. The most common phthalates included on restriction lists for the leather industry are bis(2-ethylhexyl)phthalate (DEHP), benzyl butyl phthalate (BBP), dibutyl phthalate (DBP), di-“isononyl” phthalate (DINP), D-“isodecyl” phthalate (DIDP) and di-n-octyl phthalate (DNOP). All these chemicals are included on the SVHC list (Candidate List), and currently (2012) there is a proposal to restrict the placing of products containing DEHP, BBP and DBP on the market in the EU.

The use of biocides is in Europe controlled and regulated by the EU Biocidal Products Directive [15]. Registration of a biocide is expensive and only a few active biocide substances will in the future be available for the leather industry in the EU. The directive will include a list of active substances that are permitted to use by the leather industry (a so-called positive list). Many eco-labels and RSL does already today include restrictions of the use of some biocides.

Perfluorinated chemicals such as PFOS and perfluorooctanoic acid (PFOA) are usually restricted by brands and eco-labels. Furthermore, the EU regulates the content of PFOS in consumer products on the market. The use of PFOS and PFOA is also restricted by the Stockholm Convention on POPs although some exemptions exist. PFOS are still produced and used in several countries and can be used in the coating of leather.

Finally, it should be mentioned that the automotive and upholstery industries often introduce restrictions on the VOC emissions from leather. The VOC is measured by heating the leather in a closed chamber, and the emitted VOCs are determined by a mass spectrometer.

5 Conclusions

The leather industry is a traditional industrial sector using a high number of chemicals as it is not uncommon that tanneries use 300–400 different chemicals in their production.

Globally, it can be estimated that the tanning industry use around 3 million tons of chemicals for the production of leather. The chemicals will end up in the product or waste or will be directly discharged to the water, air or soil. Although a major part of the chemicals are standard organic chemicals and standard inorganic chemicals, it is important for tanneries to have a careful control of the chemicals both for environmental and health reasons.

The main incentives for tanneries to implement a careful management of chemicals are environmental legislation and production specification lists developed by different customers. In addition, there are several voluntary eco-labels and product labels on the market.

It is expected that due to legislation and increased customer awareness of the content of chemicals in leather, an increased focus will develop on the use of chemicals in the leather industry, especially regarding to the content of eventually hazardous chemicals in the leather product.

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Managing E-Waste in Developed and Developing Countries

Suthipong Sthiannopkao

Abstract Electronic goods contain a range of toxic materials requiring special end-of-life handling. This chapter surveys policies adopted by countries across the spectrum of development to deal with waste from electronics and also practices that now in fact exist for handling this hazardous waste. Developed countries have conventions, directives, and laws to regulate the disposal of such e-waste, most based on the extended producer responsibility concept. Manufacturers take back items collected by retailers and local governments for safe destruction or recovery of materials. Compliance, however, is difficult to assure, and frequently runs against economic incentives.

The expense of proper disposal leads to the shipment of large amounts of e-waste to China, India, Pakistan, Nigeria, and other developing countries. Shipment is often through middlemen, and under tariff classifications that make quantities difficult to assess. There, despite the intents of national regulations and hazardous waste laws, most e-waste is treated as general refuse, or crudely processed, perhaps by burning or acid baths, to recover only a few materials of value. Harm to the environment, workers, and area residents is inevitable, often from release of dioxins, furans, and heavy metals.

The faster growth of e-waste in the developing than in the developed world presages continued expansion of an informal processing sector that, while on its own terms is inexpensive and efficient, remains hazard-ridden.

Keywords E-waste, Extended producer responsibility, Informal waste processing, Recycling, Take-back

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Contents

1 Introduction

Electronic products become e-waste when they are deemed at the end of their useful life. Nonfunctioning or obsolescent TVs, computers, printers, photocopiers, cell phones, fax machines, home appliances, lighting equipment, games and such, when no longer wanted, come to constitute e-waste. These electronic products contain many materials requiring special end-of-life handling, most prominently lead, mercury, arsenic, chromium, cadmium, and plastics capable of releasing dioxins and furans.

The fate of e-waste is guided in vastly different ways, both physically and in policy, in different parts of the world. Developed countries have gone to great lengths to devise fairly complex, high-cost systems to handle e-waste, following directives written to spare the environment – although the majority of e-waste across Europe and North America still goes unrecycled [1]. Elaborate collection systems are deployed, backed by information campaigns. Especially developed clean recovery technologies are used, from disassembly stations to plasma furnaces carefully engineered to prevent release of dioxins. In systems at the other end of the scale, in developing and transition countries for which China, India, Pakistan, and Nigeria may be taken as the archetypes, common practice is to smolder plastic off cables, as the cheapest means known of recovering the copper. Precious metals may be leached by acid baths from circuit boards and the used acid, laden with toxic metals, dumped into the ground or nearby stream [2]. The surrounding population may be largely unaware of any danger from toxicity.

Worlds apart are the practices, yet the official policies and regulatory guidelines in developing countries show much influence from those of the developed world. While waste import bans are common in the developing world, the topography of recycling and disposal costs seems to assure a flow of e-waste out of the developed world down to the points of lowest-cost disposal.

This chapter presents a characterization of the e-waste situation, particularly in terms of intervention attempts made in order to manage it safely. The more prominent agreements, policies, systems, and laws at the national and international level are surveyed. Samples are provided of the environmental and human consequences of large-scale movements of toxic e-waste to the developing world. Trends for the next several years are noted, too.

1.1 A Current Sense of Crisis

The sense of crisis around e-waste arises from three considerations. The first is the sheer volume of units of obsolescent electronics – recently 400 million items per year in the USA alone, for example. Next is the fact of e-waste as a global phenomenon, present nearly everywhere there are people. Finally, there is the rate at which the e-waste volume is increasing, 5–10% yearly. China's e-waste will likely overtake the USA's by the year 2020 [3]. India anticipates a growth from about 400,000 tons in 2011 to 500,000 in 2012 [4]. Indeed, by the year 2030, the developing world is forecast to discard twice the number of personal computers annually as the developed world, some 600 million versus 300 million [5].

To insert a timely caveat, data for quantities of e-waste, particularly when crossing borders, tend to exist in the form of estimates and be given as general ranges; among the reasons is that most used electronics need not be specified as such on tariff forms. E-waste, including functioning units, is typically shipped as scrap plastic or metal and may also be mixed in a container with other types of used goods, such as automobile parts [6].

1.2 Behind the Switch to Transboundary Shipment

The 1970s and 1980s saw the enactment in developed countries of wide-ranging laws to manage the treatment of hazardous waste, along with other long-overdue regulations of chemical use in the environment. When waste with hazardous contents required special treatment and could no longer be simply dumped in landfills, within a short time it became more economical to load materials containing hazardous waste onto ships and trains for transport beyond the boundaries and jurisdiction of those places in which they were produced or collected. The containerization of shipping helped speed this change. Before the mid-1980s, nearly all the hazardous waste produced in the USA stayed there, nor did that produced in industrialized continental Europe go far. Most was shipped either to eastern Europe or the UK for processing [7]. However, the trend changed rapidly. Between 1980 and 1988, for example, the number of companies seeking USEPA approval to ship hazardous waste abroad rose from 12 to 522 [8].

Destination countries for this waste often welcomed the hard currency paid by its senders. China, in the early 1990s, invited the arrival of containers of waste, the government collecting a fee of US$50 per ton. A number of operators small and large became established in the business of disposing of waste without possessing the equipment or technology for safely processing it, and without regulatory oversight. In the cheapest way possible, component materials of value were removed, and the remaining matter disposed of by the most expedient means available, generally by burying, burning, or discharging into waterways. By no means was this an altogether new economic sector; an estimated 1% of the urban population in developing countries engages in scavenging waste as a livelihood [9]. The crude processing of hazardous waste represents an extension of an existing form of employment.

Egregious examples also occurred of hazardous materials disposed of abroad with wanton disregard for safety, as, for example, when a landowner near the town of Koko in Nigeria was induced by a shipper from Italy to allow the stacking of barrels of highly toxic waste, some radioactive, on his property, in return for a small monthly rent [10].

It was against the background of this trend to ship waste abroad that the impetus for control of the transboundary movement of hazardous waste materials began in the late 1980s and early 1990s. This need to address the large gap between developed and developing countries in handing e-waste, both physically and in the realm of policy, culminated in a variety of agencies putting forth initiatives.

2 Initiatives in Developed Countries Affecting E-Waste

2.1 The Basel Convention

The most important of these initiatives that would bear on e-waste was the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal. The Basel Convention was intended to keep hazardous waste within countries capable of safely handling it. For some time before it came into force in 1992, the OECD had seen the need for such an agreement. Environmental and industry NGOs both contended at the time of the Convention's negotiations to influence its contents. The latter inveighed against further waste export restrictions as stifling world economic growth. The political mood, however, and ultimate terms of the agreement ran contrary to this position, according to Kempel [7], a delegate.

This most comprehensive agreement, with 178 nations party to it (signed, though not yet ratified, by the USA), charges countries wherein hazardous waste is produced with responsibility for the safe disposal of such products, while banning hazardous material exports to developing countries – except when written "prior informed consent" from the accepting nation had been obtained. Extended producer responsibility (EPR) is thus a core concept of the Basel Convention [11]. The materials and their concentrations coming under regulation are defined in the Convention's Annex 1; these do not extend to functioning second-hand goods. While it does provide rules for determining liable parties in cases of infringement, penalties are not given, being left to individual states to enact.

2.2 EU's Waste Electrical and Electronic Equipment Directive and RoHS

The European Union WEEE (Waste Electrical and Electronic Equipment) Directive was written into law in 2003, and adapted by all member states by 2007. The directive covers all types of electrical goods, for which it establishes ten categories, and sets targets for their collection, recovery, and recycling. It notably calls for free take-back of used products, as well as the establishment of collection points [12]. Its sister directive is RoHS, "Restriction of Hazardous Substances." This directive is aimed at the design phase of products, and limits, by percent weight of homogenous components, six specific materials: lead, mercury, cadmium, hexavalent chromium, and two flame retardants added to plastics, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE). The EU WEEE Directive and RoHS have been influential in shaping legislation in other developed regions, such as Korea, Japan, Australia, the USA, and Canada.

2.3 The 3Rs and StEP

The 3Rs "Reduce, Reuse, Recycle" Initiative was introduced by Japan at a 2004 G8 Summit. Japan has promoted use of the 3Rs domestically and on the international stage. "Reduce" – preventing the creation of waste – is presented as the first priority. Among this initiative's other goals are furthering the technologies of reuse, the cooperation of developed with developing countries on recycling and reuse programs, and removing barriers to the international movement of materials for recycling and remanufacture [13]. This last objective is seen by some as conflicting with tenets of the Basel Convention, which stress producer-nation responsibility.

Solving the E-waste Problem (StEP) is a UN-led initiative, organized in 2004, to enhance and coordinate various efforts around the world on the reverse supply chain, the reuse of recycled materials. Its five categories of concentration are policy, redesign, reuse, recycling, and capacity building. The idea of redesign with disposal in mind has growing promise [3]. One aspect is designing for ease and safety of eventual disassembly and recycling; another is design with minimal use of toxic materials. In workaday terms, StEP organizes meetings and produces and disseminates reports, all on a fairly large scale.

2.4 In the USA: Legislation and NGOs

While the US Congress has not yet ratified the Basel Convention, 25 of the 50 states within the USA have enacted laws dealing with e-waste [14]. These state laws, however, do not limit the international movement of electronic waste. Once e-waste has reached even a state-approved collection agency, its fate is not easily traced, and 50–80% of American e-waste has been reckoned to arrive in China, India, or Pakistan [15]. Finally, in September, 2010, a national law was proposed in the American Congress, known as the Responsible Electronic Recycling Act (HR2284), an act designed to substantially control the shipment to developing countries of waste electronics containing hazardous materials. The legislation is expected to be passed by the US Congress [16]. HR2284 has fairly broad backing, having been introduced jointly by one member from each of the major political parties, and enjoys the support of the Electronics TakeBack Coalition (ETBC), as well as companies such as Apple, Hewlett-Packard, and Samsung. It specifies a comprehensive list of toxic substances banned from export, including CRTs (unless broken and "furnace ready" for an already-designated recycler). Under the bill, used goods for export need to be fully functional and tested as such within the USA. HR2284 also funds a research initiative into recovery of rare earth materials [17].

Three American-based nongovernmental organizations have been particularly active in e-waste issues. The Basel Action Network (BAN), Silicon Valley Toxic Coalition (SVTC), and ETBC constitute an associated network of environmental advocacy NGOs in the USA. They partner on the issue of international support for the more strict export-limiting amendment to the Basel Convention known as the Basel Ban. Promoting domestic collection and recycling is another joint cause, as is investigative research – the fruits of which have considerably raised the profile of BAN. Though an advocacy group, BAN, in its investigative role, has frequently been the source of data cited in research papers and other media about e-waste issues.

The organizations' common objective, in short, is promoting national-level solutions for hazardous waste management [18]. One recent initiative has been e-Stewards, a system for auditing and certifying recyclers and take-back programs so that conscientious consumers know which ones meet high standards [19].

3 Policies and Systems in Developed Countries

The European Union and Japan have been leaders in formulating and then implementing e-waste regulations. The Swiss are credited with establishing the first comprehensive e-waste management system, covering collection to disposal.

In EU countries, the principle behind directives for collection, recovery, and reuse has been EPR, making producers responsible for the take-back of e-waste. Canada and Australia are among other countries developing systems based on these principles. Japan's "Reuse, Recycling and Recovery" system differs in some ways, while still promoting take-back by manufacturers. The most salient difference is the direct payment of recycling costs by Japanese consumers.

3.1 Registry, Collection, Logistics

E-waste management in all these countries can be seen as consisting of three elements: the national registry, the collection system, and logistics [3]. The national registry is primarily a list of producers and their collection obligations; the registry may be kept by a variety of agencies, which may also check compliance.

Systems for e-waste collection are usefully grouped into two types. A *collective system* is usually nonprofit and nongovernmental, and founded by trade associations, which concentrate on certain product categories for efficiency in finding markets for reuse. In the *clearing house system*, producers, recyclers, waste businesses, and such compete to provide services. The government sets the ground rules for allocation and monitoring, and provides the national registry to a coordinating body, from which that body may assign producer obligations; it also establishes waste collection points.

Logistics of e-waste collection commonly involve three channels. Municipal collection sites usually accept any amount of waste from citizens, without cost. In-store retailer take-back schemes may be free or depend on repeat purchases. Direct producer take-back is generally for business customers and may require a replacement purchase.

Once collected, dismantling, preprocessing, and end processing are the stages leading to safe disposal or recycling of e-waste. Dismantling and preprocessing may be largely mechanical and require pneumatic wrenches and drills or other only moderately specialized equipment. Worker training need not be extensive. End processing by best available technology for metal recovery, a prime goal of e-waste processing, does require a heavy investment, up to US$100s of millions. Integrated metal smelters using extractive metallurgy to separate constituents are used for complex items such as circuit boards. Highly skilled workers are needed [20].

Analyses of developed countries' e-waste management shows Japan to have perhaps the best-functioning system, in terms of scope and compliance levels. Korea, Canada, and Australia have well-advanced systems as well. Switzerland's system is seen as a model of comprehensive management, and the Swiss, Norway, Belgium, Sweden, and the Netherlands have all exceeded minimum EU e-waste directives' collection and recycling targets.

3.2 Take-Back in Japan

Japan has had home appliance recycling laws since 2001, including for CRTs. The end user has to pay a recycling fee, retail outlets provide collection points, and recycling is by the producing company. For a fee, local governments will also collect the goods to be disposed of. Recycling fees paid by consumers range from about 1,800 to 5,000 yen (about US$20–55), depending on the type of item. In the absence of a producer company to take back goods, another company is designated for that role. In this way about 74% of e-waste reaches a recycler [21], compared to a US average of about 12.5% [22]. Domestic recycling follows best practices, such as the careful separation of materials, decontamination, step-by-step disassembly, and destruction of some components by plasma arc furnaces, to not release toxic compounds.

Many computer and other IT device makers offer take-back programs even where not mandated by law. In the USA, Apple, Sony, Sharp, Mitsubishi, Samsung, Hewlett-Packard, Dell, LG, Lenovo, Panasonic, and Toshiba have free collection point or mail-in take-back programs of their products. Apple and Hewlett-Packard provide some form of payment for the value of the taken-back item. Other companies, Hitachi, Phillips, and Funai, do not now have take-backs [23].

4 E-Waste Policies and Handling in Developing Countries

The policies and systems just outlined notwithstanding, a great portion of waste from developed countries is sent for processing or disposal to the developing world. China, India, Pakistan, and Nigeria have become the leading destinations. While all four are parties to the Basel Convention and have other forms of regulations intended to address the importation of hazardous waste, shippers and waste processors find it possible to transport waste labeled, for example, as used goods, which the Basel convention does not cover, in order to get it landed. The enforcement of rules bearing on the import or handling of e-waste is generally not seen as a priority by the local enforcers, who can often be induced to overlook transgressions [24].

4.1 China

China, in addition to ratifying the Basel Convention, has a 2002 law banning hazardous waste imports. In 2005, the Management Measure for the Prevention of Pollution from Electronic Products became effective. It has been referred to as China’s RoHS, specifying limits on materials similar to the EU Restriction of Hazardous Substances directive. A new waste disposal law enacted in 2009, Regulations for the Administration of the Recovery and Disposal of Electric and

Electronic Products, targets e-waste more specifically, by funding safe electronic recycling facilities. Manufacturers, retailers, and recycling companies are to be responsible for collecting and safely handling e-waste, and recyclers are to be licensed. Obligations and penalties, however, are loosely defined in the law's wording [25].

An archetype of "backyard" e-waste processing is Guiyu, a set of towns in southeast China. Guiyu had become a major imported e-waste processing area by 1995, and has about 5,500 shops employing around 150,000 people [26]. The majority of the workers come from elsewhere in China. They typically labor without goggles, gloves or proper ventilation, indeed without basic personal safeguards. Many are minors. Fengjiang, south of Shanghai, is another large processing area, handling mainly domestically produced e-waste.

Consumers in Japan or other developed countries may pay to have e-waste collected; in China a component of the informal processing system is circulating peddlers who pay householders for unwanted electronics, after a bit of doorstep haggling. Chi et al. [27] cite this as an example of the efficiency of the informal system: the peddlers take care of collection and transportation as part of a self-organizing, demand-driven system that continuously sets market values for e-waste. They do not consider a prohibition of the informal sector as practical. Backers of this pragmatic approach see that while government and private sector investment for formal processing systems is growing, such systems will not match the reach, efficiency, and volume of the pervasive and cheap informal sector. Investment should therefore also be made in workable basic technical solutions to ameliorate polluting aspects of informal e-waste processing.

4.1.1 Human Effects of E-Waste in Guiyu

The vast amount of waste electronics processed in Guiyu over a relatively long period has made it a prime area for investigating the effects of crude e-waste disposal methods on the air, water, soil, and people. Leung et al. [28] took soil samples where it had long been common to burn such things as cable sheathing to recover copper wire, and to use open-pit acid leaching for separating metals of value. Their study focused on polybrominated diphenyl ethers and polychlorinated di-benzo-p-dioxins along with dibenzofurans, that is, PBDEs and PCDD/Fs. In duck ponds and rice paddies, these carcinogens were found in levels exceeding international guidelines for agricultural areas. China itself has not yet set such guidelines for these materials. Wong et al. [29], in their 2007 study of the Guiyu area, looked at a wide variety of pollutants in the soil, air, and water, and measured high levels of air-borne PBDE dioxins and polycyclic aromatic hydrocarbons. Their presence is attributed to incomplete combustion of plastic chips, insulation, and PVC materials. Elevated levels of heavy metals were found in sediments near paddies – and commonly grown rice cultivars, it should be noted, have, among all plants, an exceptionally high capability for taking up and concentrating cadmium [30]. Li et al. [31] have found umbilical cord blood cadmium levels above WHO standards in over 25% of neonates in the Guiyu area.

4.2 India and Pakistan

India is second to China in processing e-waste. Seventy percent of the e-waste processed or disposed of in India is believed to originate abroad, with Delhi as its primary destination. Bangalore handles more that is domestically produced; India by itself produces 400,000 tons of e-waste annually. With only three facilities currently existing in India to properly handle e-waste, the overwhelming majority goes into the informal sector. As in China, unwanted electronic equipment is seen as worth money, and sold by households or businesses to doorstep collectors.

Wath et al. [32] point out that India lacks actual legislation dealing with e-waste. The Ministry of Environment and Forests (MoEF) issues rules and guidelines for waste management; those bearing on e-waste are the 2004 "Municipal Solid Waste Management Rules" and the 2008 "Hazardous and Waste Management Rules." More specific new regulations, codified as the "2010 E-waste Management and Handling Rules," become effective in 2012. These set hazardous substance limits on lead, mercury, cadmium, hexavalent chromium, PBBs, and PBDEs, that is, the six RoHS materials. Also called for are collection centers and EPR rules for recycling [33]. By judicial ruling, the import of e-waste into India is considered illegal. In practice, this ruling seems easily evaded through such dodges as labeling e-waste as charitable donations, scrap metal, or reusable products [34]. The net effects of the ministerial regulations and judicial rulings on the informal recycling sector, or on the e-waste illegally imported each year, are likely to be modest.

Research near Bangalore [35] into the effects of crude disposal processes on the environment and workers found elevated levels of trace elements Cu, Zn, In, Sn, Pb, and Bi in soil near informal recycling shops. Among the workers, hair samples held high levels of Cu, Sb, Bi, Cd, and Ag.

Pakistan has also emerged as a major destination for e-waste, receiving large volumes from the EU, Australia, and the USA, with transshipment often through Hong Kong or Singapore. Pakistan has ratified the Basel Convention, and has produced its own waste legislation. Pakistan's Environmental Protection Act of 1997 prohibits the import of hazardous waste. The National Environment Policy of 2005 and Import Policy Order of 2009 further define and restrict hazardous materials. Despite this policy framework, a large recycling industry imports what is commonly but inaccurately labeled as second-hand equipment. All but of a small percentage of the imported used electronics are dismantled as electronic scrap – for example, only 2% of imported used computers are reused. Dismantling is by crude methods, by hand rather than by machine, by workers with no protective gear. Lead, cadmium, barium, mercury, chromium, and other toxic elements are released into the environment, as there is no formal system in place to handle the quantities produced [36].

4.3 Nigeria

Nigeria is a major destination for e-waste from Europe and Asia. Attention was drawn to Nigeria and to Africa in general as a victim of e-waste in the 2005 BAN documentary “The Digital Dump” [37]. An earlier attempt to bring attention to the problem of Africa as a too-acquiescent waste destination was a convention held in Bamako, Mali, in 1991. Representatives of 51 Organization of African Unity (now African Union) countries, on the grounds that the work in Basel would still allow too much waste past their borders, passed the Bamako Convention as a supplement to the Basel Convention. It was markedly more restrictive, in casting a wider definition of what was hazardous then nearly categorically banning the import of such, with transgressions to be viewed as criminal acts. Although Bamako officially came into came into force in 1998, calls to use it against e-waste have had not produced results [38]. The value of Bamako may be said to be that it is an already extant piece of regulation with at least the potential for use: the stimulus that occurred to produce it may not come again.

Nigeria has as well its Harmful Wastes Act, which, rather than listing banned substances, broadly bans materials by their effects, defining such materials as those which “. . .subject a person to risk of death or. . .incurable impairment.” Trading in such can be punished by life imprisonment [39]. Nigeria’s more recent National Environmental Regulations (Electronics Sector) explicitly prohibits unusable electronic goods [40].

Poorer countries are the natural market for working used electronics, and it has been estimated 500 shipping containers of used electronics enter Lagos, Nigeria each month [37]. Each container can hold about 350 large televisions, or about 800 computer monitors or CPUs. In reality, most of this used equipment will not be functionable. To characterize the situation, if a shipper wishes to remain on good terms with the receiver, the container will include enough functioning items to allow the receiver a decent profit after covering shipping costs [6]. A representative of the Nigerian electronics trade group CAPDAN thought up to 75% of a container might be junk electronics the recycler wanted to be rid of, perhaps to avoid high home-country recycling costs. These were commonly dumped in swampland outside Lagos, there to be picked over by scavengers. Unlike in Guiyu, there seems here to be little extraction of metals by acid leaching. Most pollution comes from burning insulation from wires and cables, or igniting the vast piles of televisions and computers, to reduce the piles’ size [6]. Even for the resold usable products, their fate at the end of their second life is, very likely, to be added to the pile in the swamp.

4.4 Other Developing Countries

The e-waste situation in China, India, Pakistan, and Nigeria can be found, on smaller scales, in a surrounding swath of countries, including Bangladesh, Cambodia, Ghana, Indonesia, Malaysia, Sri Lanka, Thailand, and the Philippines. Among these there is currently a rather low level of imported e-waste: though to the degree that China manages to restrict its intake of e-waste, the likely effect is a corresponding deflection of waste to nearby developing countries, to undergo crude processing.

Most local e-waste in these countries is seen as having a positive money value, and is thus pulled by the small profit to be turned at each step through an informal recycling network that collects, trades, transports, and processes it. Collecting, a low barriers-to-entry vocation, is quite thorough for e-waste of any value. Most all the system operates outside the guidance of regulations [3]. The legal framework bearing on e-waste in these states is nearly always in the form of department-issued regulatory guidelines rather than statutes specifically for electronic waste (e.g., in Malaysia [41]). Table 1 shows the dispositions of several developing Asian nations regarding the regulations, inventories, collection, and processing of e-waste [3, 42, 43].

4.5 Nonrecovery of Valuable Metals

Electronic equipment today makes use of many precious and special metals; its manufacture has therefore become an important contributor to world demand for metals. Developed countries, particularly in the EU, have sought to establish through legislation a circular flow economy to preserve such valuable resources. Nevertheless, most are lost, and the primary reason has been the vast, often illegal outflow of e-waste to developing and transition countries lacking recycling infrastructure. The crude recovery methods of the developing world get at the most easily recoverable high-value metals, usually copper and very small amounts of gold, of which the typical cell phone has 24 mg, and silver (250 mg). Other rare metals with a soaring demand in electronics, such as indium, ruthenium, and palladium, are lost among the tons of waste because low-tech methods cannot recover them [44].

In addition, these precious and special metals have very low concentrations in ores; mining, smelting, and refining these metals therefore have a particularly large environmental impact. Recovering these metals from defunct electronic equipment would result in a fraction of the effect on the environment [20].

5 Comparing E-Waste Management in Developed and Developing Countries

In terms of the three elements, a national registry, a collection system, and logistics that constitute e-waste handling in developed countries, what do we find in developing countries? A national registry keeping track of produced electronics for the purpose of eventual manufacturer take-back is in a nascent stage in China and India. For developing countries, a first step is to make an inventory of e-waste. Abbas [36] reports such inventorying is essentially not done in Pakistan. India has set and run trials on an inventory system during the past decade [4], but it has not reached an effective usage level [45]. China has committed to making an e-waste inventory. Its new e-waste law, effective in 2011, does call for a government-maintained catalogue of electronic items domestically produced [46]. Collection of most e-waste remains in the hands of the informal sector in the developing world. In China and India, its separation from general refuse is in the hands of local recyclers.

Table 1 Regulations and management strategies for e-waste in some developing Asian countries

Levels	1	2	3	4
Practice	Rudimentary			Best
Legal framework	Legal framework nonexistent or only as plan	A legal framework to be issued/ enforced in the near future	Some enforcement, but the legal framework is not uniformly conducted	Full enforcement and model legal framework for other countries
	Cambodia, Bangladesh, Vietnam, Indonesia, Philippines	Sri Lanka, India	China, Malaysia, Thailand	–
Inventory	There is an inventory for municipal solid waste, but no designated inventory for e-waste	An e-waste inventory is under planning and preparation	E-waste inventory is conducted, but has lack of information and data.	E-waste inventory is fully conducted and publicly available
	Sri Lanka, Bangladesh, Vietnam	China, Thailand, Indonesia, Philippines, Malaysia	Cambodia, India	–
Separate collection of e-waste	Unregulated pick-up of e-waste of value only, by local collectors	E-waste is well collected by local collection mechanisms. Pilot separation and collection systems have been set up	A collection system for e-waste is operational and leads to environmentally sound disposal	Collection systems are fully operational. Collection is recognized as a model system by other countries
	Cambodia, Bangladesh, Sri Lanka, Vietnam, Indonesia, Philippines	Malaysia, China, Thailand, India	–	–
Recycling technology	Only recyclable and reusable e-waste is recycled and reused, by local stakeholders	There is a plan to set up e-waste facilities	There are e-waste recycling facilities, which accommodate a minority of all e-waste in the country	State-of-the- facilities can accommodate all e-waste in the country
	Sri Lanka, Indonesia, Philippines, Cambodia, Vietnam, Bangladesh	–	China, Thailand, India, Malaysia	–

Adapted from [3]

In both China and India (and to a lesser extent in Pakistan) some facilities have been built enabling the proper technology for e-waste disposal. Among these countries, China at least possesses a large capacity in such things as the smelting furnaces needed for recycling nonferrous metal. China is thus seen as the large-scale handler of e-waste that, with the help of partnering and technology transfer, has the potential for building facilities for handling a significant amount of it properly [20]. The vast scale of e-waste both imported and domestically produced, its rate of increase, cost of transport, and above all the high cost of facilities for its benign disposal, indicate that, despite the adoption of tighter official regulations in China, India, Pakistan, and Nigeria, their informal sectors will continue to handle the great majority of e-waste.

6 Conclusions

In developed countries, e-waste is collected to recover some materials of value and to be safely rid of the lead, cadmium, mercury, dioxins, furans, and such toxic materials as they contain. In developing countries, e-waste is collected principally to recover a few metals of value.

Major e-waste importing countries have laws restricting hazardous waste imports. The policies of developed countries in this area have served as models for official policies in the developing world. Developing countries, however, harbor in their economies an entrenched sector, in several respects honed to a high degree of efficiency, whose profitability depends on the retrieval of material from e-waste using methods harmful to the environment.

The direct release of toxic materials into the environment by the burning, burying, dumping, or discharge into waterways of the by-products of crude recycling methods will likely make zones where this work is done unsafe for habitation. Those living in such areas or working with the waste without protective equipment will risk the effects of exposure.

The faster rate of growth of e-waste produced in the developing world than in the developed world likely means that by the year 2018, more e-waste will be produced in places unable to process it properly than in places that can [5]. Where it exists as an efficient and pervasive bottom-up market-driven system, the informal sector may best be reformed by specifically targeting its most dangerous practices.

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Mass Emissions of Pollutants from E-Waste Processed in China and Human Exposure Assessment

Hong-Gang Ni and Eddy Y. Zeng

Abstract Electronic waste (e-waste) has become a pressing global pollution issue. The situation in China is more severe, due to largely primitive recycling of e-waste generated domestically and imported from outside China. In China, the improper e-waste recycling operations have resulted in severe contamination of the ambient environments by toxic pollutants. All data suggest that the contaminant levels in various environmental media near e-waste recycling sites are substantially higher than those at reference sites. People living near e-waste recycling sites and adjacent regions are subject to increased health hazard. Long-range transport of e-waste-derived pollutants can also subject residents in adjacent regions to unintended health risks. Given the special circumstances in China, implementation of improved e-waste recycling technologies and rigorous law enforcement should be the ultimate resolution for containing the spreading of e-waste-derived pollution.

Keywords China, Electronic waste (e-waste), Human exposure, Mass emission, Pollutant

Contents

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1 Introduction

1.1 Background

The main aims of this chapter are to provide estimates for the amounts of pollutants emitted from processed electronic waste (e-waste) and assess the magnitudes of human exposure to these pollutants. Specifically in this chapter, e-waste is defined as the sum of discarded personal computers, electronic/electrical equipment, electronic entertainment devices, cell phones, television sets, and refrigerators. In another word, e-waste explicitly refers to electronics at their end of life cycle and disposed by end users rather than surplus electronics (brand new products). In addition, e-waste also does not include reusable (e.g., repairable electronics or second hand electronics) and secondary scraps (e.g., noble metals, plastics, and rubbers).

The global demand for electronic equipment has continued to grow in recent years. Various electronic products, such as household electronic appliances, telecommunications equipment, and consumer electronic goods are in increasing use. Again, fast growing amounts of surplus electronics around the globe continue to be generated with rapid advances in technology, falling prices, and planned obsolescence. For example, approximately 30 million computers are discarded in the USA and 100 million phones are disposed of in Europe each year. The U.S. Environmental Protection Agency (USEPA) estimated that only 15–20% of e-waste is recycled, while the rest goes directly to landfills and incinerators [1]. Apparently, disposal of e-waste is becoming an increasingly challenging task around the world [2]. Technical solutions are available but in most cases a legal framework, a collection and transport system, and other logistics need to be implemented before a technical solution can be applied. Besides, to avoid costly treatment processes, some exporters deliberately transport difficult-to-recycle e-waste to other regions such as developing countries rather than recycling by themselves.

In addition, the concern about e-waste not only focuses on its vast quantity generated daily, but also more on the need to handle the toxic chemicals embedded in it. It is well known that e-waste contains lead, beryllium, mercury, cadmium (Cd), and brominated flame retardants (BFRs) among other chemical materials [3]. Furthermore, highly toxic chemicals such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) can be formed during the recycling process [4].

Although China has officially banned e-waste importation, such ban in some cases has resulted in underground illegal e-waste trading activities. In fact, e-waste problems are not limited to China alone; other developing countries such as India, Cambodia, Indonesia, Pakistan, Thailand, and Nigeria also have to deal with similar issues [2, 5].

1.2 Central Issue

China generates a large portion of the world's e-waste and gradually pollutes its environment in the process. The most urgent issue related to e-waste in China is the widespread use of primitive recycling methods, which has resulted in intensive environmental and human exposure to toxic chemicals released during the recycling processes and caused possibly severe environmental and human health hazards [6–9]. One example is the likelihood for e-waste processing workers to be readily exposed to toxic chemicals derived from e-waste. Moreover, e-waste processing workers may unintentionally carry hazardous materials home on their skins and clothing, subjecting their families to unintended exposure [10].

Several groups of e-waste-derived toxic chemicals, which have gained worldwide attention in recent years, include halogenated polycyclic aromatic hydrocarbons (such as chlorinated polycyclic aromatic hydrocarbons; ClPAHs), BFRs, dioxins and dioxin-like compounds, and heavy metals. Among them, BFRs and metals are embedded materials, whereas halogenated and parent PAHs and dioxins/dioxin-like compounds are produced during recycling processes. As the main components of BFRs, polybrominated diphenyl ethers (PBDEs) can lead to impaired learning and memory functions. Meanwhile, PBDEs can also interfere with thyroid and estrogen hormone systems [7, 11]. Dioxins or dioxin-like compounds are comprised of three structurally related families of chemicals: PCDDs, PCDFs, and polychlorinated biphenyls (PCBs). These compounds have caused considerable concerns because of their acute toxicity. Finally, some halogenated PAHs have been shown to elicit dioxin-like toxicity and mutagenic properties [12].

Manufacture of cell phones and personal computers consumes 3% of gold and silver mined worldwide each year, and 13% of palladium and 15% of cobalt as well. Electronics contain approximately 60 elements, some valuable and hazardous, or both [13]. Recycling the valuable elements is the driving force behind the intensive activities engaged in disposal of e-waste.

Recycling of printer circuit boards is deemed as the most important source of heavy metals to the ambient environment. These heavy metals may be entering into human body from various exposure routes such as ingestion, inhalation, and dermal absorption. Exposure to high levels of heavy metals can lead to acute and chronic toxicity, such as damage to central and peripheral nervous systems, blood composition, lungs, kidneys, liver, and even death [14].

1.3 Scope and Objectives

The e-waste issue can be discussed from multiple angles, e.g., international trade, management, and recycling techniques. This chapter is intended to address the environmental consequences of e-waste disposal if not conducted properly.

Our recent review [15] has summarized data related to environmental and human exposure to persistent halogenated compounds derived from e-waste in China. However, no information on heavy metals derived from e-waste recycling processes was given in that review. In addition, numerous studies carried out in China in recent years have surveyed the environmental occurrence of organic pollutants [16–21] and heavy metals [22–25] derived from e-waste recycling activities, which provides sufficient data for another integrated assessment of the e-waste issue in China. Therefore, this chapter will summarize the concentration ranges of organic pollutants and heavy metals in various environmental media near e-waste contaminated and reference sites in China. Based on this information, mass emissions of organic pollutants from e-waste processed in China will be estimated, and the magnitude of human exposure to e-waste-derived pollutants will be assessed as well.

2 Approach

To obtain the mass emissions of pollutants from e-waste recycling processes, it is essential that the inputs of pollutants are truly e-waste related. To fulfill this requirement, a causal analysis is desirable. However, the concept of causation is rather problematic because causal mechanisms are complex [26]. Nonetheless, we are compelled to identify causes, in an attempt to minimize the uncertainties associated with our estimates. In this chapter, the strict empiricist, David Hume's empirical criterion, was adopted. This approach requires only a combination of (1) e-waste processing and environmental pollution are associated in space and time (contiguity); (2) e-waste processing precede to environmental pollution (temporal succession); and (3) e-waste processing is always conjoined with environmental pollution (consistent conjunction). These are always the cases judged from a number of previous studies [6, 27–35].

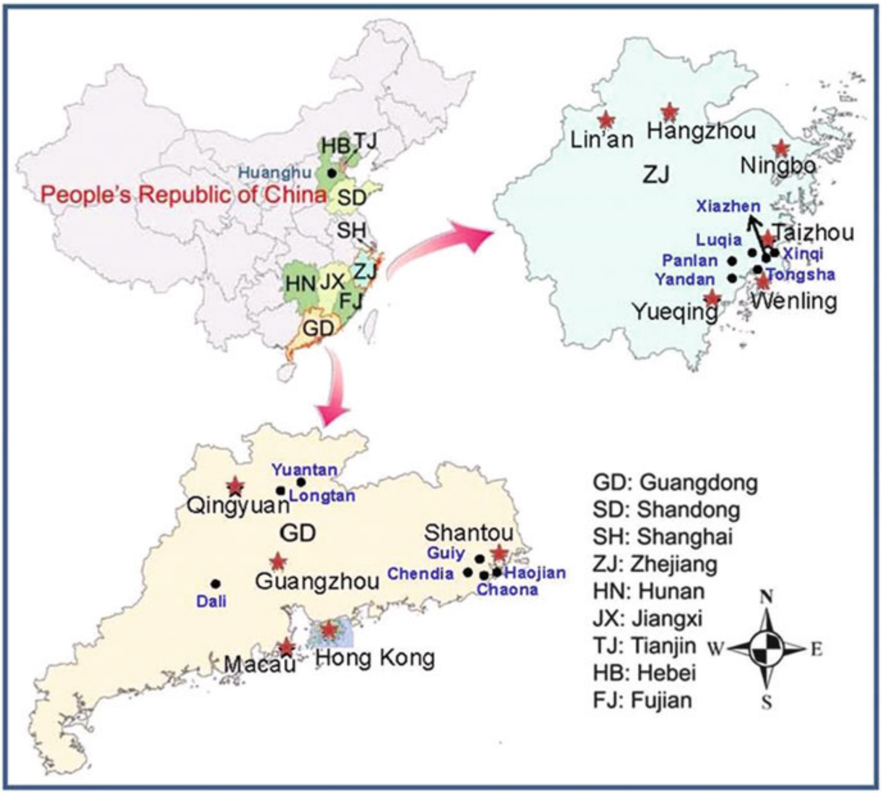

Fig. 1 Map of the main sampling locations mentioned in this chapter

Many reports have demonstrated serious environmental impacts from e-waste recycling activities in developing countries and regions [6, 27–35]. Previous studies conducted in Taizhou of Zhejiang Province [33] and Guiyu of Guangdong Province [36] have confirmed that improper e-waste recycling operations do lead to serious environmental pollution in surrounding areas (Fig. 1). However, e-waste recycling processes are not necessarily the only cause for the environmental occurrence of some pollutants (e.g., BFRs and heavy metals) as other sources than e-waste recycling may also be present. To our best knowledge, no definitive evidence is available to implicate that e-waste recycling processes are the exclusive sources of BFRs, dioxin-like chemicals, or heavy metals. It should be noted that although numerous studies on the occurrence of PBDEs and PCDD/Fs in Chinese soil have been published, only a few reports have focused on soil impacted by e-waste recycling.

It is expected that soil PBDEs and PCDD/Fs may also have stemmed from other sources than e-waste recycling processes, as only 3% of the global production of flame retardants is used in electronic products [36]. Apparently, only a small portion of BFRs occurring in the environments is derived from e-waste.

Nevertheless, various toxic chemicals can be released into the ambient environmental media during primitive e-waste recycling processes [2, 3, 37, 38]. Because e-waste recycling is intended to recover noble metals such as copper (Cu) and gold [39], e-waste-derived metal pollution is inevitable and should also be investigated. In fact, several reports or reviews on metal pollution from e-waste in China have been published [2, 14, 17, 24, 36, 40, 41]. However, these previous studies only investigated metals in the environmental media around e-waste recycling sites, and no control sites were involved. Consequently, it is difficult to assess the impacts of e-waste recycling processes on the environment.

Because causation of e-waste and pollutants is very difficult to identify as mentioned above, comparative analysis between e-waste and non-e-waste sites is a suitable choice for identifying the environmental impacts from e-waste recycling processes. To achieve this goal, we chose several typical e-waste recycling sites in China as the target regions to conduct comparative analyses. Data acquired from various environmental media near several major e-waste recycling sites and control sites in China were subject to comparative analysis.

3 Disposal of E-Waste in China

3.1 Importation and Domestic Generation

Importation from developed countries and domestic generation are two main sources of e-waste in China. According to a report by the United Nations Environment Programme (UNEP), “Recycling – from E-Waste to Resources” [13], the amounts of e-waste generated from obsolete computers, cell phones, and televisions by 2020 in China will be approximately 4, 7, and 1.5 times, respectively, higher than the levels in 2007. If classified by device type, the estimated amounts of e-waste currently generated in China are 0.3 million tons from personal computers, 0.5 million tons from refrigerators, and 1.3 million tons from television sets, resulting in 2.1 million tons/year as the total amount of e-waste generated domestically. This figure is considerably similar to another estimate of 2.3 million tons, which makes China as the world’s second largest producer of e-waste behind the USA (approximately 3 million tons/year) [13].

Worse yet, China has been a major dumping ground of e-waste from developed countries despite the fact that e-waste importation has been declared illegal [42]. In fact, importation of e-waste to China has been lasting for more than 10 years and is still underway. Of the huge amount of e-wastes generated worldwide each year, 70% is being exported to China [43]. Notably, only public information, such as data from official documents and reports or peer-reviewed publications, is used in this chapter. As the main recipient of e-waste, Guangdong Province usually receives the majority of imported e-waste, and then diverts some of it to other provinces or municipalities such as Hunan, Zhejiang, Shanghai, Tianjin, Fujian, and Shandong (Fig. 1).

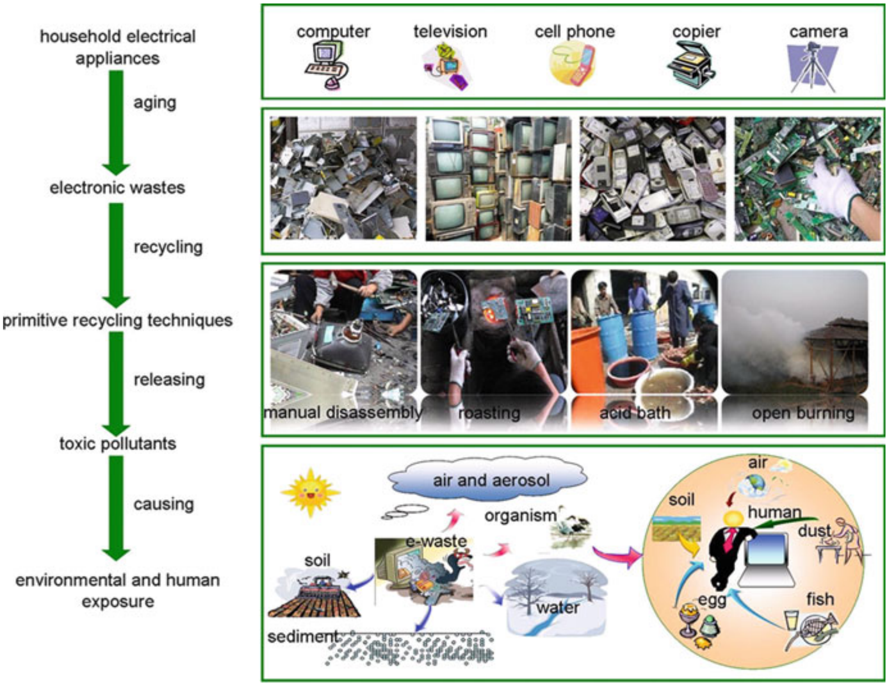

Fig. 2 Abridged general view of environmental and human exposure to e-waste-derived pollutants in China

3.2 *Procedures of Disposal*

The biggest concern about e-waste is obviously the release of embedded toxic chemicals to the environment, and a secondary concern is regarding the use of unhealthy and environmentally damaging methods for dismantling electronics to recover useful and valuable materials. As shown in Fig. 2, most methods for recycling and disposal of e-waste in China are primitive. For example, dismantling of e-waste often takes place with bare hands with no protection. Other unsafe practices include cathode-ray tube cracking and dumping, circuit board recycling, acid stripping of chips, plastic chipping and melting, and dumping of waste residues [2, 5]. To recover copper from e-waste, for instance, wires are pulled out, piled up, and burned. This emits dioxins and other pollutants [42]. Toxic cyanide and acids used to remove gold from computer circuit boards are also released into the environment [42]. These methods are able to not only recover gold, platinum, and other valuable materials but also unleash toxins to the surrounding environment.

There are many e-waste disposal sites in China, among which Guiyu of Guangdong Province (Fig. 1) is a focal point of international attention as it is perhaps the largest e-waste recycling site in the world. In addition, Longtang and Dali of Guangdong Province, Taizhou of Zhejiang Province and Huanghua of Hebei Province are also significant e-waste processing regions (Fig. 1). In fact, a large number of dismantling sites in China still remain unknown to the public.

4 Emissions of Pollutants from E-Waste

4.1 Organic Pollutants from E-Waste

4.1.1 Chlorinated Polycyclic Aromatic Hydrocarbons

To our best knowledge, very few studies on halogenated and parent PAHs associated with e-waste have been conducted. During e-waste recycling processes, ClPAHs may be produced by chlorination of PAHs [38]. The concentration of ClPAHs (List 10 of Appendix) in soil from an e-waste recycling site in Taizhou reached 26.8 ng/g dry sample weight (Table 1). The mean concentration of ClPAHs (List 10 of Appendix) in e-waste debris (59.1 ng/g) was lower than that in dust (103 ng/g) from an e-waste recycling workshop [38]. This indicates that the e-waste recycling process, rather than electronic devices themselves, is the major contributor of ClPAHs [38], similar to PCDD/F which is also derived from e-waste open burning other than e-waste itself [38]. No information on halogenated PAHs in other environmental media than soil associated with e-waste recycling operation is available to date.

4.1.2 Brominated Fire Retardants (BFRs)

PBDEs are a group of chemicals widely used as fire retardants in various commercial products. They have also been found in almost all environmental media around e-waste recycling sites, presumably due to unintended releases during primitive recycling operations. Herein a summary of the levels of PBDEs around e-waste recycling and reference sites is presented.

In recent years, a number of PBDE measurements in air from e-waste recycling sites have been conducted. A report published in 2007 indicated that the air PBDE concentration (List 2 of Appendix) in Guiyu (21.5 ng/m^3) was approximately 140 times higher than that in Hong Kong (0.15 ng/m^3) and 70 times higher than that in Guangzhou (0.29 ng/m^3) (Table 1 and Fig. 1) [44]. In 2009, a study on the diurnal variability of PBDEs in the atmosphere of Guiyu showed that the average concentrations of PBDEs (List 1 of Appendix) were 11.7 ng/m^3 in daytime and 4.83 ng/m^3 at night, while the concentrations at a reference site were 0.38 ng/m^3 in daytime and 0.24 ng/m^3 at night [35]. This difference suggested that e-waste recycling activities posed higher impacts on the local atmosphere than on

Table 1 Concentrations of chlorinated polycyclic aromatic hydrocarbons (ClPAHs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) in ambient air, soil, and human samples collected from e-waste recycling and reference sites in China

Location	Sample	ClPAHs	PBDEs	PCBs	PBBs	PCDD/Fs	PBDD/Fs	Reference
Exposed, Guiyu	Air	–	11.7^{a}	–	–	–	–	[35]
Control, Chendian	Air	–	0.38^{a}	–	–	–	–	[35]
Exposed, Guiyu	Air	–	21.5^{b}	–	–	–	–	[44]
Control, Hong Kong	Air	–	0.15^{b}	–	–	–	–	[44]
Control, Guangzhou	Air	–	0.29^{b}	–	–	–	–	[44]
Exposed, Guiyu	Air	–	–	–	–	64.9–2365^{c}	21.9–118^{d}	[18]
Control, Chendian	Air	–	–	–	–	7.12–461^{c}	0.912–6.31^{d}	[18]
Exposed, Taizhou	Air	–	0.09–3.1^{e}	4.2–11^{f}	–	2.9–51^{c}	–	[45]
Exposed, Taizhou	Soil	(ND–96.4)^{g}	–	–	–	–	–	[38]
Control, urban	Soil	ND	–	–	–	–	–	[38]
Exposed, Guiyu	Soil	–	28–4,351^{h}	–	–	0.55–39^{c}	–	[7]
Control, reservoir	Soil	–	1.6–5.0^{h}	–	–	0.23–0.83^{c}	–	[7]
Exposed, Taizhou	Soil	–	–	–	–	0.85–10.2^{c}	–	[46]
Control, Wenling	Soil	–	–	–	–	0.073–0.46^{c}	–	[46]
Exposed, Guiyu	Serum	–	580^{i}	69^{j}	–	–	–	[6]
Control, Haojiang	Serum	–	190^{i}	65^{j}	–	–	–	[6]
Exposed, Taizhou	Milk	–	–	–	–	21.0^{c}	–	[33]
Exposed, Taizhou	Placenta	–	–	–	–	35.2^{c}	–	[33]
Exposed, Taizhou	Hair	–	–	–	–	33.8^{c}	–	[33]
Control, Hangzhou	Milk	–	–	–	–	9.35^{c}	–	[33]
Control, Hangzhou	Placenta	–	–	–	–	11.9^{c}	–	[33]
Control, Hangzhou	Hair	–	–	–	–	5.59^{c}	–	[33]
Exposed, Guiyu	Serum	–	382^{i}	–	–	–	–	[47]
Control, Haojiang	Serum	–	158^{i}	–	–	–	–	[47]
Exposed, Luqiao	Hair	–	870^{k}	1.6^{l}	–	–	–	[47]
Exposed, Tongshan	Hair	–	7.63^{m}	32.8^{n}	26.2^{o}	–	–	[48]

(continued)

Table 1 (continued)

Location	Sample	ClPAHs	PBDEs	PCBs	PBBs	PCDD/Fs	PBDD/Fs	Reference
Exposed, Panlang	Hair	–	4.70[m]	28.2[n]	28.6[o]	–	–	[48]
Exposed, Xiazheng	Hair	–	11.1[m]	68.4[n]	44.1[o]	–	–	[48]
Exposed, Xinqiu	Hari	–	29.6[m]	182[n]	57.8[o]	–	–	[48]
Control, Yandang	Hiar	–	4.50[m]	13.3[n]	25.7[o]	–	–	[48]
Exposed, Guiyu	Milk	–	–	9.50[p]	–	–	–	[49]

Note: Concentrations of PBDEs and PCBs in air samples were expressed in ng/m^3, while those of PCDD/Fs and PBDD/Fs in air were expressed in pg/m^3. ClPAHs, PBDEs, and PCDD/Fs in soil samples were in ng/g dry weight. For PCDD/Fs in human samples, pg WHO-TEQ$_{1998}$/g lipid (World Health organization Toxic Equivalency) was used. For PBDEs, PCBs, and PBBs in human samples, concentrations were expressed in ng/g lipid, except for those from Tongshan, Panlang, Xiazheng, Xinqiu, and Yandang where ng/g dry weight was used

[a] Appendix, List 1
[b] Appendix, List 2
[c] Appendix, List 4
[d] Appendix, List 6
[e] Appendix, List 3
[f] Appendix, List 5
[g] Appendix, List 10
[h] Appendix, List 9
[i] Appendix, List 15
[j] Appendix, List 20
[k] Appendix, List 7
[l] Appendix, List 8
[m] Appendix, List 16
[n] Appendix, List 19
[o] Appendix, List 20
[p] Appendix, List 17

distant areas. The same trend was also observed in Taizhou, another prominent e-waste recycling region in China [45], i.e., higher levels of PBDEs (List 3 of Appendix) in air around e-waste sites than those in other urban sites (Table 1). Furthermore, occurrence of PBDEs in tree barks around e-waste recycling sites also confirmed this notion because tree bark can be taken as a passive air sampler for organic pollutants [50]. The average concentration of PBDEs (List 7 of Appendix) in tree bark from Luqiao (an e-waste recycling site) in Taizhou was 1.4 μg/g lipid weight. These results suggested that ambient air in e-waste recycling sites has been severely polluted by PBDEs, which was also confirmed by the composition of PBDEs [50].

Only a few studies have focused on soil impacted by e-waste recycling processes among a large number of publications concerning the occurrence of PBDEs in China's soil ecosystems. A study carried out in Guiyu surveyed the spatial distribution of PBDEs (List 9 of Appendix) in five types of soil and obtained total PBDE concentrations (based on dry sample weight) in the decreasing order of acid leaching site (2,720–4,250 ng/g) > printer roller dump site (893–2,890 ng/g) > duck pond (263–604 ng/g) > rice field (34.7–70.9 ng/g) > reservoir (control site) (2.0–6.2 ng/g). A possible explanation is that PBDEs were stripped off from printer circuit boards in acid bath and then released into the adjacent soil. Interestingly, the levels of PBDEs were significantly higher in combusted residues (33,000–97,400 ng/g dry sample weight) than in acid leaching impacted soil (2,720–4,250 ng/g dry sample weight) [7]. This may suggest that combusted residues have the potential to impact the ambient environments [7]. Similarly, sediment impacted by wastewater discharge from e-waste recycling sites contained higher PBDE levels than those from reference areas. For instance, concentrations of PBDEs in river sediment from Liangjiang River of Guiyu (Fig. 1) were higher than those in sediments receiving wastewater from a non-e-waste source [51]. Penta-BDEs were the dominant components in sediment from Guiyu with total concentrations ranging from 11.7 to 6,270 ng/g [51].

Levels of PBDEs in birds were also examined [52, 53], but data associated with e-waste recycling activities in China are scarce. A noteworthy study on the occurrence of PBDEs in birds was reported by Luo et al. [53], which is used to elucidate possible correlation between the levels of PBDEs in bird and e-waste recycling operations. The concentrations of PBDEs (List 13 of Appendix) in five bird species collected from 2005 to 2007 in Qingyuan County (the second largest e-waste recycling sites behind Guiyu in South China) of Guangdong Province (Fig. 1) ranged from 37 to 2,200 ng/g lipid weight while those of organochlorine pesticides (OCPs; List 14 of Appendix) ranged from 530 to 4,300 ng/g lipid weight [53]. This distribution pattern was different from those obtained by other studies, which indicated that the levels of OCPs in birds were higher than those of PCBs or PBDEs [52, 54–61]. The similar concentrations between the two groups of chemicals indicated that industrial sources (PBDEs) are more important than agricultural sources (OCPs) in the region.

E-waste-derived PBDEs may enter human body via various exposure routes. Bi et al. [6] found that the median PBDE (List 15 of Appendix) concentration

(580 ng/g lipid) in Guiyu residents' serum was approximately three times higher than that of Haojiang (190 ng/g lipid) where aquaculture dominates (Fig. 1 and Table 1). Similarly, the mean concentrations of PBDEs (List 15 of Appendix) in serum of Guiyu residents were 382 ng/g lipid for the exposure group and 158 ng/g lipid for the control group (Table 1) [47]. In addition, concentrations of PBDEs (List 16 of Appendix) in hair of residents around e-waste recycling sites in Zhejiang Province (Fig. 1) were considerably higher those from a reference site (Table 1) [48]. In another e-waste recycling site, Luqiao of Taizhou (Fig. 1), the level of PBDEs (List 7 of Appendix) in hair was as high as 870 ng/g lipid (Table 1) [48].

4.1.3 Dioxins and Dioxin-Like Compounds (PCDD/Fs)

Similar to PBDEs, higher levels of PCDD/Fs (List 4 of Appendix) and PCBs (List 5 of Appendix) in ambient air were also observed around e-waste recycling sites of Taizhou (Fig. 1) compared to other urban sites (Table 1). In Guiyu, a previous study obtained atmospheric concentrations of PCDD/Fs (List 4 of Appendix) as 64.9–2,765 pg/m^3 (Table 1), the highest values in the worldwide so far [18]. In addition, high levels of PBDD/Fs (List 6 of Appendix) were also observed in the same study (Table 1) [18], which implicated strong impacts of e-waste recycling activities on the local environment. Moreover, dioxin and dioxin-like compounds derived from e-waste recycling sites may also impact adjacent areas. For example, the levels of atmospheric PCDD/Fs (List 4 of Appendix and Table 1) and PBDD/Fs (List 6 of Appendix and Table 1) in Chendian, about 50 km away from Guiyu (Fig. 1), were at the high end of the global range observed in urban areas [8]. The average concentration of PCDD/Fs (List 4 of Appendix) in the air around e-waste sites in Taizhou was 14.3 ng/m^3 [45], lower than that in Guiyu but still indicative of impacts from e-waste disposal activities (Table 1).

In tree bark from Luqiao of Taizhou (Fig. 1), the mean concentrations of PCDD/Fs (List 4 of Appendix) and PCBs (List 8 of Appendix) were 0.1 and 6.5 μg/g lipid weight, respectively. Among all the target analytes, 2,3,4,7,8-PeCDF and PCB-126 were the dominant contributors to toxic equivalency (TEQ). The high levels of PCDD/Fs and PCBs in tree bark suggested the impact of e-waste recycling operations on the local environment [50].

Numerous studies have been conducted on the occurrence of dioxin or dioxin-like compounds in soil from e-waste recycling sites. Ma et al. [46] measured PCDD/Fs (List 4 of Appendix) in surface soil from Fengjiang (e-waste site) and Wenling (reference site) (Fig. 1), as well as in several cultivated surface soils from several provinces in China. Concentrations of PCDD/Fs (List 4 of Appendix) in soil from the e-waste site (854–10,200 pg/g dry weight) were significantly higher than those in both the reference site (72.8–456 pg/g) and the cultivated soils (3.44–33.8 pg/g) (Table 1). E-waste recycling operations were obviously responsible for the higher PCDD/F levels in ambient air of the e-waste sites. Another study [7] also obtained higher levels of PCDDs/Fs (List 4 of Appendix) in soil from e-waste recycling sites (including acid leaching and printer roller dump sites) in Guiyu than those from a reference site (a reservoir). At the same time, this study also suggested that combustion of e-waste was the predominant mechanism for the levels of PCDD/Fs in the ambient environment compared to other disposal activities [7]. In this context, the high PCDD/F levels at the acid leaching site may have been resulted from the proximity to possible combustion sources.

In summary, improper e-waste recycling operations are the major contributors of dioxin and dioxin-like compounds to the terrestrial environment in China [7]. The lower concentrations of dioxin and dioxin-like compounds at reference sites than at e-waste recycling sites suggest the likelihood for these chemicals to transport atmospherically from where they are generated to distant areas. We can also infer that dioxin and dioxin-like compounds initially derived from burning of e-waste can enter ambient air and dust and finally deposit into soil. This notion is supported by the significant positive correlation between the levels of PCDD/Fs in dust and soil samples from Taizhou.

No significant difference was found between the levels of PCBs in serum samples (List 18 of Appendix) collected from residents in Guiyu (exposure site) and Haojiang (control site; Table 1) [6]. In contrast to the distribution of PCBs in serum, PCBs in hair exhibited different distribution patterns. Hair samples collected from Tongshan, Panlang, Xiazheng, and Xinqiu of Taizhou (exposure site) contained higher levels of PCBs (List 19 of Appendix) and polybrominated biphenyls (PBBs; List 20 of Appendix) than those from Yandang (control site, Fig. 1 and Table 1) [48]. It is obvious that various exposure routes should be responsible for this difference [33]. For example, exposure of hair to PCBs and PBBs via atmospheric deposition is more direct than that of serum. Again, these pollutants in serum may have undergone various complex biological processes of absorption, distribution, and metabolism [62]. Besides, deposits on hair are likely to mirror short-term pollution without accumulation effects. A recent study [49] showed that concentrations of PCBs (List 17 of Appendix) in human milk from Guiyu reached as high as 9.50 ng/g lipid weight. Overall, levels of PCBs and PBBs in human tissues from e-waste recycling sites tend to be higher than those from control sites. It should be pointed out that PCBs and PBBs are expected to mainly derive from their historical use in electronic products. In fact, considerably high levels of PCBs have been detected in sediment and other environmental compartments near e-waste recycling sites of China [32, 63]. This underscores the long-lasting effects of historical use of PCBs on the global environment and the likelihood for PCBs embedded in e-waste to transport within various environment compartments on a global scale. Apparently, PCBs have remained an important group of organic pollutants in e-waste and therefore need to be addressed adequately as part of the e-waste problem [32, 63].

Improper disposal of e-waste has been regarded as the major source of PCDD/Fs occurring in China's environment [46]. Consequently, e-waste recycling should be somewhat responsible for human exposure to dioxins in China. A comparison of dioxins in human samples from e-waste recycling and reference sites would either confirm or disapprove the notion. The levels of PCDD/Fs (List 4 of Appendix) in human milk samples from a group of pregnant women in Taizhou (e-waste site) were higher than those at Hangzhou (reference site; Fig. 1 and Table 1) [33]. Meanwhile, the TEQ values in Taizhou human samples (21.0–33.8 pg WHO-TEQ/g lipid) were also higher than those in reference site samples (5.59–11.9 pg WHO-TEQ/g lipid) [33]. In addition, all Taizhou human milk samples and 80% of the Hangzhou human milk samples contained PCDD/Fs at levels exceeding the European Union's maximum permitted level in milk (3 pg WHO-TEQ/g lipid) [33, 64]. Again, the Taizhou human milk samples had the highest levels of dioxin and dioxin-like compounds in China during 2000–2005 while the Hangzhou samples contained similar levels to those from non-e-waste sites around the world [65, 66]. Overall, the levels of PCDD/Fs in human samples from Taizhou were at the high end of the global range [33]. This again demonstrates that heavy body burdens of dioxin and dioxin-like compounds in residents of e-waste recycling sites are largely attributable to unsafe e-waste recycling processes.

4.2 *Heavy Metals*

Besides the organic pollutants mentioned above, e-waste recycling activities are also releasing various heavy metals such as Hg, Cd, Cr, Cu, Ni, Pb, and Zn [14]. These e-waste-derived heavy metals pose extremely high risk to the environment and humans [67], especially at e-waste processing sites. Numerous previous studies suggested that most environmental matrices around e-waste sites, such as air, soil, sediment, and dust, have been severely contaminated by these heavy metals (Table 2) [71–75].

Heavy metals in air mainly associate with atmospheric suspended particles. A previous study [68] reported concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, and Mn) in total suspended particles (TSP) in ambient air of Guiyu, including $PM_{2.5}$ (fine particles with aerodynamic diameter less than 2.5 μm). For example, Cr (1,161 ng/m^3) and Zn (1,038 ng/m^3) were the most enriched metals in TSP and $PM_{2.5}$ followed by Cu (483 ng/m^3), Pb (444 ng/m^3), Mn (60.6 ng/m^3), and As (10.2 ng/m^3) (Table 2). These values were much higher than those from other Asian regions. In particular, the concentrations of Cr and Zn in $PM_{2.5}$ were 4–33 times higher than those in Shanghai, Tokyo, Ho Chi Ming, Taichung, and Seoul. Clearly, these high levels of metals in TSP and $PM_{2.5}$ indicated a high inhalation exposure risk for e-waste processing workers and local residents.

Surface dust from e-waste sites also contained enriched metals. Elevated mean concentrations of heavy metals, such as Pb (52,770 mg/kg), Cu (13,400 mg/kg), Zn (5,080 mg/kg), and Ni (605 mg/kg), were found in surface dust collected from e-waste recycling workshops in Guiyu (Table 2) [14]. The mean concentration of Pb (52,770 mg/kg) was 29 times higher than that in floor dust samples from printer circuit board component separation workshops in East Delhi, India. This may indicate that Pb pollution in e-waste sites of China was much more serious than

Table 2 Concentrations of heavy metals in ambient matrixes affected by e-waste recycling activities in China

		Cd			Co			Cr			
Sites	Samples	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Reference
Guiyu	Surface dust (mg/kg)	55.3		11.0–104	21.3		18–25	108		83–146	[14]
Guiyu	Soil (mg/kg)			5.51–42.9						137–477	[2]
Guiyu	TSP (ng/m3)	7.25		2.1–21.1				1,161		181–2,155	[68]
Guiyu	PM2.5 (ng/m3)	7.26		2.5–15.7				1,152		155–1,968	[68]
Guiyu	Indoor dust (mg/kg)										[29]
Taizhou	Surface soil (mg/kg)	4.53	2.7	0.6–12.5				93.4	91.3	16.4–269	[69]
Taizhou	Sediment (μg/g)	6.26	6.67	1.37–13.9				256	372	55.8–387	[70]
E-waste site	TSP (ng/m3)		5.37								[71]
E-waste site	Soil (mg/kg)	17.1		3.05–46.8				68.9		23.6–122	[72]

		Cu			Ni			Pb			
		Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	
Guiyu	Surface dust (mg/kg)	13,400		4,100–25,400	605		292–1,020	52,770		31,300–76,000	[14]
Guiyu	Soil (mg/kg)			1,374–14,253			85.2–722			856–7,038	[2]
Guiyu	TSP (ng/m3)	483		292–1,064	9.93		5.1–17.3	444		106–1,063	[68]
Guiyu	PM2.5 (ng/m3)	126		30.3–369	7.19		2.79–15.6	392		87.2–1,208	[68]
Guiyu	Indoor dust (mg/kg)										[29]
Taizhou	Surface soil (mg/kg)	362	225	77.9–1,641	63.6	66.2	11.7–120	372	176	81.3–2,374	[69]
Taizhou	Sediment (μg/g)	4,647	2,750	51.2–14,000	133	147	57.9–221	369	336	55.8–869	[70]
E-waste site	TSP (ng/m3)		314						395		[71]
E-waste site	Soil (mg/kg)	11,140		1,500–21,400	60.1		12.2–132	4,500		629–7,720	[72]

(continued)

Table 2 (continued)

		Zn			Mn			As			
		Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	
Guiyu	Surface dust (mg/kg)	5,080		2,340–9,130							[14]
Guiyu	Soil (mg/kg)			546–5,298							[2]
Guiyu	TSP (ng/m3)	1,038		163–1,881	60.6		15.4–109	10.2		3.6–22.7	[68]
Guiyu	$PM_{2.5}$ (ng/m3)	924		130–1,629	25.41		11.6–46.9	6.04		1.1–15.0	[68]
Guiyu	Indoor dust (mg/kg)							12.3	12.8	5.4–17.7	[29]
Taizhou	Surface soil (mg/kg)	332	273	144–661							[69]
Taizhou	Sediment (μg/g)	825	823	112–1,740				11.7	11.8	6.36–16.6	[70]
E-waste site	TSP (ng/m^3)										[71]
E-waste site	Soil (mg/kg)	3,690		682–8,970							[72]

		Sb			Hg			
		Mean	Median	Range	Mean	Median	Range	
Guiyu	Surface dust (mg/kg)							[14]
Guiyu	Soil (mg/kg)							[2]
Guiyu	TSP (ng/m3)							[68]
Guiyu	$PM_{2.5}$ (ng/m3)							[68]
Guiyu	Indoor dust (mg/kg)	43.9	30	6.1–232				[29]
Taizhou	Surface soil (mg/kg)				56	0.65	0.2–654	[69]
Taizhou	Sediment (μg/g)				1.48	1.32	0.16–3.82	[70]
E-waste site	TSP (ng/m^3)							[71]
E-waste site	Soil (mg/kg)							[72]

the counterparts of India. The concentrations of Cu and Zn also exceeded the New Dutch List optimum values by 31–994 and 7–73 times and the action value by 6–188 and 1.4–14 times, respectively. Furthermore, the levels of Sb (6.1–232 mg/kg) in indoor dust from 13 e-waste recycling villages in Guiyu were 3.9–147 times higher than those from the control sites, indicating that e-waste recycling is also an important source of Sb pollution [29].

Six heavy metals, including Cd, Cr, Cu, Ni, Pb, and Zn, were measured in soil samples collected from an e-waste recycling site, Guiyu [2]. Their concentrations in soil were extremely high compared to those from control sites (Table 2). All the heavy metal levels, except for Cr, exceeded the action values of the New Dutch List. These metals in soil may derive from dumping and burning of circuit boards or other metal chips. The high levels of heavy metals in soil can pose high potential health risk to children via the hand-to-mouth route. Another recent study [72] on metals in soil of former e-waste incineration sites in South China obtained average concentrations of 17.1 mg/kg for Cd, 11,140 mg/kg for Cu, 4,500 mg/kg for Pb, and 3,690 mg/kg for Zn, which greatly exceeded the action values of the Dutch standard. Again, these results highlighted the apparent influences of e-waste processing activities on local ambient environments.

Similar to soil, sediment near e-waste processing sites also contains high levels of heavy metals. The mean concentrations in surface sediment samples collected from Nanguan River draining through an e-waste recycling area of Taizhou were 151 mg/kg for Ni, 448 mg/kg for Pb, 7.48 mg/kg for Cd, 307 mg/kg for Cr, 1,003 mg/kg for Zn, 5,800 mg/kg for Cu, 1.81 mg/kg for Hg, and 13 mg/kg for As [70], much higher than those for control site (an upstream site of Nanguan River, the concentrations were 57.9, 55.8, 1.37, 55.8, 112, 51.2, 0.158, and 6.36 mg/kg for Ni, Pb, Cd, Cr, Zn, Cu, Hg, and As, respectively, Table 2). These were much higher than the sediment screening benchmarks by the USEPA Region IV (EPA Reg. IV) and the Netherlands quality criteria dredged material [76]. Clearly, the occurrence of abundant heavy metals in the surface sediment of Nanguan River has stemmed from e-waste recycling operations in Taizhou.

4.3 Mass Emissions of Organic Pollutants from E-Waste in China

4.3.1 Methods for Mass Emission Estimation

Pollutant mass loading is a critical measure useful for quantifying the level of concern from improper e-waste recycling activities. Our previous review [15] has estimated the annual loadings of various organic pollutants derived from e-waste processed in China. However, the volume of e-waste generated domestically has increased from 1.1 to 2.3 million tons/year since then. Therefore, the mass loadings of e-waste derived organic pollutants are re-estimated in this chapter.

A mass loading is estimated in two steps. First, the gross amount of e-waste imported to and generated in China is estimated. Second, the annual mass loadings of individual e-waste-derived pollutants are estimated from the pollutant concentrations in e-waste debris multiplied by the amount of e-waste generated in and imported to China each year.

The gross amount of e-waste annually occurring in China ranged from 16 to 37 million tons, including 2.3 million tons generated domestically [13] and 70% of the total amount of globally generated e-waste (approximately 20–50 million metric tons) [13]. For PBDEs, the annual amount of e-waste occurring in China is replaced with the volume of plastics in e-waste (accounting for approximately 20% of the total weight in electronic products [77]).

It should be recognized that there are large uncertainties in mass loading estimation due to the large variability in the data used, especially the volumes of e-waste and chemical contents in e-waste. Another source of uncertainty is due to the fact that some target chemicals are not embedded in e-waste, but formed during the recycling process. In this context, the estimated mass loadings of PCDD/Fs and ClPAHs are possibly underestimated.

4.3.2 Annual Loadings of E-Waste Derived Organic Pollutants

Based on the values of $C_{\mathrm{PCDD/Fs}}$ [46], C_{ClPAHs} [38], and C_{BFRs} in e-waste, the annual mass emissions of selected PCDD/F and ClPAH congeners and BFRs from e-waste are estimated (Table 3). The lowest annual mass emission of PBDEs is about 82,207 tons/year, with 70,607 tons/year from importation and 11,600 tons/year from domestic generation (Table 3). Nona- and deca-BDEs are the most important congeners as they are the major constituents of BRFs in electronic equipment [77]. In addition, the annual mass emissions of PBBs, TBBPA, and PBPs are also estimated with the same procedure (Table 3). Obviously, importation is responsible for the majority of annual mass emissions of e-waste-derived organic pollutants in China (Table 3).

As expected, the estimated annual mass emissions of PCDD/Fs from e-waste are relatively low (Table 3). The amount of 2,3,7,8-TCDD annually accumulated from e-waste is estimated at 2.1 g/year only. However, this is an underestimate because dioxins are mainly formed during combustion of e-waste, but are not embedded in e-waste [67]. Therefore, the amounts of PCDD/Fs inherited from e-wastes are not indicative of the true levels of environmental and human exposure to e-waste-derived PCDD/Fs. Also, ClPAHs originate from incineration of solid waste including e-waste [38]. Therefore, if halogenated PAHs and dioxin and dioxin-like chemicals stemming from primitive e-waste recycling operations are taken into account, the annual mass emissions of these chemicals should well exceed our estimation. Since the toxicity of some halogenated PAHs is similar to that of dioxins [12, 78], further investigations into halogenated PAHs associated with e-waste recycling operations are warranted.

Table 3 Estimated annual mass loadings of e-waste-derived polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), polybrominated biphenyls (PBBs) and polybrominated phenols (PBPs), chlorinated polycyclic aromatic hydrocarbons (ClPAHs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the environment of China

Compounds		Concentration	Annual loading		
			Domestic	Imported	Total
PBDEs	penta-BDE	170[a]	0.084[b]	0.48–1.20[b]	0.564–1.37[b]
	hexa-BDE	2,200[a]	1[b]	6.16–15.4[b]	7.6–16.9[b]
	hepta-BDE	2,500[a]	1.15[b]	7.00–17.5[b]	8.2–18.7[b]
	octa-BDE	12,000[a]	5.52[b]	33–84[b]	39–90[b]
	nona-BDE	4,200,000[a]	1,932[b]	11,760–29,400[b]	13,692–31,332[b]
	deca-BDE	21,000,000[a]	9,660[b]	58,800–147,000[b]	68,460–156,660[b]
Sum		**25,216,870**[a]	**11,600**[b]	**70,607–176,518**[b]	**82,207–188,118**[b]
TBBPA		8,100[a]	3.72[b]	23–57[b]	27–61[b]
PBBs	tera-BB	5[a]	0.021[b]	0.01–0.03[b]	0.03–0.05[b]
	penta-BB	45[a]	0.021[b]	0.13–0.33[b]	0.15–0.35[b]
	hexa-BB	200[a]	0.083[b]	0.56–1.40[b]	0.64–1.48[b]
Sum		**250**[a]	**0.125**[b]	**0.70–1.75**[b]	**0.83–1.88**[b]
PBPs	mono-BP	70[a]	0.41[b]	0.20–0.50[b]	0.61–0.91[b]
	di-BP	4,400[a]	2.02[b]	12.0–30[b]	14–32[b]
	tri-BP	56[a]	0.21[b]	0.16–0.40[b]	0.37–0.60[b]
	tetra-BP	35[a]	0.21[b]	0.10–0.25[b]	0.31–0.47[b]
	penta-BP	170[a]	0.84[b]	0.48–1.20[b]	1.32–2.04[b]
Sum		**4,731**[a]	**2.09**[b]	**13–33**[b]	**15–35**[b]
ClPAHs	3,9-Cl_2Phe	0.94[c]	–	–	14.9–34.9[d]
	3-ClFlu	0.52[c]	–	–	8.3–19.5[d]
	8-ClFlu	13.2[c]	–	–	211.2–488.1[d]
	1-ClPr	14.9[c]	–	–	238.9–550.8[d]
	3,9,10-Cl_3Phe	5.43[c]	–	–	86.4–200.4[d]
	7-ClBaA	10.6[c]	–	–	169.6–392.6[d]
	6-ClBaP	13.5[c]	–	–	216.5–499.5[d]
Sum		**59.1**[c]	–	–	**946–2,187**[d]
PCDD	2378-TCDD	0.72[e]	–	–	2.1–5.01[f]
	12378-PeCDD	2.71[e]	–	–	8.4–20.9[f]
	123478-HxCDD	3.49[e]	–	–	10.5–25.1[f]

(continued)

Table 3 (continued)

			Annual loading		
Compounds		Concentration	Domestic	Imported	Total
	123678-HxCDD	10.2[e]	–	–	31.4–75.3[f]
	123789-HxCDD	12[e]	–	–	37.6–89.9[f]
	1234678-HpCDD	82.9[e]	–	–	259.3–623[f]
	OCDD	138[e]	–	–	432.8–1,039.2[f]
Sum		**250**[e]	–	–	**784.1–1,881.8**[f]
PCDFs	2378-TCDF	99.2[e]	–	–	1.07–22.47[f]
	12378-PeCDF	24.8[e]	–	–	4.3–10.3[f]
	23478-PeCDF	36.7[e]	–	–	5.3–12.3[f]
	123478-HxCDF	89.6[e]	–	–	16–37[f]
	123678-HxCDF	29.9[e]	–	–	19.2–44.2[f]
	234678-HxCDF	32.5[e]	–	–	132–306[f]
	123789-HxCDF	2.58[e]	–	–	220.8–510.8[f]
	1234678-HxCDF	1210[e]	–	–	400–925[f]
	1234789-HxCDF	295[e]	–	–	472–1,092[f]
	OCDF	68.6[e]	–	–	157.7–364.9[f]
Sum		**1,889**[e]	–	–	**39–90**[f]
	23478-PeCDF	36.7[e]	–	–	58.7–135.7[f]
	123478-HxCDF	89.6[e]	–	–	142.9–330.09[f]
	123678-HxCDF	29.9[e]	–	–	51.2–118.194[f]
	234678-HxCDF	32.5[e]	–	–	51.2–118.2[f]
	123789-HxCDF	2.58[e]	–	–	4.3–10.3[f]
	1234678-HxCDF	1210[e]	–	–	1,936–4,477[f]
	1234789-HxCDF	295[e]	–	–	472.5–1,092.5[f]
	OCDF	68.6[e]	–	–	110–254[f]
Sum		**1,889**[e]	–	–	**3,021–6,987**[f]

[a] Concentrations in plastics (ng/g) [77]

[b] tons/year

[c] ng/g

[d] kg/year

[e] pg/g

[f] g/year

5 Human Exposure

5.1 Exposure to Organic Pollutants

The current e-waste recycling operations in China may pose significant risk to the environmental and human health (Fig. 2). Because environmental exposure to organic pollutants originated from e-waste has been discussed in Sect. 4.1, only a review of human exposure to e-waste-derived organic pollutants is presented here. It is logical that workers engaged in e-waste recycling operations are more likely to expose to chemicals derived from e-waste than the general population. Consequently, their family members are also part of the susceptible population as mentioned in Sect. 1.2.

The highest level of serum BDE-209 (3,100 ng/g lipid) was observed in a male subject in Guiyu. No other human samples have been reported to contain this high concentration of BDE-209 [6]. People residing in Guiyu will also inevitably be affected by e-waste-derived toxic pollutants. A previous report [8] suggested that Guiyu residents were exposed to considerably high levels of PCDD/Fs (List 4 of Appendix). The average daily intakes of PCDD/Fs (List 4 of Appendix) for these residents ranged from 68.9 (in summer) to 126 pg of WHO-TEQ/kg/day (in winter) for adults and from 122 (in summer) to 223 (in winter) pg of WHO-TEQ/kg/day for children, respectively. The average daily intake for children was about twice as much as that for adults. Therefore, children appear to suffer more than adults from improper e-waste disposal practices. Actually, these values are also much higher than the WHO 1998 tolerable daily intake limits (1–4 pg of WHO-TEQ/kg/day [64]) and daily intake limits in areas around medical solid waste incinerations [79, 80]. Li et al. [8] also pointed out that 80% of children in Guiyu suffer from respiratory diseases. However, it is unclear whether this high incidence of a disease can be attributed to e-waste disposal activity, which merits further study. It is notable that dioxins from Guiyu not only pose potentially adverse effects on the local environment and human health but also affect the adjacent areas (such as Chendian; Fig. 1) via atmospheric transport [8]. A similar study [33] conducted at another large e-waste recycling site, Taizhou, also obtained similar results, i.e., the estimated daily intake of PCDD/Fs (List 4 of Appendix) in 6-month breast-fed infants from Taizhou (e-waste site) was twice that from Hangzhou (reference site) [33].

Polybrominated diphenyl ethers derived from e-waste recycling operations have also posed serious human health issues, especially for residents around e-waste recycling sites. Yuan et al. [47] recruited 49 subjects from Guiyu (exposure site) and Chendian (50 km from Guiyu; reference site) and found that residents of the e-waste recycling site were subject to higher levels of exposure to PBDEs (List 15 of Appendix) than those of the reference site. Although no association between the duration of exposure to PBDEs and oxidative DNA damage was observed, intensive exposure to PBDEs may affect the levels of thyroid-stimulating hormone and genotoxic damage among the exposed population [47]. Consequently, Yuan et al. [47] inferred that other e-waste-derived toxic chemicals than PBDEs may have also interfered with the balance of thyroid hormone homeostasis. However, these hypotheses still need further confirmation.

In general, food consumption has been perceived as the dominant human exposure route for the general population [81–83]. Other exposure routes (such as dermal contact, water drinking, and dust inhalation) contribute relatively less to the total human exposure. For example, previous studies indicated that more than 90% of total exposure was resulted from food ingestion [84]. Since large amounts of toxic chemicals derived from e-waste can distribute widely in the environment and eventually enter the food chain [85], level of human exposure to these toxic chemicals via food ingestion is expected to rise for years to come. Zhao et al. [19] found that the levels of BFRs and dioxin-like compounds derived from e-waste via dietary intake for the exposed residents from Taizhou (Fig. 1) were approximately 2–3 times higher than those for the residents of a control site (Hangzhou; Table 1). This again confirmed that e-waste recycling activities continuously impose a health threat on the environment and humans in China, particularly to residents near e-waste recycling sites. On the other hand, exposure routes for e-waste processing workers may be vastly different from those for the general population. Nondietary intake of PCDD/Fs was estimated to account for about 85% of total daily intake for e-waste processing workers, which is much higher than that (<30%) for the general population [46]. Consumption of polluted food by e-waste processing workers may further exacerbate exposure to PCDD/Fs.

Clarification of the human exposure mechanisms is a steep challenge. In most cases, we may only observe modes of action rather than mechanisms of action. A mode of action is more general and phenomenological, which implies a common toxicological result but not necessarily indicates the same underlying mechanism. The mechanism of action, on the other hand, is a specific way with which chemicals induce effects in organisms. Therefore, the concentrations of toxic chemicals in organisms can be readily used to mirror the magnitude of exposure. This approach can also be used to assess human exposure to toxics originated from e-waste. Table 1 summarizes the levels of several e-waste-derived organic pollutants in human tissues from both e-waste recycling and control sites. Not surprisingly, the levels of the e-waste-derived organic pollutants were always higher in residents living near the e-waste sites than those at control sites. As mentioned above, nondietary exposure is more significant than dietary exposure for e-waste processing workers. Table 1 shows that residents at reference sites also expose to e-waste-derived organic pollutants with a magnitude between the e-waste processing workers and general population. This is similar to the difference between the levels of e-waste-derived organic pollutants for e-waste recycling and reference sites.

As discussed above, the specific mechanism governing exposure to a toxic chemical is difficult to characterize, i.e., the causality between an effect (e.g., disease) and the level of the toxic chemical causing the effect is difficult to identify. In this context, investigations into body burdens of toxic chemicals in patients may obtain useful information for examining the correlation between the levels of pollutants and related effects. Zhao et al. [21] determined the body burdens of PBBs (List 20 of Appendix), PBDEs (List 16 of Appendix), and PCBs (List 19 of Appendix) in cancer patients living near e-waste recycling sites of Zhejiang Province, China and found that the concentrations (181–192 ng/g lipid) of PBBs in kidney, liver, and lung tissues [21] were almost two orders of magnitude higher than those reported for the U.S. general population (3–8 ng/g lipid) [86]. The concentrations (174–182 ng/g lipid) of PBDEs [21] were comparable to those for the U.S. general population (23–399 ng/g lipid) [86], but almost two to three orders of magnitude higher than those for the populations of Japan (0.7–2.9 ng/g lipid) [87], Singapore (0.5–12 ng/g lipid) [88], and Europe (3.9–18 ng/g lipid) [89–93]. As for PCBs, the levels (257–399 ng/g lipid) were similar to those from the population of European industrialized countries [21]. This is perhaps PCBs have been banned in most commercial uses for several decades and the current levels are essentially reflective of historical residues. Overall, the levels of these compounds in cancer patients' tissue samples are indicative of high cancer incidences near e-waste recycling sites [21].

5.2 *Exposure to Heavy Metals*

Previous studies have found that heavy metal levels in human body are related to e-waste recycling activities. Higher levels of heavy metals have been found in human blood, urine, and hair from e-waste recycling sites. Heavy metals can poison humans at low concentrations through bioaccumulation in the food chain. For instance, Pb interferes with behavior and learning abilities, copper (Cu) causes liver damage, and chronic exposure of (cadmium) Cd increases the risk of lung cancer and kidney damage [71].

The improper e-waste recycling activities in Guiyu apparently contributed to elevated blood levels of Pb and Cd in children living there. Huo et al. [94] evaluated the mean blood lead levels (BLLs) in 1–6 years old children living in Guiyu (exposure site) and Chendian (control site). BLLs in children of Guiyu ranged from 4.4 to 32.7 μg/dL with a mean of 15.3 μg/dL, which were significantly higher than thoes in children living in Chendian (Table 4). On the other hand, BLLs in children of Guiyu and Chendian were not only higher than the Chinese mean level (9.29 μg/dL), but also higher than those in adjacent areas such as Shantou (7.9 μg/dL), Zhongshan (7.45 μg/dL) and Shenzhen (9.06 μg/dL), indicating that Pb contamination may have spread from Guiyu to nearby Chendian. In addition, there was a significant correlation between the BLLs in children and numbers of e-waste workshops [94]. Another study [95] tested 278 children under 8 years old from Guiyu and Chendian for Pb and Cd in blood. Similar to the previous survey, children from Guiyu had significant higher blood levels of Pb and Cd than those from Chendian (Table 4). Approximately 71% and 20% of the children from Guiyu had BLLs >10 μg/dL and blood Cd levels >2 μg/L, respectively, whereas the numbers were 39% and 7.3% for children from Chendian ($p < 0.01$). In addition,

Table 4 Concentrations of heavy metals in human samples from e-wasting recycling and reference sites in China

Location	Exposed group	Samples	Pd	Cd	Cr	Reference
Exposed, Guiyu	Children	Blood	15.3 (4.4–32.7)[a]			[94]
Control, Chendian	Children	Blood	9.94 (4.1–23.1)[a]			[94]
Exposed, Guiyu	Children	Blood	13.17 (4.1–37.8)[a]	1.58 (0.00–9.72)[a]		[95]
Control, Chendian	Children	Blood	10.04 (2.2–25)[a]	0.97 (0.00–3.49)[a]		[95]
Exposed,Guiyu	Neonates	UCB			306.2 (0.45–6,030)[b]	[96]
Control, Chaonan	Neonates	UCB			19.95 (1.66–56.5)[b]	[96]
Exposed, Guiyu	Neonates	UCB			99.90 (20.2–630)[b]	[96]
Control, Chaonan	Neonates	UCB			32.48 (8.6–197)[b]	[96]
Exposed, Guiyu	37 (average)	Blood	11.45[a]			[71]
Control, Haojiang	40 (average)	Blood	9.1[a]			[71]
Exposed, Guiyu	37 (average)	Urine	0.041[c]			[71]
Control, Haojiang	40 (average)	Urine	0.034[c]			[71]
Exposed, Longtang	Residents	Hair	14.97[d]	0.34[d]		[75]
Exposed, Longtang	Workers	Hair	40.07[d]	1.15[d]		[75]
Control, Yuantan	Residents	Hair	2.94[d]	0.05[d]		[75]
Exposed, Taizhou	–	Hair	85.3 (1.9–730)[d]	0.94 (0.01–13.7)[d]	1.59 (0.4–7.2)[d]	[97]
Control, Ningbo	–	Hair	2.98 (1.09–8.8)[d]	0.209 (0.18–0.33)[d]	1.16 (0.7–2.5)[d]	[97]
			Ni	Cu	Zn	
Exposed, Guiyu	Children	Blood				[94]
Control, Chendian	Children	Blood				[94]
Exposed, Guiyu	Children	Blood				[95]
Control, Chendian	Children	Blood				[95]
Exposed, Guiyu	Neonates	UCB				[96]
Control,Chaonan	Neonates	UCB				[96]
Exposed, Guiyu	Neonates	UCB				[96]
Control, Chaonan	Neonates	UCB				[96]
Exposed, Guiyu	37 (average)	Blood				[71]

(continued)

Table 4 (continued)

			Ni	Cu	Zn	
Control, Haojiang	40 (average)	Blood				[71]
Exposed, Guiyu	37 (average)	Urine				[71]
Control, Haojiang	40 (average)	Urine				[71]
Exposed, Longtang	Residents	Hair	0.59[d]	17.67[d]	112.5[d]	[75]
Exposed, Longtang	Workers	Hair	0.74[d]	29.81[d]	139[d]	[75]
Control, Yuantan	Residents	Hair	0.81[d]	9.85[d]	123[d]	[75]
Exposed, Taizhou		Hair	1.77 (0.007–9.4)[d]	53 (10.9–537)[d]		[97]
Control, Ningbo		Hair	0.81 (0.37–3)[d]	10.7 (5.3–14)[d]		[97]

Data in parenthesis are ranges of heavy metal levels, and other data are mean values

UCB umbilical cord blood

[a] μg/dL

[b] μg/L

[c] μg/mL creatinine

[d] μg/g

children's blood Pb and Cd levels were related to their fathers' engagement in e-waste-related work and the duration of time that children played outside every day [95].

In another epidemiological study concerning neonates in Guiyu (with Chaonan as a control site), chromium (Cr) levels in umbilical cord blood were measured and DNA damage of cord blood lymphocyte was assessed [96]. The mean Cr levels in umbilical cord blood of neonates from Guiyu in 2006 and 2007 were 303 and 100 μg/L, respectively, which were significantly higher than the results for the control group (Table 4). High levels of Cr in neonates were found to correlate with their mothers' exposure to e-waste recycling activities. The authors attributed the DNA damage to high Cr levels in umbilical cord blood, based on the correlation between the two parameters ($p < 0.05$). However, the DNA damage might be due to a combination of different factors.

Wang et al. [71] detected levels of Pb, Cu, and Cd in blood and urine from e-waste processing workers (working for 1–5 years) in Guiyu (with Haojiang as a control site) (Table 4). The results indicated that individuals processing e-waste had elevated Pb levels in their blood and urine and that working history with e-waste was a predictor for increased blood Pb levels.

Wang et al. [98] found that human scalp hair could be a useful biomarker to assess the extent of heavy metal exposure for individuals living in areas with intensive e-waste recycling activities. Scalp hair samples collected from Taizhou (e-waste recycling site) were analyzed for heavy metals. The levels of Cu (53 μg/g), Pb (85 μg/g), and Cd (0.94 μg/g) were significantly higher than those in hair samples from control areas (Ningbo in Zhejiang) (Table 4). Another study [75] measured heavy metals in hair from occupationally and non-occupationally exposed populations in an e-waste recycling area (Longjiang town of Qingyuan City) and from residents in a control rural town (Yuantan town of Qingyuan City). The levels of five heavy metals were in the order of Zn $>$ Pb, Cu $>$ Cd $>$ Ni, with the highest levels found in the occupationally exposed workers (Table 4). The levels of Cd, Pb, and Cu were significantly higher in residents from the e-waste recycling area than in the control area. The similarity in the heavy metal concentration patterns between children and occupationally exposed workers indicated that children are particularly vulnerable to heavy metal pollution caused by e-waste recycling activities.

Humans can expose to heavy metals through various routes, e.g., inhalation, dust ingestion, and dietary ingestion among others [14, 36]. Zhao et al. [22] estimated the total daily dietary intakes of five heavy metals As, Cd, Cr, Hg, and Pb for residents living in five villages located in Zhejiang Province. The highest dietary intakes of the five heavy metals were all observed at four e-waste disassembly localities. The dietary intakes of As for residents were approximately 1.3–3.4 times higher than the provisional maximum tolerable daily intake (2 μg/kg body weight, which is equivalent to 140 μg/day for an adult with a body weight of 70 kg) [99]. Apparently, residents living in the e-waste recycling regions exposed the higher levels of As, Cr, Hg, and Pb than those living in the control sites [22]. High levels of heavy metals in rice from a typical e-waste recycling site were reported [36]. Daily intake of Pb via rice consumption in this area was 3.7 μg/day/kg body weight, exceeding FAO tolerable daily intake (3.6 μg/day/kg body weight) [100], and the Cd daily intake (0.7 μg/day/kg body weight) through rice accounted for 70% of the total tolerable daily intake (1 μg/day/kg body weight). Heavy metals can enter human body via rice ingestion and pose a potential risk to human health.

6 Future Perspectives

It has been widely perceived that banning importation of e-waste from developed countries to China is an effective strategy for containing the nearly out-of-control e-waste situation in China. However, it should be recognized that developing countries (especially China) are also generating large amounts of e-waste. For example, a recent study [42] forecast that developing countries will generate more obsolete computers than developed countries by as soon as 2017, and by 2025 the developing world will generate twice the amount of obsolete computers from developed countries. Therefore, control of both e-waste importation and domestic generation should be regarded as a better approach to dealing with e-waste issues in China.

Apparently, e-waste management and disposal have become a global issue. A complete ban of e-waste flow streams appears highly unlikely because of the financial temptation. Even if such a ban is implemented, it still may not solve the global e-waste problem because it deals with only a diminishing percentage of the overall supply of e-waste. A more effective measure should be to reduce the harmful environmental impacts of backyard recycling operations. In this context, setting up regional e-waste disposal centers may be a more realistic way to minimize e-waste-related pollution, with the help of technical advances in e-waste recycling. As far as China's e-waste situation concerned, our previous viewpoint [67] suggested that there are numerous laws and regulations about inter-boundary transport and disposal of e-waste in China. However, the lack of rigorous law enforcement, as well as a virtually unlimited supply of underclass labor, has undermined any effort to encounter the ongoing problem that does not seem to be abated anytime soon. Clearly, both technological advances and effective law enforcement are the keys in battling the adverse consequences of e-waste in China and globally.

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Lists of Organic Pollutants

List 1	PBDEs	BDE-28, 47, 85, 99, 100, 153, 154, 138, 183, 66, 209.
List 2	PBDEs	BDE-3, 7, 15, 17, 28, 49, 71, 47, 66, 77, 100, 119, 99, 85, 126, 154, 153, 138, 156, 184, 183, 191.
List 3	PBDEs	BDE-28, 47, 66, 99, 100, 153, 154.
List 4	PCDDs	2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD.
	PCDFs	2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,6,7,8-HxCDF, 1,2,3,4,7,8,9-HxCDF, OCDF.
List 5	12 coplanar PCBs	PCB-77, -81, -105, -114, -118, -123, -126, -156, -157, -167,-169, -189.
	6 indicator PCBs	PCB-28, 52, 101, 138, 153, 180.
List 6	PBDD/Fs:	2,3,7,8-TBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 2,3,7,8-TBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD.
List 7	PBDEs	BDE-28, 47, 100, 99, 153, 154, 183, 209.
List 8	PCBs	PCB-81, 77, 123, 118, 114, 105, 126, 167, 156, 157, 169, 189, 28, 52, 101, 153, 138, 180.
List 9	PBDEs	BDE-3, 7, 15, 28/33, 47, 49, 71, 66, 77, 85, 100, 99, 119, 126, 138, 154, 153, 183, 190, 197, 203, 207, 209.
List 10	ClPAHs	9-ClFle, 9-ClPhe, 2-ClAnt, 9-ClAnt, 3,9-Cl2Phe, 10-Cl2Ant/1,9-Cl2Phe, 9,10-Cl2Phe, 3-ClFlu, 8-ClFlu, 1-ClPyr, 3,9,10-Cl3Phe, 5,7-Cl2Flu, 3,8-Cl2Flu, 3,4-Cl2Flu, 6-ClChr, 7-ClBaA, 6,12-Cl2Chr, 7,12-Cl2BaA, 6-ClBaP.
List 11	PBDEs	BDE-28, 47, 49, 100, 119, 99, 118, 153, 154, 153, 138, 183, 181, 196, 203, 207, 208, 209.
List 12	PCBs	PCB-28/31, 52, 60, 66, 74, 85, 90, 92, 99, 101, 105, 107, 110, 114, 115/87, 117, 118, 119, 123, 128, 130, 137, 138, 141, 146, 147, 149/139, 153, 154, 158, 163/164, 166, 167, 171, 174, 175, 177, 178, 180, 183, 187, 190, 191, 194, 195, 202, 205, 206, 207, 208, 209.
List 13	PBDEs	BDE-28, 47, 100, 99, 154, 153, 183, 203, 196, 206, 207, 208, 209.
List 14	OCPs	α–HCH (hexachlorocyclohexane), β–HCH, γ–HCH, δ–HCH, *p*, *p*'–DDT (dichlorodiphenyltrichloroethane), *p*, *p*'–DDE, *p*, *p*'–DDD.
List 15	PBDEs	BDE-28, 47, 85, 99, 100, 153, 154, 183, Octa-BDE, 196, 197, 203, 206, 208, 209.
List 16	PBDEs	BDE-3, 15, 17, 18, 47, 66, 100, 99, 154, 153, 183, 209.
List 17	PCBs	PCB-18, 28, 37, 44, 49, 52, 70, 74, 77, 81, 87, 99, 101, 105, 114, 118, 119, 123, 126, 128, 138, 151, 153, 156, 157, 158, 167, 168, 169, 170, 177, 183, 187, 189, 194, 199.
List 18	PCBs	PCB-28, 52, 60/56, 70, 74, 90/101, 95, 99, 105, 118, 138, 149, 153, 156, 157, 158, 167, 170, 180, 183, 187, 194, 203.
List 19	PCBs	PCB-8, 18, 28, 52, 44, 66, 101, 153, 138, 187, 128, 180, 170, 195, 206, 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189.
List 20	PBBs	PBB-1, 2, 3, 4, 7, 9, 10, 15, 18, 26, 29, 30, 31, 38, 49, 52, 53, 80, 101, 103, 153, 155, 209.

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Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, with a Case Study in China

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Abstract The ongoing process of globalization and global trade of products have been an important topic in media as well as in social and economic science. Overlaid by the well-known global trade pathways for feedstock and products, a reverse flow of end-of-life products has been happening for many years. This is especially true for the case of electric and electronic equipment (WEEE). Global flows of WEEE occurred to become an emerging topic of waste management in the past two decades. E-Waste has to be distinguished from materials like paper or PET-bottles, although their recycling is of environmental concern as well. WEEE is not directly recyclable but needs to be processed in several steps to extract the valuable material to be recycled. Several research projects have been carried out on the global flow of WEEE, all suffering from scarce and scattered data and a lack of uniform labelling. To assess the volume of e-waste shipped around the world, an extensive literature research has been carried out. The tool of substance flow analysis (SFA) has been identified as valuable instrument to track global WEEE trade. Data from the e-waste flows have been combined with literature-based chemical data on lead (Pb) and brominated flame retardants (BFRs) and with information on the material composition of WEEE. Several levels of e-waste

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trade have been addressed: from a global view down to the country level of China to finally focus on a case study of a municipality (Guiyu, China). The processes of informal recycling in China and Guiyu have been introduced to assess the releases of hazardous substances to the environment. The release stages have then been prepared for further use in environmental modelling presented in the chapter "Human and Environmental Impact Produced by E-waste Releases at Guiyu Region (China)" to be found in this publication.

Keywords Brominated flame retardants, E-waste, Substance Flow Analysis SFA, Informal Recycling, Waste Electric and Electronic Equipment WEEE

Contents

1 Introduction

According to an estimation by Zoeteman et al. [1], the flow of obsolete electric and electronic devices is constantly growing by 3–5% each year. Brigden et al. [2] assume that the total volume of obsolete appliances adds up to a volume of 20–50 million tons every year. Despite the fact that 172 countries signed the Basel

Table 1 Categorization of WEEE according to EU Directive 2002/96/EG

No.	Category	Content examples
1	Large household appliances	Freezers, washing machines
2	Small household appliances	Vacuum cleaners, toasters
3	IT and telecommunications equipment	PCs, telephones, printers
4	Consumer equipment	TVs, radios
5	Lighting equipment	Fluorescent lamps, metal halide lamps
6	Electrical and electronic tools (no large-scale stationary industrial tools)	Drills, saws, gardening tools
7	Toys, leisure and sports equipment	Game consols, electric train sets
8	Medical devices (no implanted/infected products)	Dialysis, nuclear medicine
9	Monitoring and control instruments	Smoke detectors, thermostats
10	Automatic dispensers	Dispensers of all kind (hot drinks, food, money, etc.)

Source: Directive 2002/96/EG [5]

Convention on Control of Transboundary Movements of Hazardous Wastes and their Disposal and 69 ratified the ban on all kinds of hazardous waste export from wealthy OECD-countries to non-OECD countries, large amounts of waste electrical and electronic equipment (WEEE) are shipped overseas for recycling, the majority to China as reported by Brigden et al. [2] and Puckett et al. [3], lesser quantities to India and Western Africa reported by Kuper and Hojsik [4]. WEEE contains a variety of harmful substances like endocrine disruptors and persistent organic pollutants (POPs). Additionally, hazardous substances may be formed during "informal recycling." This often practised "informal treatment" without proper equipment for metal extraction and labour safety heavily affects the environment and human health of workers and the inhabitants of whole stretches of land.

In 2003, the European WEEE-Directive 2002/96/EG [5] was implemented to reduce the amount of electronic waste and foster reuse, recovery and recycling of electric and electronic equipment. Closely connected to this, the restriction of hazardous substances Directive 2002/95/EG [6] (RoHS) was adopted by the EC in 2003 with the aim to restrict the use of hazardous substances in the manufacture of electric and electronic products.

The European Commission distinguishes between ten categories of e-waste, based on different uses such IT- and communication equipment or large/small household appliances in the Directive 2002/96/EG [5] (see Table 1).

In an attempt to quantify the global transport of hazardous substances that are connected to the e-waste flow, a substance flow analysis (SFA) has been performed. This includes different stages:

(a) Identification of global transportation routes.
(b) Research on the composition of typical e-waste exports with identification of priority groups with reference to WEEE-Directive categories.
(c) Compilation of the chemical composition of single categories with a special focus on lead (Pb) and brominated flame retardants (BFRs) called polybrominated diphenylethers (PBDEs) and tetrabromobisphenol A (TBBPA).

On the ground of flow data and concentrations that were either collected from literature or calculated on the basis of published data, the SFA addressed three levels: The global layer to allow an overview over the annual generation of e-waste; the country-level, in this case China as most important importing country for e-waste; and the regional level, focusing on the town of Guiyu, a former rice growing municipality changing to Chinas most important location of informal e-waste recycling as Puckett et al. [3] and Puckett [7] described and a heavily polluted place as shown by Leung et al. [8].

2 Additives: Concentration and Distribution in E-Waste

From the number of additives present in plastics the group of BFRs has been chosen due to their potential as endocrine disruptors and due to them being precursors of dioxins and dioxin-like compounds during informal recycling. Lead has been chosen because of its wide use in different fields of appliance in WEEE. Wäger et al. [9] identified the e-waste categories of small and large household appliances and IT/telecommunication and consumer equipment responsible for 98% of the amount of plastic and plastics as the main field for the appliance of BFRs as additives in WEEE. Morf and Taverna [10] stated the cathode ray tubes (CRTs), the close-grained metal fraction and printed circuit boards (PCB) as main sources lead to be found in. For lead it is often the case that the additive and reactive use of the substance cannot be discerned reliably. CRTs as a main field of application for lead therefore are observed separately. For the BFRs, data are given in Table 2, based on an SFA performed by Morf et al. [11] and adjusted to the categories from WEEE-Directive 2002/96/EG [5] (see Annex 1). It has been decided to base the later calculations on the data derived from Morf et al. [11] because they were the most comprehensive ones found during literature review.

Table 3 shows typical lead contents of WEEE based on results from Ewasteguide.info [12]. The data given in Table 2 are used as basic data for all following SFAs (if no other sources are mentioned). Ewasteguide.info [12] only provides data for categories 1–5.

3 Application of Substance Flow Analysis to Illustrate Global E-Waste Trade

3.1 The Method

Brunner and Rechberger [13] consider material flow analysis (MFA) to be a valuable tool for the tracing of stocks and flows of materials in a system defined in time and extension. Therefore the related SFA is supposed to be a valuable tool

Table 2 Average BFR concentrations in EEE, calculations based on Morf et al. [11], category numbers conform to WEEE categories presented in Table 1

Average concentration of flame retardants (rounded)	PentaBDE		OctaBDE		DecaBDE		TBBPA	
	New	Old	New	Old	New	Old	New	Old
1	0.000	0.001	0.054	0.054	0.478	0.478	0.329	0.327
2	0.000	0.000	0.071	0.071	0.633	0.633	1.114	1.114
3	0.000	0.000	0.935	2.094	2.555	6.314	9.449	5.950
4	0.000	0.090	0.083	0.415	1.174	1.719	4.408	4.047
8	0.000	0.000	0.051	0.051	0.702	0.702	13.118	13.118

"Old" data refer to e-waste from appliances produced before 1998, "New" data to those produced later than 1998, conform to Morf et al. [11]

Table 3 Typical lead contents in WEEE, assumptions marked

Categories	Leadglass (mg/kg)	Lead content (mg/kg)	Assumptions
1	0	16,000	Ewasteguide [12]
2	0	5,700	Ewasteguide [12]
3	19,000	2,900	Ewasteguide [12]
4	19,000	2,900	Estimation = categorie 3
5	0	0	Ewasteguide [12]
Additional average		2,900	Robinson (2009)

Source: Ewasteguide.info [12]

for the tracing and the assessment of international e-waste flows. To perform an SFA requires to define the respective substances and to do comprehensive analysis of the system. This includes definition of system boundaries in time and scale as shown by Brunner and Rechberger [13]. The SFA starts with an analysis of the flow of material or "goods" (MFA), in this case study assessing the shipment of e-waste as commodities. In the following step, the substances layer, tracing certain components of e-waste, such as additives, is analysed. This layer includes, as far as data are available, the identification of potential "release points" of the observed substances, meaning processes at which substances are released to the environment.

A substantial aspect for an SFA is the definition of the system which is described by the SFA. An SFA is always limited in its extent due to process properties and data availability. The time frame chosen for the SFA is strongly related to the character of the process. If the SFA is based on statistical data, a period of 1 year has been recommended as an appropriate time span by Brunner and Rechberger [13]. The spatial system boundary as second aspect defines the physical extension of the process. Regarding the fact that an SFA does not always stand on its own but is used as a basis for further investigation, it is useful to include the demands of further steps in the setting of the system boundaries. Consideration of stocks is an important aspect of an SFA as the life span of electronic devices is usually longer than one year, which is the system boundary for this case study. For this study, it has been decided to abandon stocks due to the fact that products enter as trade goods and are usually not put into service in the region observed. The appropriateness of the tools of SFA/MFA for research on e-waste has been shown by Morf et al. [11] and Morf

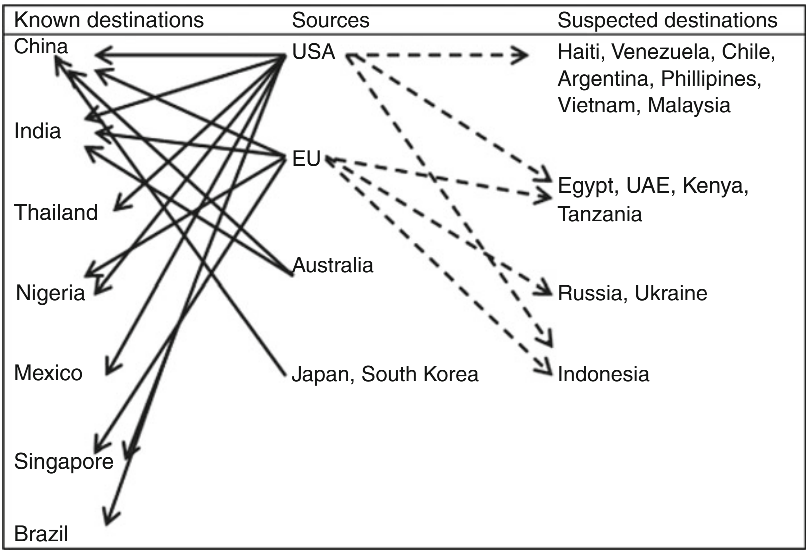


Fig. 1 Known (*full lines*) and suspected routes (*dashed lines*) of e-waste from PCIJ [17], modified by H. Tien

and Taverna [10]. As there are varying possibilities for an SFA approach, two pathways have been chosen to assess the volumes of additives. First the category approach for China and Guiyu working with the e-waste categorization from Directive 2002/96/EG [5] and second the single appliances approach for China focussing on the volumes of special appliances.

3.2 Basic Data

The term WEEE comprises a variety of different kinds of appliances, which had to be addressed separately in the substance flow analyses, as production and export of different categories varies, as does the content of hazardous material. An important input for an SFA is the composition of e-waste.

Information on shipment routes of E-waste and the respective composition of transported categories was compiled from four different sources: The statistical data from EUROSTAT [14], information published by Sander and Schilling [15], Zoeteman et al. [1] and Lepwasky and McNabb [16]. The latter compiled their data from official UN COMTRADE data. Zoeteman et al. [1] use statistical data on the consumption of electronic products and several estimation methods.

Figure 1 shows the known and suspected global shipping routes of e-waste, modified from a figure from PCIJ [17] (Phillipine Centre for Investigative Journalism), which they based on a collection of results from several NGOs.

Table 4 Global export and import of WEEE per EU-WEEE category, estimations for China 2005, from Zoeteman et al. [1], modified, full table see Annex 2

Import China (million tons)	From EU	From USA	From Japan
Cat 1	0.39	0.55	0.21
Cat 2	0.07	0.073	0.032
Cat 3	0.14	0.146	0.066
Cat 4	0.14	0.146	0.066
Sum	0.74	0.91	0.38

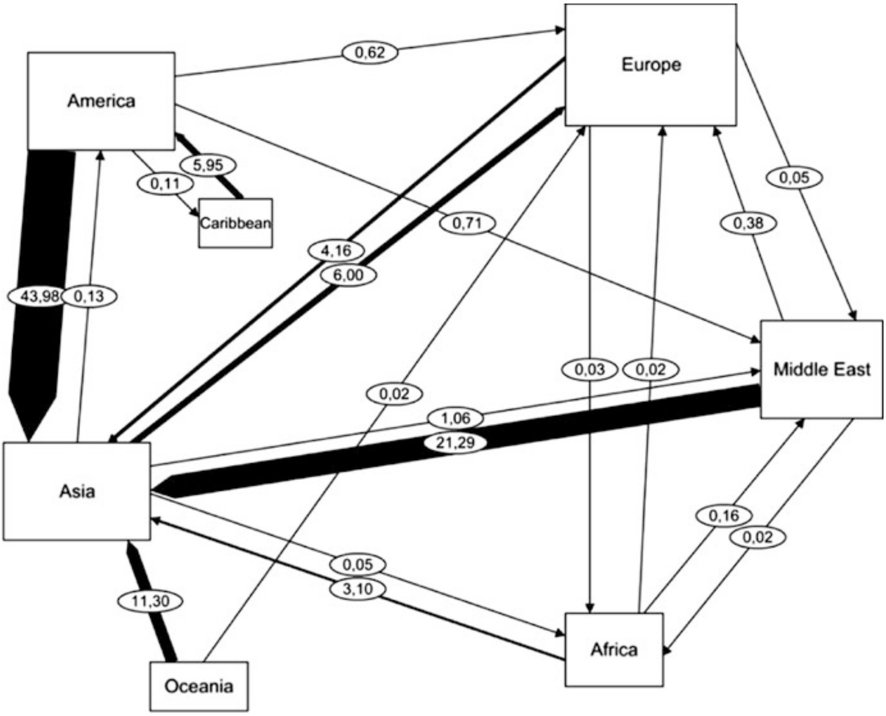


Fig. 2 Flow chart of e-waste trade. Data based on the COMTRADE-based calculations from Lepwasky and McNabb [16], values in percent of whole trade volume between named regions

Zoeteman et al. [1] present an estimation on global e-waste flow for the year 2005. They identified USA, EU-25, and Japan as the important exporting actors and China, India and West Africa as the common importers of e-waste. The calculations of Zoeteman et al. [1] (Table 2 of their article) are based on a number of assumptions and presented in Table 4.

Analogue to Fig. 2 e-waste flows presented by Zoeteman et al. [1] have been turned into percentage shares and are presented in Fig. 3.

There are several gaps to be highlighted comparing the results derived from Lepwasky and McNabb [16] and Zoeteman et al. [1]. The first base their work on

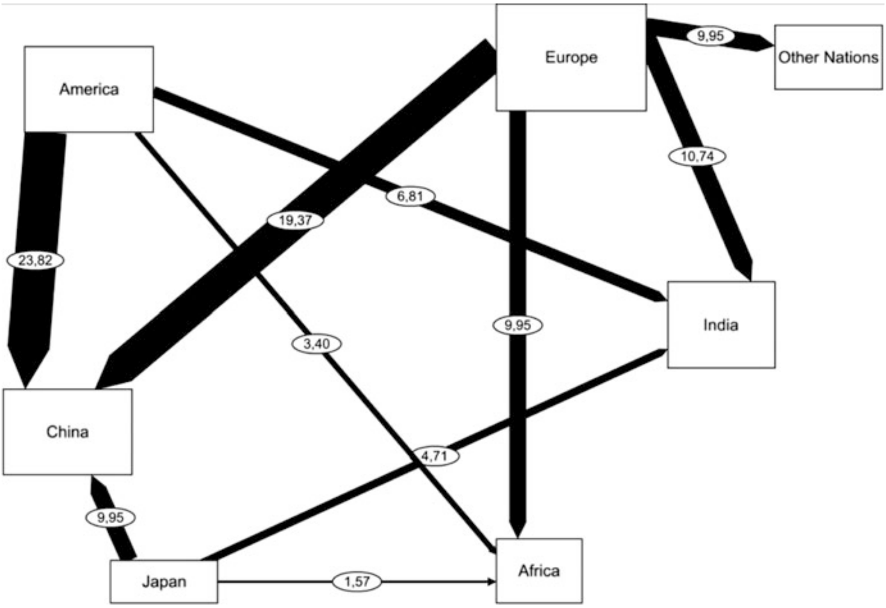


Fig. 3 Flow chart of e-waste trade. Data based on calculations from Zoeteman et al. [1], values in percent of whole trade volume between named regions

the COMTRADE database and point out several inadequacies included in those data. The excursiveness of the COMTRADE data has been called remarkable over the years by Lepwasky and McNabb [16]. In their chapter "data issues" they point out that their work does not include monitors and television sets. They conclude that their paper is highly underestimating the effective flows. Thus the results have been introduced first to show the limitations of official sources and second at least to give a further evaluation of trade routes. Zoeteman et al. [1] base their calculations on a number of assumptions considering the consumption of electronics and the amount of e-waste per capita generated. Comparing the results it comes up that the considered amount of e-waste alleged by Zoeteman et al. [1] is about seven times higher than the volume figured out by Lepwasky and McNabb [16]. This can partly be explained by the mentioned problems with the COMTRADE pointed out by database Lepwasky and McNabb [16]. More of concern is the identification of shipments. First there is the fact that in contrast to Zoeteman et al. [1], Lepwasky and McNabb [16] identified shipments from developing to developed countries. As a second difference the destinations of e-waste shipments and their importance vary. Lepawsky and McNabb consider Europe to be of minor importance and introduce the middle east as an emerging source of e-waste. The results derived from Zoeteman in contrast consider Europe to be the second largest exporter of e-waste and do not mention the middle east. Both approaches have in common that USA/America is identified as the world's largest exporter of e-waste what is conform with literature on the e-waste topic. Conspicuously Africa does not play

Table 5 Volume of WEEE derived from category "treated outside EU" of EUROSTAT database 2009

Sum EU (w/o Norway)	Mass [to]	Percentage
Category 1	858	17.47
Category 2	67	1.36
Category 3	1,653	33.67
Category 4	2,231	45.45
Category 5	1	0.02
Category 5a	0	0.00
Category 6	2	0.03
Category 7	1	0.02
Category 8	2	0.04
Category 9	0	0.01
Category 10	95	1.93
Sum Categories 1–10	4,910	100.00

Source: EUROSTAT [14]

an important role in the calculations of Lepawsky and McNabb. This again is a contrast to the common opinion that Africa is a relevant destination for WEEE as stated by Kuper and Hojsik [4]; Brigden et al. [18] and the results based on Zoeteman et al. [1]

Whereas Zoeteman et al. [1] ground on assumptions it has been decided to introduce statistical data from EUROSTAT [14]. The European statistic service EUROSTAT [14] collected data on WEEE. For this approach the most recent data from 2009 have been taken into account.

Summing up the data out of the EUROSTAT data sheet "treated outside the EU" the amounts of WEEE exported are presented in Table 5. It is an interesting fact that the official source of EUROSTAT avoids the term "export".

The results based on EUROSTAT cannot be compared directly to the data from Zoeteman et al. [1] or Lepwasky and McNabb [16]. They present the amount of e-waste generated but do not report export destinations. What can be compared is the structure of e-waste. Comparing Tables 4 and 5 it can be established that while Zoeteman et al. [1] point out household appliances as important trade fraction, data from EUROSTAT [14] allow the conclusion that IT and consumer equipment is of special importance in e-waste trade.

3.3 SFA on Global Scale

Official data on trade and flow of e-waste are few. Data and assumptions from published papers were used to gather more information. As an assumption on the average composition and the amount of e-waste produced per person in European countries, data from the UK were used (see Fig. 4, original source is Giraffe Innovation Ltd. and WEEEman.org [19], now available on www.edenproject.com). Taking into account composition, production and global transport data, an estimate of global annual e-waste generation, its components and mass of

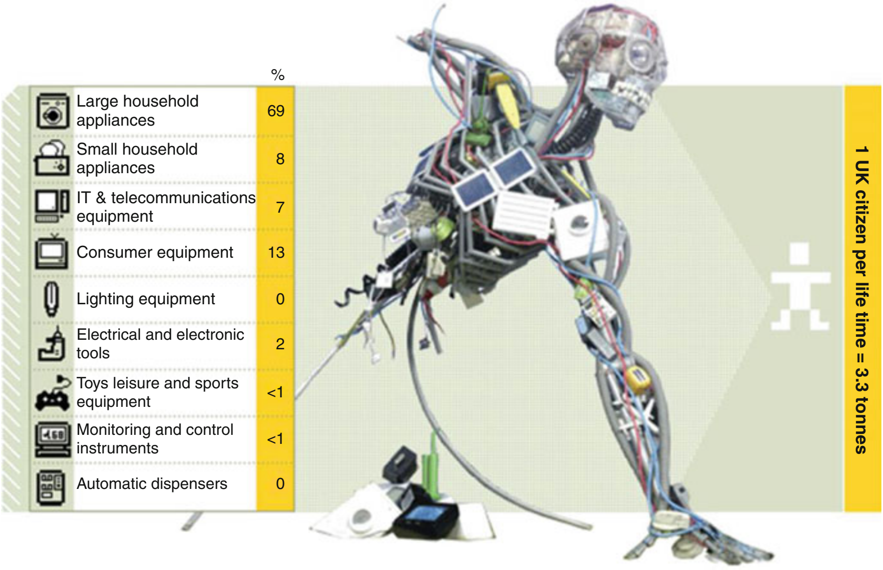


Fig. 4 The WEEEman, structure and composition of e-waste by Giraffe Innovation Ltd. and WEEEman.org [19] ©Giraffeinnovation. The WEEEman shows the composition of the lifetime e-waste volume generated by a UK citizen during his lifetime. Total volume is 3.3t, composition in %

contaminants was made. The results presented in Table 6 show a very high amount of lead, BFRs, plastics, and metals as well as CRT glass generated as part of e-waste every year. While components like metals and plastics depict valuable fractions additives like BFRs are fractions of e-waste heavily affecting human health and environment when released. Table 6 is based on the estimated range of annual waste generation (20–50 million tons) by Brigden et al. [2]. The total volume has been divided into amounts per categories from Directive 2002/96/EG [5] based on the consumption pattern presented by Giraffe Innovation Ltd. and WEEEman.org [19]. These per category volumes have been combined with the concentration data derived from Morf et al. [11] for the BFRs and Ewasteguide.info [12] for metals, plastics, and CRT-glass.

It has to be noticed that there is a share of 0% for the lightning equipment. It can be assumed that there is going to be a change regarding this aspect as the classic lightning bulb was usually not called e-waste but the new lighting equipment is considered to be.

The shares for categories 7 and 9 were given with less than1% and adjusted to 0.5%. Category 8 (medical devices) has been left out by the authors of the WEEE-man maybe because of its minor importance.

Generally these results are intended to give an overview of the cumulated amount of contaminants and fractions entering the waste stage every year.

Table 6 Annual generation of e-waste and contaminants based on following data: annual amount of e-waste taken from Brigden et al. [2], concentrations of TBBPA and Octa/Deca-BDEs based on Morf et al. [11], concentrations of lead, plastics, metals, and CRT-glass taken from Ewasteguide.info [12]

[t/a]		Lead	TBBPA	T-OctaBDE	T-DecaBDE	Plastics	Metals	CRT-glass
Flows	20,000,000	243,000	35,400	2,950	15,800	4,730,000	12,500,000	779,000
Flows	50,000,000	608,000	88,600	7,360	39,400	11,800,000	31,200,000	1,950,000

The composition of e-waste concerning Directive 2002/96/EG [5] categories is based on Giraffe Innovation Ltd. and WEEEman.org [19]. Data adjusted to three significant numbers

3.4 Uncertainty Data Compilation

The estimation of global flows has been performed in a number of researches. Non-governmental watchdog organizations (watchdog-NGOs) like the Basel Action Network or Greenpeace play an important role in the identification of shipping routes of e-waste. Often there is a difference between official data and data gathered by the NGOs. This is mainly due to illegal exports, not turning up in official statistics, as well to differing definitions what e-waste is and how it is labelled. Puckett [7] pointed out that there is currently no internationally uniform rule of labelling e-waste on transboundary transportation routes. Therefore the data concerning e-waste flows or concentrations have to be viewed regarding the data uncertainty. The issue of data uncertainty is aggravated by the fact that even little is known about the variations of the data, if the deviation has a factor like one to two or is even in the range of an order of magnitude. Facing the number of parameters affecting the accuracy of the e-waste-flow information deviations have not been introduced into the SFA calculations but the uncertainty issue is highlighted by the authors.

3.5 SFA for China Including Processes of Informal Recycling for the Year 2005

The SFA for China is based on trade data by Zoeteman et al. [1] for the year 2005 and on the information on chemical composition derived from Ewasteguide.info [12] and Morf et al. [11]. The STAN-software from Vienna Technical University was applied which has been used by Cencic and Rechberger [20] before for MFA and modelling of systems. Figure 5 depicts the structure of the STAN-approach designed.

The processes of informal recycling such as physical dismantling, migration to dust, and shredding and dismantling have been addressed in the SFA as best as possible on the ground of available information, e.g. from Chi et al. [21]. During the physical dismantling process the e-waste devices are divided into the most interesting elements such as the PCB, copper windings and cables, metal casings, and the toner cartridges. The PCBs are heated and treated by acid extraction in order to recover their high content of precious metals. The final end-use of the recovered toner is uncertain.

Plastics and metals are also of high interest. The plastic materials are normally mechanically shredded, manually sorted and then remelted. Then, new products are produced by heated extrusion. However Puckett [7] states that 25–30% of the plastics are burnt in open fires in order to recover valuable metals such as copper. The metals are only extracted and not further processed due to the fact that the informal recycling facilities in China do not have the proper technology to perform the metal recycling via smelting.

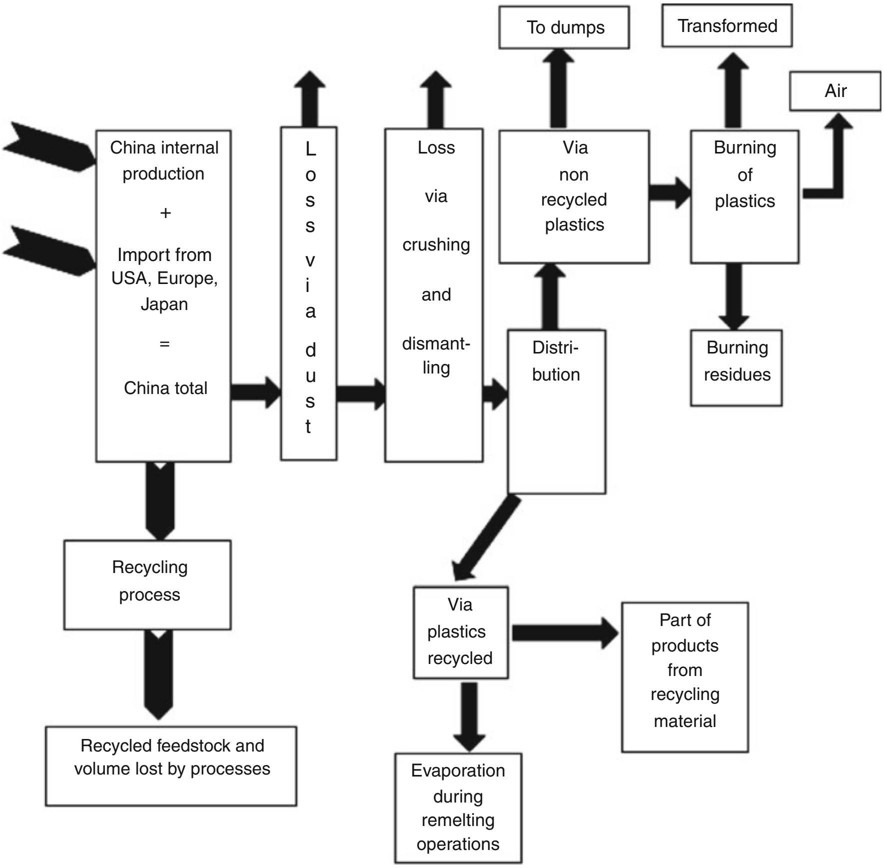


Fig. 5 Simplified depiction of the STAN-approach developed for the China case

Finally, despite the attempt to recycle, much of the dismantled components of the e-waste appliances end up being dumped in open landfills as supported by Sepúlveda et al. [22].

In STAN-software, so-called transfer coefficients (TCs) describe the transfer of substances, in our case contaminants, from one process to another. They have been derived for this study from publications and personal communication. Table 7 presents the results of the SFA with special focus on China for 2005. The e-waste volumes per category from Zoeteman et al. [1] have been combined with the concentration data derived from Morf et al. [11] and Ewasteguide.info [12] to access the volumes of contaminants and fractions. These data were then viewed introducing TCs for the processes of migration to dust, crushing and dismantling, and thermal treatment. The distribution into the different pathways (recycling, burning, dumping) is based on TCs developed in discussion with Puckett [7]. The TCs used can be found in Annex 3.

Special attention has to be set on the TCs taken from Sakai et al. [24] as they are taken from a study on Japanese e-waste recycling.

Table 7 Fate estimation of hazardous substances derived by the SFA for China

Fraction/substance	Pathway	Volume [t/a]
DecaBDE	Total volume	4,590
	Loss via dust	0.0041
	Loss via crushing and dismantling	0.0208
	To dumps	569
	To exhaust (off-gas)	0.00228
	Transformed to secondary products via burning	1,270
	To burning residues	0.736
	To plastics recycled	2,760
OctaBDE	Total volume	871
	Loss via dust	0.000775
	Loss via crushing and dismantling	n.a.
	To exhaust (off-gas)	0.000433
	To dumps	108
	Transformed to secondary products via burning	241
	To burning residues	0.1400
	To plastics recycled	523
TBBPA	Total volume	12,300
	Loss via dust	n.a.
	Loss via crushing and dismantling	n.a.
	To dumps	3,120
	To exhaust (off-gas)	
	Transformed to secondary products via burning	6,800
	To burning residues	160
	To plastics recycled	2,210
Lead	Total volume	55,300
	Lead recycled	44,200
	Lead waste	11,100
Metals	Total volume	3,060,000
	Lost metals	613,000
Plastics	Plastics recycled	746,000
	Plastics burned	341,000
	Plastics dumped	152,000
CRT glass	Total volume	332,000

Calculations have been performed with STAN, based on data by Zoeteman et al. [1] for the flows and concentration data from Tables 2 and 3

4 Alternative Approach: The Single Appliances Approach for China

4.1 The Approach

The present section offers a different way to address the e-waste flow in China from the one already presented in previous sections. The main idea is focusing on single appliances and not on categories. By doing this, the information obtained for the

Table 8 Estimation of obsolete WEEE in China, based on Yang et al. [23]

Year WEEE (million units)	2003	2004	2005	2006	2007	2008	2009	2010
PCs	4.48	7.31	9.81	10.73	12.68	15.13	15.57	19.57
TVs	33.51	28.81	32.32	40.88	44.49	44.60	48.43	55.73

different appliances is more accurate while the overall picture is missing information. This is due to the fact that it is easier to determine concentrations of a certain additive in a single appliance (i.e. televisions and computers) than in a whole category (e.g. category 3: IT and telecommunications equipment). In addition, focusing on a single appliance, it is possible to estimate the different parts into which an electronic device is dismantled. Therefore, it seems that it allows the possibility to develop a more detailed and precise study.

In the present approach, the electronic devices taken into account are computers and televisions. These devices have been chosen because of their important growth in the e-waste production during the last years. The availability of information has been also important to select the studied appliances.

4.2 Amounts of the Target Single Appliances in China

The starting point in the single appliance approach is to determine the amount of the target devices that reach China every year. In previous sections data from Zoeteman et al. [1] have been used as a basis for the definition of the global e-waste flow in China. However, for the single appliances approach more specific information on the entering flow of e-waste appliances in China has been found in a report developed by Yang et al. [23]. Therefore, this document has been taken as the basis of the present section.

The report made by Yang et al. [23] determines the amount and composition of the e-waste flow in China (i.e. the quantity and the type of products that it includes). The document distinguishes among: TVs, computers, mobile phones, air-conditioners, refrigerators, etc. Nevertheless, as aforementioned, this approach focuses on televisions (category 4) and computers (category 3).

Table 8 provides the amounts of the electronic devices (millions units) accumulated in China over the years.

The following table presents the estimated weight per unit for the e-waste appliances studied (Table 9).

Table 10 is the result of the multiplication of the amount of each WEEE in millions of units by its weight per unit. As a consequence the following table provides the weight of the electronic devices (millions tons) accumulated in China over the years.

From these data the percentages of these appliances on the e-waste category that they belong to can be estimated. Once the amount of the studied appliances has been defined, the following subsection presents the content of additives of the selected e-waste devices.

Table 9 Unit weight for the WEEE considered, based on Yang et al. [23]

WEEE	kg/unit
PCs	27
TVs	25

Table 10 Estimate of obsolete WEEE in China, based on Yang et al. [23]

Year WEEE (millions tons)	2003	2004	2005	2006	2007	2008	2009	2010
PCs	0.12	0.20	0.26	0.29	0.34	0.41	0.42	0.53
TVs	0.84	0.72	0.81	1.02	1.11	1.12	1.21	1.39

4.3 *Content of Additives in the Considered Appliances*

An extensive research has been done with the purpose to collect enough and valuable data about the content of additives inside the considered appliances. Nevertheless, despite there exists a lot of information on the content of additives in electronic devices, this is not well classified.

In order to follow the same line of the category approach, the content of Lead and BFRs is estimated. Due to the lack of data on the content of TBBPA in televisions and computers, this additive is removed from the single appliance approach. Therefore this section focuses on the content of Pb and PBDEs.

As aforementioned, the advantage of studying an electronic device on its own is that it is easier to determine the concentration of the device or even of the elements in the appliance.

In previous sections, the most common ways of informal recycling have been introduced. It is known that a computer is not entirely recycled and that it is divided into the most interesting elements before going to the informal recycling processes as reported by Chi et al. [21]. The selection of the interesting elements takes place during the physical dismantling process already introduced in Sect. 3.5.

Once the most interesting elements in e-waste appliances and the most common pathways of recycling them have been established, the content of the selected additives (Pb and PBDE) in these parts for computers and televisions is explained in more detail below.

4.3.1 Content of Additives in Televisions

The total content of Lead and PBDEs in the TVs has been calculated. In the case of Lead, Fig. 6 presents the distribution of this compound in the different parts of a TV set. It is important to mention that due to the lack of data on the Pb content in Printed Circuit Board (PCBs), this element has not been taken into account for televisions.

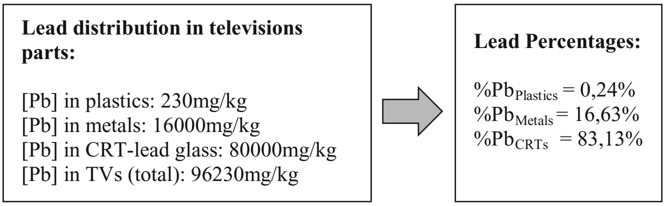


Fig. 6 Lead distribution and percentages in TVs, based on Morf and Taverna [10]

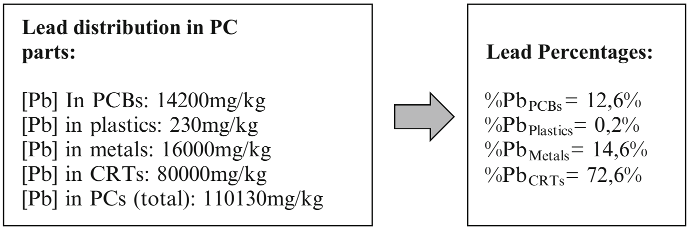


Fig. 7 Lead distribution and percentages in PCs (based on Morf and Taverna [10] and Gullett et al. [27]

In the case of PBDEs, their content is supposed to be placed mainly in plastics [9]. Therefore it is easier to estimate the PBDE content rather than the Pb one because plastics are the unique source of BFRs (PBDEs) in a television. The estimated concentration of PBDEs in the television plastic is 24.5 g/kgPlastic [25]. Nevertheless, the content of PBDEs is known in the television plastics and not in the whole device; therefore, it is essential to know the percentage of plastics in a TV set in order to determine the content of PBDEs. This value is around 16.00% (estimation made using documents from Kim et al. [25] and Tasaki et al. [26] as a basis).

4.3.2 Content of Additives in Computers

As done for the televisions, the lead content and distribution in the different parts of a computer is shown in figure 7.

Concerning the PBDEs content in computers, no specific information about this compound has been found. Therefore, since computers belong to the category 3, the PBDE content of this category presented in Sect. 2 (Table 2) has been assumed as the one in computers. The considered value is 28.03 g/kgPlastic, it is the result of the sum of the content of the different PBDE congeners in appliances from Table 2 (appliances produced before 1998 as conservative scenario). In addition the plastic content in a computer is around 22.99% based on Puckett et al. [3].

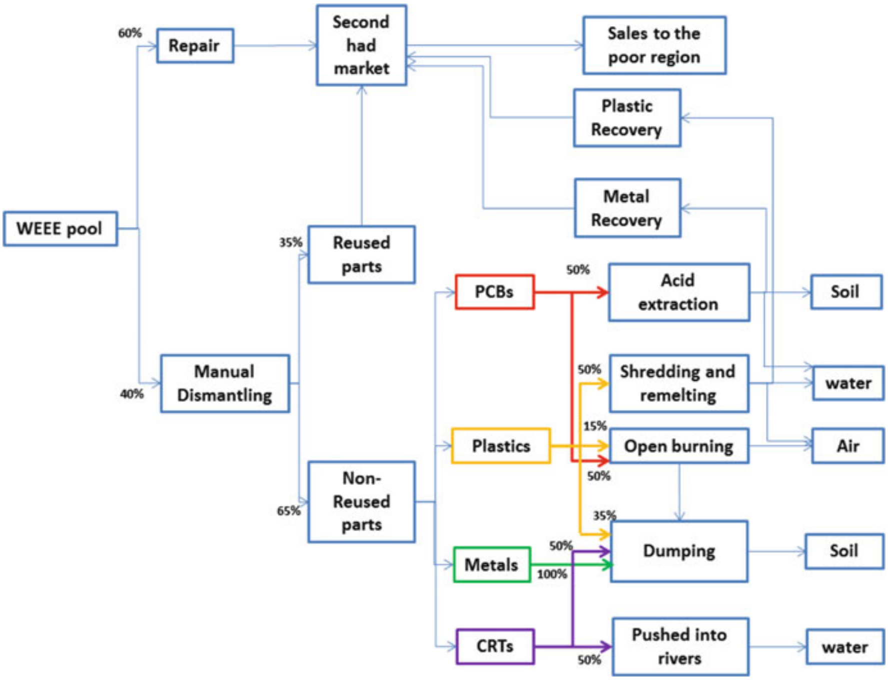


Fig. 8 Scenario for e-waste appliances (TVs and PCs) in China, based on Yang et al. [23]

4.4 Appliances E-Waste Flow and Its Additives

In previous subsections, the amounts of the targeted e-waste appliances and their content in the selected additives have been presented for the case of China. The next step is to define scenarios in order to determine the distribution of the additives (Pb and PBDEs) among the informal recycling processes. Furthermore, the estimation on the predicted emissions to the environmental targeted compartments is also done.

As a general trend, the amount of TVs and PCs discarded (obsolete) is normally repaired or manually dismantled (see Fig. 8). Then the repaired part goes to the second-hand market, and it is usually sold to the poor regions whereas the dismantled part can either be reused or not. On the one hand, the reused parts also end up into the second-hand market being sold to the poor regions. On the other hand, the non-reused parts (PCBs, plastics, metals and CRTs) are treated with some informal recycling process and might have effects on the different environmental compartments.

In order to estimate the emissions to each environmental compartment, it is important to point out the effects of the informal recycling processes to soil, water and air. However, as already mentioned in the category approach, it is a complicated issue due to the fact that there exists scarce data on this topic. Therefore, in some cases the distribution of the emissions into the different environmental compartments has had to be assumed.

On the one hand, the acid solution used in acid extraction process affects mainly to water and soil when it is discharged to the environment. Nevertheless there is an important part of this solution that is removed as metal recovered which is sold in the second-hand market.

On the other hand, the process of shredding and remelting plastics recycles an important share of the plastic e-waste. These recycled plastics are normally sold in the second-hand market.

Concerning the open burning process, it has hazardous effects on the air. However, since there is a part that is not well burned, a residue is generated. This residue of the combustion along with metals and CRTs are normally dumped in open-air landfills. The effects of this activity impact the soil compartment. Moreover, CRTs are often pushed into rivers affecting in the water compartment.

4.5 Predicted Additive Emission into the Environmental Compartments

The aim of the scenario presented above is to determine the emission of the selected additives present in the different e-waste devices into each environmental compartment. However, each appliance has its particularities, and consequently there exist differences among the devices and their emissions. For example, since the PCBs are not taken into account for the televisions, the acid extraction pathway is not considered for this appliance. Furthermore, each appliance involves a different e-waste amount and a different content of additives.

Another important point to bear in mind is the already mentioned transfer coefficients (TC) issue. It is well known that the process that leads Pb to reach the soil compartment is very complex requires a lot of time and involves a lot of parameters such as pH or meteorological conditions. In addition, there always exists the uncertainty about the possibility of the Pb remaining in the device and not ending up into the soil. In the present approach (single appliances), the transfer coefficients used for the category approach have been taken as valid. As a particular example, it has been assumed that approximately 0.017% of the dumping leachates have effects on the water surface referring to Choi et al. [28]. However, in the cases that a TC is unknown, the total amount of the additive present in the device has been considered to reach the predicted environmental compartment, being more conservative.

Table 11 shows a summary of the additive emission values into the environmental compartments obtained for the different appliances.

Concerning the results obtained in the present approach, it seems important to highlight that they are rather difficult to compare with the categories angle. It is due to the fact that both approaches are different and even based on different reports, the

Table 11 Additive emissions into the predicted environmental compartments, based on Yang et al. [23]

Emission to:	Air		Soil		Water	
(kg Additive/year)	Pb	PBDEs	Pb	PBDEs	Pb	PBDES
PCs	1.62×10^2	8.77×10^1	9.07×10^2	8.77×10^1	5.60×10^3	8.77×10^1
TVs	1.03×10^1	1.38×10^2	1.87×10^1	1.38×10^2	1.45×10^4	1.38×10^2

categories approach is based on Zoeteman et al. [1], whereas the single appliances one takes into account an article developed by Yang et al. [23].

Furthermore, the categories approach for the global SFA in China does not define the predicted environmental whereas in the single appliances one, some assumptions have been had to be done in order to provide an emission value into these environmental compartments. In addition, as aforementioned the single appliances approach takes into account that the total amount of the additive present in the device reaches the predicted environmental compartment when a TC is unknown.

4.6 Comparison Between the Results of the Category: And the Single Appliances Approach

Conducting the two different approaches (category based and single appliances approach) highlights the sensitiveness of an SFA towards data uncertainties. Both approaches have their advantages and disadvantages. The category approach based on Directive 2002/96/EG [5] offers the possibility to include large groups of e-waste into the calculations. Further most statistical data refer to this categorization or are at least adaptable. The category approach allows a comprehensive acquisition of data. A less objective point of the category approach is the uncertainty concerning the concentration of additives. The concentrations of PBDEs and lead vary among all the single appliances and the category approach has to work with average concentrations per category. This is the aspect the single appliances approach comes into action as this approach focuses on single products which allows a comprehensive look on the additives distribution inside the single appliances and the consequences for the steps of recycling. In contrast to the category approach this focus can hardly cover the total flow of e-waste. The decision which approach to use should be based on two aspects. Observing a comprising system with several types of e-waste implies the use of the category approach, if a special process with homogeneous e-waste input is the object of research, the single appliance approach is easier to handle and allows more accuracy. A second aspect is the later use of the data produced by the SFA. If the SFA is performed to provide data for further research such as environmental modelling or life cycle assessment (LCA) the demands of the consecutive steps should be regarded while designing the SFA. The two approaches are comparable in their results, as far as comparable input data are used.

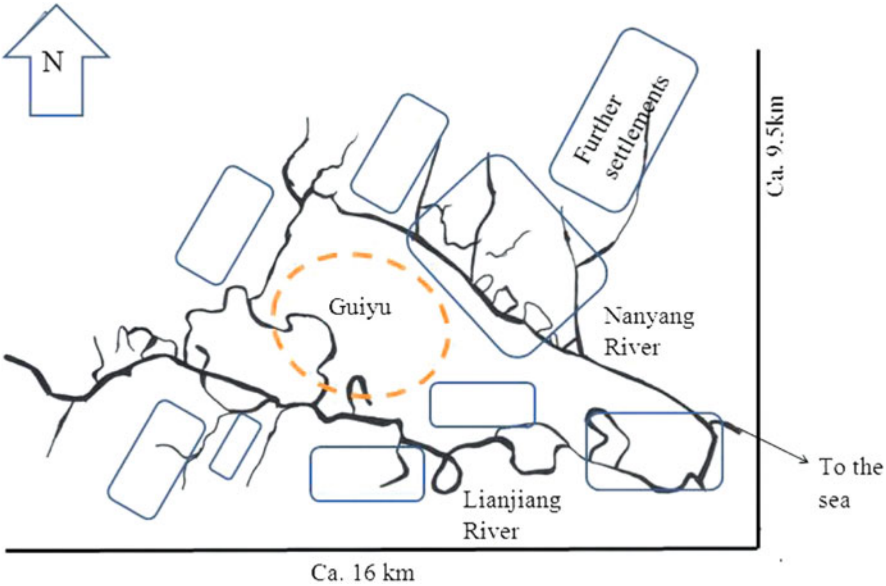


Fig. 9 Map for the Guiyu region

5 SFA for the Region of Guiyu, Based on the Category Approach

5.1 Introduction

Located in the province Guangdong in the south east of China, Guiyu turned its face from a community of rice growing farmers to one of the most polluted landscapes to be found as described by Puckett et al. [3]. Guiyu is considered to be an example for the trashing of developing countries and for the global consequences of western way of the use pattern concerning electric and electronic equipment by Puckett et al. [3]. For the case of Guiyu a time range of one year is for the SFA. The territorial borderline should be defined considering the later on planned involving of a multimedia fate models. The following Fig. 9 is based on a photo from Google Earth® from 19 August 2011 in connection with the map of Luo et al. [29]. The area that is suspected to be the centre of recycling is marked with dashed lines, the other marks are further settlements that presumably are involved in the informal recycling. The drawings are not true to scale but give and overview over the large rivers which are fed by a number of channels and brooks.

The system has got an acreage of approximately 150 km^2. Later conversation with Jim Puckett [7], an expert on the Guiyu topic, brought up a suspected extend of the central recycling area of approximately 10–15 km^2.

5.2 Composition of the Incoming WEEE

The TCs for the SFA for Guiyu are the same as the ones used in Sect. 4 (see Annex 3) and based on literature review and personal communication with Jim Puckett [7] who has visited Guiyu three times and is very knowledgeable on that issue, and Monica Danon-Schaffer [30] as an expert in the behaviour of the BFR group of polybrominated diphenylethers (PBDEs) in dumpsites and landfills as apparent from Danon-Schaffer [31]. Beyond the three steps of SFA from global to spatial Guiyu scale, the SFA for Guiyu itself has been divided into three connected sub-SFAs. The first one provides an overview of the substance flow through the system of Guiyu, the second SFA identifies release points of contaminants, and the third SFA models of a hypothetic dumpsite for e-waste remains in Guiyu. Information on how much e-waste is transported to Guiyu is scarce. As suggested by Lee [32], and supported by Puckett [7], an estimate of 1 million tons per year seems to be reasonable and has been chosen as input data for this regional SFA. The composition with regard to categories was assumed to be equal to the one derived from EUROSTAT [14] data. A hint on private use of the incoming WEEE has not been in the literature.

5.3 SFA and Resulting Flows

The results of step 1 and 2 of the Guiyu-SFA are presented in Tables 12 and 13. The process of acid treatment of PCBs has not been investigated due to the lack of data concerning the process itself and the unknown extension of application for the Guiyu case. For the conceptual diagrams of the STAN-approach for Guiyu, see Annex 4.

There is varying information on the leakage of lead from the dumps of Guiyu. Based on the SFA two approaches concerning lead given by van Oers [33] and Thomas et al. [34] have been chosen. The calculations are supposed to be highly uncertain as Thomas et al. [34] mentioned. The results based on van Oers [33] are presented in table 14.

The data from Thomas et al. [34] have been taken as emission factors for lead from CRTs in landfills (Table 15).

To assess the relevance of the Guiyu dumpsites, essential data were missing. Therefore it has been decided to introduce a model dumpsite for Guiyu. It is based on climate data from Hong et al. [35], data from Danon-Schaffer [31] and personal communication with Danon-Schaffer [30]. The dumpsite topic has potential for further research as it may concern a long-term problem. The defaults for the model dump are presented in Table 16, the results can be found in Table 17.

Danon-Schaffer [31] includes several leachate concentrations for PBDEs in her thesis. BDE congener BDE-209 (i.e. C-DecaBDE) has been chosen. The calculations given in Tables 12 and 13 are based on the assumption that the rainfall is constant over time. The table numbers refer to Danon-Schaffer [31]. There is no information

Table 12 Results of the SFA for Guiyu performed with STAN based on 1 million tons input and the composition derived from EUROSTAT

Results [t/a]	Cat	Goods	OctaBDE	DecaBDE	TBBPA	Lead	PbCRT-Frac
Inflow	1	174,700	9.43	83.5	57.5	2,800	0
	2	13,600	1.0	8.6	15.2	77.5	0
	3	336,700	315	860	3,180	976	64,000
	4	454,500	37.7	534	2,000	1,320	86,400
CRT glass	3 + 4	0	0	0	0		150,000
Plastic waste	1–4		109	594	4,630	29.4	0
Metal waste	1–4		0	0	0	1,020	0
Metals recycled	1–4		0	0	0	4,080	0

Table 13 Results of the SFA with a closer look towards the release points [t/a] (rounded)

Pathway	DecaBDE [t/a]	OctaBDE [t/a]	TBBPA [t/a]	Lead in plastics [t/a]
Input	1,490	363	5,260	73.4
To dust	0.00132	0.000323	n.a.	n.a.
Loss shredding and disassembly	0.00669	n.a.	n.a.	n.a.
Transformed via burning	408	99.2	2,900	0
Solid residues from burning	0.237	0.0580	68.2	20.2
Emission to exhaust	0.000736	0.00018	0.00296	Fly ash: 0.0238
To dumping	186	45.4	1,350	9.17
Recycling material	892	218	946	44.0
Loss via reextruding	n.a.	n.a.	n.a.	n.a.

Table 14 Predicted lead emissions via leachate from Guiyu dumps, based on van Oers [33]

Input [t/a]					Output (kg/y)		
Dumping pathway	Lead flow from SFA	Deviation	Emission factor	Deviation	Value	Max	Min
From plastics burning	20.20	6.86	2.30E-03	2.30E-04	46.4	68.4	27.6
Lead in plastics dumped	9.17	3.15	2.30E-06	2.30E-07	0.0211	0.0312	0.01250
Lead in metals dumped	1,020	147	1.84E-07	1.84E-08	0.188	0.236	0.144

The deviation of the lead flow is based on the assumption of a constant uncertainty of 10% in the SFA, the deviation of the emission factor is assumed to be 10% as well. These uncertainties probably are highly underestimated (see Sect. 3.4)

on the effective acreage of the dumpsites, so in four approaches it has been assumed that the dumpsite is 0.15, 0.5, 1.0, and 2.0 as big as the central recycling area of 15 km^2. Further it is assumed that the surface water stays long enough for BDE-209 (decaBDE) to reach steady state, which has been confirmed by Danon-Schaffer [30].

Table 15 Emissions of lead in from the Guiyu dumps from broken CRT-Glass, based on the SFA for Guiyu and data from Thomas et al. [34]

Input [t/a]					Output [kg/y]		
Pathway	Lead flow from SFA	Deviation	Emission factor	Deviation	Value	Max	Min
CRT glass	150,000	15,200	6E-05	6E-06	9,020	10,925	7,297

The deviation of the lead flow is based on the assumption of a constant uncertainty of 10% in the SFA, the deviation of the emission factor is assumed to be 10% as well. These uncertainties probably are highly underestimated (see Sect. 3.4)

Table 16 Settings and conditions for the Guiyu model dump

Aspect	Data	Source
Average temperature	25–30°C	Hong et al. [35]
Mean annual precipitation	2,000–2,500 mm	Hong et al. [35]
Central recycling area	15 km^2	Puckett [7]
Extension of recycling area in %-share of central recycling area	15%, 50%, 100% and 200%	Assumption by the authors
Dwell time of the surface water for the BDE209 to reach steady state	Given	Danon-Schaffer [30]

6 Discussion

Tracing international e-waste flows is complicated first by the absence of a uniform labelling of shipments and second by the division of trade into formal and informal sector. Scientific literature carried out on the subject of global e-waste trade and informal recycling can only focus on parts of the system. Often it can only be based on estimations and assumptions as the informal recycling sector is usually not assessable for research due to its illegal character. Data derived in this study are literature based (except personal communications) and as a consequence suffering from uncertainties which heavily affect the results and depict the need for further research to close data gaps. The need for several approaches such as single appliance approach and category approach for the characterization of additives flows underlines the uncertainty issue.

7 Conclusions

The implementation of SFA for the tracing of hazardous substance in international informal e-waste treatment has occurred to be a useful method. As the quality of results heavily depends on the quality of input data uncertainties restrict the relevance of results. Thus the results show a direct connection between the attitude towards the treatment of e-waste in developed countries and health and environmental consequences in the receiving countries. The e-waste subject in developing

Table 17 Results for the annual leaching of BDE-209, out of the Guiyu model dumpsite in dependence of several dumpsite acreages based (average temperature: 25–30°C; mean annual precipitation 2,000–2,500 mm p.a. from Hong et al. [35]; central area of recycling: 15 km^2 based on Puckett [7]; acreage of model dumpsite: 15%, 50%, 100% and 200% of the central recycling areas extension; BDE-209 partitioning has reached steady state as supported by Danon-Schaffer [30]

	Acreage of dumping area	2.25		7.5		15		30	
Table	BDE209 (pg/L) in leachate	BDE209 released (kg) abs	Deviation of precipitation	BDE209 released (kg) abs	Deviation of precipitation	BDE209 released (kg) abs	Deviation of precipitation	BDE209 released (kg) abs	Deviation of precipitation
5.1	244,000	1.24	0.14	4.12	0.46	8.24	0.92	16.47	1.83
6.3	9,240	0.05	0.01	0.16	0.02	0.31	0.03	0.62	0.07
6.4	2,740,000	13.87	1.54	46.24	5.14	92.48	10.28	185	20.55
6.5	810,000	4.10	0.46	13.67	1.52	27.34	3.04	54.68	6.08
6.7	6,580,0000	333.1	37.01	1,110	123.4	2,221	246.8	4,442	493.5
6.9	2,700,000	13.67	1.52	45.56	5.06	91.13	10.13	182.3	20.25

The table numbers refer to Danon-Schaffer [31] countries occurs to have two dimensions. First there are short-term releases of the hazardous substances during informal recycling process affecting workers health and the environment as shown in the several steps of the SFA. The second dimension is the long-term aspect as the dumps and landfills contain a tremendous amount of the same hazardous substances ready to leach out as it has been shown with the model dump. The environmental and occupational health problems in developing countries caused by high tech waste from western world is the other side of globalization and underline the responsibility for the waste we produce and the need for further legislation.

Acknowledgements The help and advice of Monica Danon-Schaffer from Tetra Tech, British Columbia, Jim Puckett from Basel Action Network and Lauran van Oers from University of Leiden, Netherlands, is highly appreciated. Finally Giraffe Innovation Ltd. (London) kindly allowed us to use the data and picture from the WEEEman study.

Annex 1: Flame retardants in electric and electronic equipment: based on Morf et al. [11], Table 29-9

Flame retardants in products (g/kg) Old: produced before 1998 New: produced later than 1998	PentaBDE		OctaBDE		DecaBDE		TBBPA		Category from WEEE-Directive
	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	
IT and office equipment									
Computers + Monitores pHH	0	0	0.17	1.91	1.8	2.74	10.09	10.36	3
Computers+monitors office	0	0	0.17	1.91	1.8	2.74	10.09	10.36	3
Servers	0	0	0.17	1.91	1.8	2.74	10.09	10.36	3
Notebooks	0	0	0.08	1.91	0.96	2.94	23.57	20.42	3
Laserprinter	0	0	0.23	3.14	3.34	4.05	9.98	7.28	3
Inkjet printers	0	0	0.16	1.1	1.65	1.62	10.61	9.33	3
Copying machines	0	0	0.32	3.14	3.29	4	7.61	4.91	3
Calculating machines	0	0.18	0.08	0.48	7.71	2.45	4.74	4.38	3
Average	0		0.1725	1.938	2.794	2.91	10.85	9.675	
Communication equipment									
Phones	0	0	0.077	0.077	0.775	0.775	5.55	5550	3
Mobile phones	0	0	0.077	0.077	0.725	0.725	3000	3000	3
Fax	0	0	0.234	3.137	3.429	4.142	14650	11950	3
Average	0	0	0.1293	1.097	1.643	1.8807	5885	6833	
Consumcer equipment									
CD player	0	0.173	0.086	0.26	1.45	1.96	4.59	4.03	4
Amplifier	0	0.039	0.086	0.26	0.93	1.12	1.79	1.68	4
Receiver	0	0.069	0.086	0.26	1.05	1.31	2.41	2.21	4
Tapedecks	0	0.247	0.086	0.26	1.74	2.42	6.14	5.34	4
Record player	0	0	0.077	0.077	0.68	0.68	0.45	0.45	4

(continued)

Flame retardants in products (g/kg) Old: produced before 1998 New: produced later than 1998	PentaBDE		OctaBDE		DecaBDE		TBBPA		Category from WEEE-Directive
	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	
Portable hifi-appliances	0	0.319	0.086	0.26	2.03	2.88	7.66	6.61	4
TV sets	0	0.025	0.077	2.8525	1.34	4.8	2.57	2.11	4
Video recorder	0	0.075	0.086	0.26	1.07	1.35	2.54	2.32	4
Video cameras	0	0.106	0.086	0.26	1.19	1.54	3.2	2.86	4
Photo cameras	0	0.027	0.086	0.077	0.88	0.84	1.52	0.92	4
Electric toys	0	0	0.077	0.077	0.83	0.83	8.1	8.1	4
Electronic music instruments	0	0	0.077	0.077	0.9	0.9	11.93	11.93	4
Average	0	0.09	0.083	0.4150	1.174	1.719	4.408	4.047	
Small household appliances									
Small household appliances	0	0	0.077	0.077	0.675	0.675	0.45	0.45	2
Warming appliances	0	0	0.077	0.077	0.675	0.675	0.45	0.45	1
Scales	0	0	0.077	0.077	0.7	0.7	1.725	1.725	2
Clocks and buzzers	0	0	0.077	0.077	0.705	0.705	1.98	1.98	2
Average	0	0	0.077	0.077	0.6888	0.6888	1.151	1.151	
Large household appliances									
Tumbler	0	0	0.051	0.051	0.45	0.45	0.3	0.3	1
Cooling appliances	0	0	0.051	0.051	0.45	0.45	0.3	0.3	1
Freezers	0	0	0.051	0.051	0.45	0.45	0.3	0.3	1
Washing machines	0	0.0013	0.051	0.051	0.46	0.46	0.33	0.32	1
Sewing machines	0	0.0033	0.051	0.051	0.46	0.47	0.37	0.36	6
Vacuum cleaners	0	0	0.051	0.051	0.45	0.45	0.3	0.3	2
Dishwasher	0	0.0023	0.051	0.051	0.46	0.46	0.35	0.34	1
Espresso machines	0	0.0053	0.051	0.051	0.47	0.48	0.41	0.39	2
Microwaves	0	0.0015	0.051	0.051	0.46	0.46	0.33	0.33	1

Stoves and cookers	0	0	0.051	0.051	0.45	0.45	0.3	0.3	1
Air handling units, ventilators	0	0	0.051	0.051	0.45	0.45	0.3	0.3	1
Average	0		0.051	0.051	0.4555	0.4573	0.3264	0.3218	
Special appliances									
Control units	0	0	0.051	0.051	1.45	1.45	51.3	51.3	
Measurement devices	0	0	0.051	0.051	1.45	1.45	51.3	51.3	8
Laboratory equipment	0	0	0.051	0.051	0.47	0.47	1.15	1.15	8
Life-saving appliances	0	0	0.051	0.051	0.65	0.65	10.5	10.5	8
X-ray units	0	0	0.051	0.051	0.47	0.47	1.32	1.32	8
Optic appliances	0	0	0.051	0,051	0.47	0.47	1.32	1.32	8
Electronic lockers	0	0	0.051	0.051	0.45	0.45	0.38	0.38	
Automatic dispensers	0	0	0.051	0.051	0.45	0.45	0.47	0.47	10
Electric tools	0	0	0.051	0.051	0.45	0.45	0.3	0.3	6
Average	0	0	0.051	0.051	0.7011	0.7011			
EEE-small parts									
Connectors, switches, etc.	0	0	0.018	0.101	0.2	1.29	0.2	0.5	
Lightning equipment	0	0	0.009	0.049	0.15	0.62	0.1	0.24	5
Cables	0	0	0	0	0	0	0	0	
Average	0	0	0.009	0.05	0.1167	0.6367	0.1	0.2467	
Means of transport									
Cars	0.004	0.008	0.025	0.032	0.27	0.37	0.22	0.23	
Car radios	0	0.059	0	0	0.23	0.37	1.24	1.04	
Trucks	0.001	0.003	0.009	0.011	0.09	0.13	0.07	0.08	
Motobikes	0.004	0.008	0.025	0.032	0.27	0.37	0.3	0.31	
Mofa/moped	0.004	0.008	0.025	0.032	0.27	0.38	0.36	0.37	
Trains (power units)	0	0.027	0.005	0.005	0.12	0.81	0.05	0.08	

(continued)

Flame retardants in products (g/kg) Old: produced before 1998 New: produced later than 1998	PentaBDE		OctaBDE		DecaBDE		TBBPA		
	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	Category from WEEE-Directive
Trains (coaches)	0	0.066	0.011	0.011	0.29	2.01	0.09	0.18	
Aircrafts > 15 to	0	0.066	0.011	0.011	0.29	2.01	0.14	0.23	
Average		0.03063	0.01388	0.01675	0.2288	0.8063	0.30875	0.315	
Construction material+textiles									
EPS-foam	0	0	0	0	0	0	0	0	
XPS-foam	0	0	0	0	0	16	0	0	
PUR-foam	0	6.49	0	0	0	0	0	14.7	
PE-foam	0	0	0	0	10	0	0	0	
PE-foil	0	0	0	1.7	10	20	0	0	
PP-foil	0	0	0	0	10	20	5.2	5.2	
PVC-foil	0	1.45	0	0	2.5	5	0	0	
Epoxy resins	0	0	0	0	0	0	2	2	
Polycarbonate	0	0	0	0	0	0	2	2	
Textiles and upholstery	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	

Based on Morf et al. [11]

Calculation based on Morf et al. [11].

Average concentration of flame retardants per category [g/kg] (rounded)	PentaBDE		OctaBDE		DecaBDE		TBBPA	
	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)	New (g/kg)	Old (g/kg)
1	0.000	0.001	0.054	0.054	0.478	0.478	0.329	0.327
2	0.000	0.000	0.071	0.071	0.633	0.633	1.114	1.114
3	0.000	0.000	0.935	2.094	2.555	6.314	9.449	5.950
4	0.000	0.090	0.083	0.415	1.174	1.719	4.408	4.047
8	0.000	0.000	0.051	0.051	0.702	0.702	13.118	13.118

Annex 2: Global Export and Import of WEEE per Category, Estimations for 2005, Table 3 in Zoeteman et al. [1]

WEEE category	Other nations' import	China import	India import	W. Africa import	Total mln tons
EU export	0.38	0.74	0.4	0.38	1.9
Cat1	0.19	0.39	0.2	0.19	0.97
Cat2	0.038	0.07	0.04	0.038	0.19
Cat3	0.076	0.14	0.08	0.076	0.37
Cat4	0.076	0.14	0.08	0.076	0.37
USA export		0.91	0.26	0.13	1.3
Cat1		0.55	0.16	0.08	0.78
Cat2		0.073	0.021	0.01	0.1
Cat3		0.146	0.042	0.021	0.21
Cat4		0.168	0.042	0.01	0.21
Japan export		0.38	0.18	0.06	0.62
Cat1		0.21	0.1	0.06	0.34
Cat2		0.032	0.017	0.005	0.054
Cat3		0.066	0.033	0.011	0.11
Cat4		0.066	0.033	0.011	0.11
Total import/ export	0.38	2.03	0.84	0.57	3.82
Cat1	0.19	1.15	0.46	0.3	2.1
Cat2	0.038	0.18	0.78	0.053	0.35
Cat3	0.076	0.35	0.16	0.11	0.69
Cat4	0.076	0.37	0.16	0.11	0.69

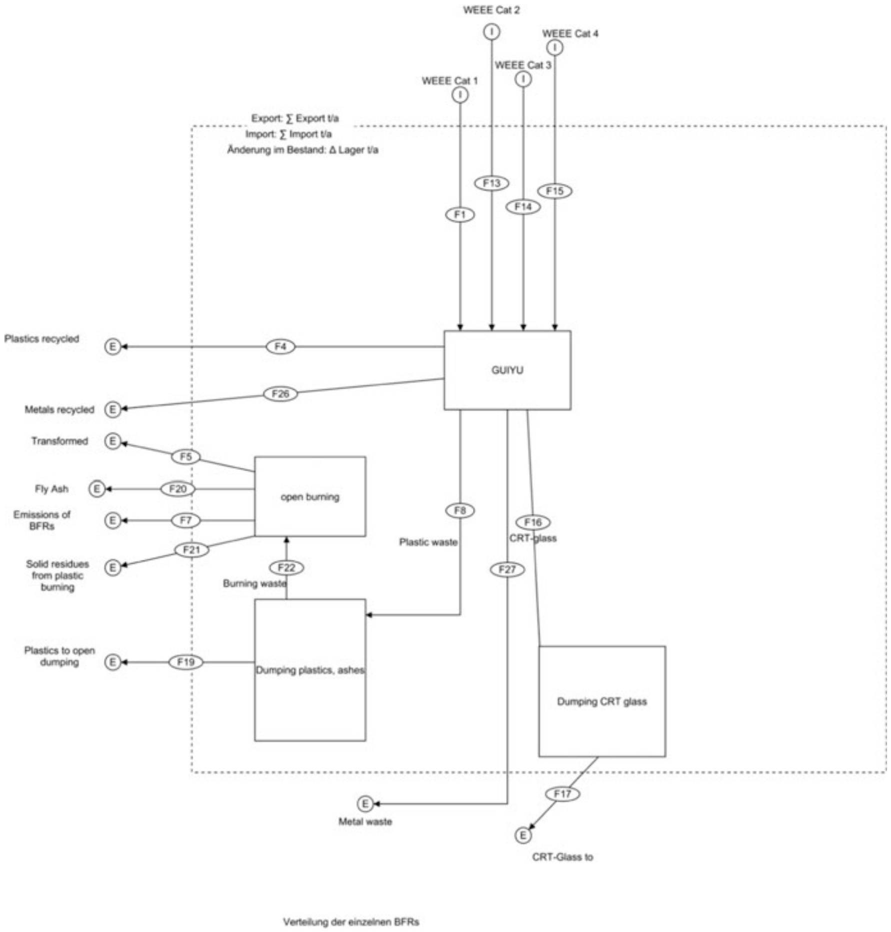
(mln tons) from Zoeteman et al. [1]

Annex 3: Overview of Transfer Coefficients (TCs) Used in the STAN-SFA for China

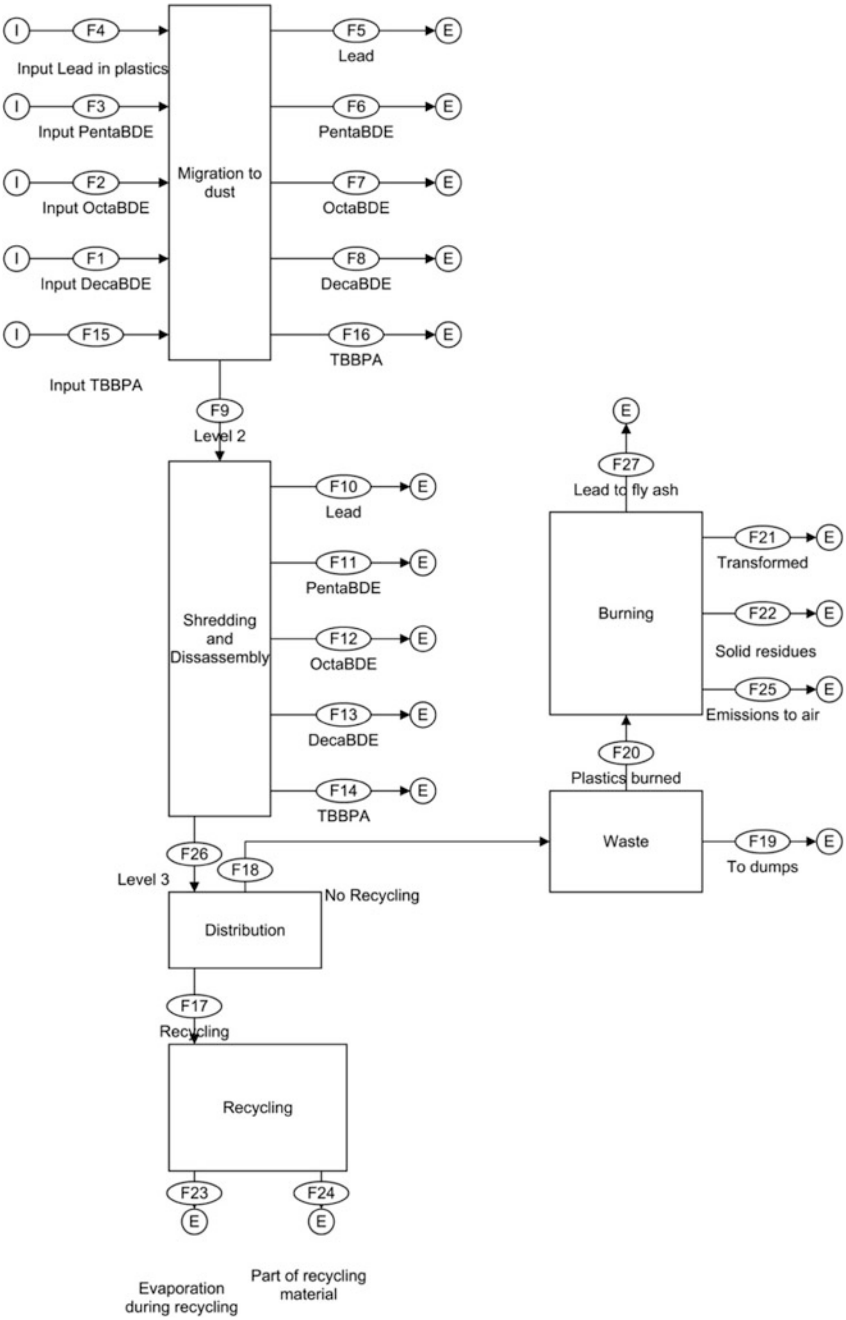
Object	Pathway	TC	Based on
PBDEs	Non-recycled plastics to open dumps	0.30625 ± 0.0625	Puckett [7]
PBDEs	Non-recycled to burning	0.6875 ± 0.0625	Puckett [7]
BFRs	Via plastics recycled and included in secondary plastic products	1	
PBDEs	To recycling pathway	0.6 ± 0.06	Puckett [7]
PBDEs	To non recycling pathway	0.4 ± 0.04	Puckett [7]
PBDEs	Loss via crushing and dismantling	4.5E-04	Sakai et al. [24]
PBDEs	Loss via migration to dust	8.9E-07	Sakai et al. [24]
PBDEs	To burning residues	5.8E-04	Morf et al. [11]
PBDEs	Transformed in burning process	0.99942	Calculated from TCs to exhaust and solid residues
Metals	Recycling rate	0.8	Sander [36]
Plastics	Recycling rate	0.6	Puckett [7]
Plastics	Plastic fraction burned	0.25–0.3	Puckett [7]
Plastics	Plastic fraction dumped	0.1–0.15	Puckett [7]
TBBPA	Share of TBBPA used in non-recyclable thermosets	0.7	Tange [37]
Pb	Emission factor to fly ash	1,180 mg/kg	Gullett et al. [27]
PBDEs	Emissions to air from burning of plastics	1.8E-06	Sakai et al. [24]
TBBPA	Emissions via exhaust	1E-06	Morf et al. [11]
TBBPA	To solid burning residues	0.023	Morf et al. [11]

Annex 4: Conceptual Diagrams for the Guiyu SFA

1. General approach concerning massflows of WEEE in Guiyu



2. Closer look on the processes of informal recycling



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Human and Environmental Impact Produced by E-Waste Releases at Guiyu Region (China)

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Abstract Over the last decades, the amount of electronic waste (e-waste) has increased rapidly in the world. It has become one of the emerging problems of the twenty-first century. About 50–80% of e-waste from industrialized countries is exported to recycling centers in developing countries such as China, India, Pakistan, and the Philippines because of the lower wages for labor and less strict environmental and safety regulations in these countries. China, however, due to its size and population not only receives enormous quantities of used devices from developed countries but also generates tremendous amounts of domestic e-waste due to its fast consumption rates of electrical and electronic (EE) products. Guiyu, a town in the Guangdong Province in the southeast of China, was identified as the largest e-waste site in the world and the second most polluted spot, due to informal recycling processes (acid extraction for metals, open burning of wires to get copper), which release chemicals to the environment, representing a threat to human health, both to "recyclers" and to nearby citizens, and the environment.

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Measured data on environmental concentrations and human health are scarce and scattered. Hence, environmental modeling was applied in order to generate an overview over the distribution of selected hazardous substances due to informal recycling in Guiyu. As all available models have a specific focus and various pros and cons, four models were chosen, which cover different geographical scales and address different environmental compartments and objectives in order to assess the potential risk of the selected chemicals to humans and the environment.

These models have been applied to different scenarios, mainly for two chemicals, decabromodiphenyl ether (DeBDE) and lead (Pb). Emissions of DeBDE and Pb that represent the input to the models are based on the SFA (Substance Flow Analysis) developed for Guiyu presented in the chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China [51]." In this chapter the results of the four models are presented and compared among them. The impact of the selected chemicals for the environment and human health at Guiyu region has been assessed on different scales, i.e., on a global, regional, and local scales.

Keywords DeBDE, E-waste, Human Health, Lead, Risk Assessment

Contents

1 Introduction

As already mentioned in the chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China," China not only generates very high amounts of domestic e-waste due to their fast consumption rates of electrical and electronic (EE) products, but also receives enormous quantities of used devices from developed countries. In particular, Guiyu was shown to be the largest e-waste site in the world and the second most polluted spot, due to informal recycling processes (e.g., acid extraction for metals, open burning of wires to get copper), which release chemicals to the environment, representing a threat to human health, both to "recyclers" and to nearby citizens [1].

Therefore, having in mind the results of the Substance Flow Analysis (SFA) for the country of China and the Guiyu region, presented in the chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China," the main objective of this chapter is to evaluate the distribution of two electronic device additives, lead (Pb) and decabrominated diphenyl ether (DeBDE), into the different environmental compartments during the e-waste recycling and their possible impact on the environment and workers'/habitants' (adults and children) health. In particular, the study is focused on the application of one dynamic fate and transport model (2 FUN TOOL) and three models which comprise steady-state multimedia fate and transport (QWASI) and exposure models (EUSES, USEtox). These models link the results from the SFA on mass fluxes to the environment (see chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China") with the distribution and subsequently accumulation of the additives in the respective region, creating a potential exposure of workers/habitants during the e-waste recycling processes and a hazard for human health.

In the present case study a high level of variability and uncertainty has been found when researching data on the e-waste additives topic. Models such as 2-FUN are very useful to treat uncertain values, and therefore they fit to the current necessities. In addition, using not only these two models but also QWASI and USEtox widens the scope of the study due to their capacity to treat different scales and to simulate the distribution of substances in different environmental compartments. With this purpose, 2-FUN and QWASI are used for local scale, EUSES for regional scale, and finally USEtox for global scale. This last model was used as a first overview giving a background view and the results can be used for both life cycle impact assessment and risk assessment. Furthermore, the fact of applying different models allows for assessment of the strengths and drawbacks of them when applied in this type of studies.

The characteristics of the applied models have been described in detail in the chapters "Environmental Fate Models [50]" and "A Revision of Current Models for Environmental and Human Health Impact and Risk Assessment for Application to Emerging Chemicals [49]" and only a brief overview is given here. Since each model has its own approach (i.e., QWASI is focused on the aquatic system), the combined results are expected to give a wider view with in-depth analyses for different aspects compared to just one model with its special characteristics.

The study is divided into two phases. In the first phase the simulation of fate and transport through different pathways that the additives take from their release during recycling processes to the environment is performed. The second phase consists of the assessment of uptake of Pb and DeBDE by local people through different exposure routes. In the first phase, the steady-state models QWASI, USETOX, and EUSES were applied, using as inputs the results obtained in the substances' fluxes calculated in the chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China," and the obtained results were analyzed. However, the EUSES model was not applied for the inorganic substance Pb as it was not considered suitable. The USEtox™ model was used to characterize the environmental risk of DeBDE and Pb for the whole China in order to provide certain background information to the case study of Guiyu. The steady-state model EUSES was implemented for the analysis of the region of Guiyu, considering the regional scale, whereas the steady-state model QWASI was implemented for the Guiyu Town, considering the local scale. In the second phase of the study, the Physiologically Based Pharmacokinetics (PBPK) Model, present in the 2 FUN Tool, was used for the Guiyu Town case study to predict the possible Pb concentration in the arterial blood of workers/habitants (adults and children), considering as inputs the results obtained with the steady-state model QWASI. Previously, additional runs using environmental monitoring data from literature as inputs were undertaken and the results were lastly compared with the results predicted when using the outputs of the QWASI model as inputs. Finally, sensitivity analysis for the dynamic 2 FUN model outputs was performed.

2 Case Study Framework

2.1 Selection of the Study Area

A literature review was made in order to identify the main Asiatic countries recycling e-waste and to select the most representative for this study. Twenty-five articles were found to be of interest and were analyzed. The country selected was China, which seems to import and recycle 80% of e-waste produced in the USA and about 10% of e-waste produced in Europe. An important recycling place in China is the Guiyu town (Fig. 1), formed by several villages located in the Chaozhou region of Guangdong Province. Guiyu is located 250 km northeast of Hong Kong and has a population of 150,000, including 100,000 migrants. At least 50% are laborers, and more than 300 companies and 3,000 individual workshops are spread over more than 20 villages of the total 28 villages engaged in e-waste recycling work (Xinhua Net 2005 [43]). This place has been defined by Greenpeace China as the second most polluted place in the world. For example, the report by the Basel Action Network and Silicon Valley Toxics Coalition published in 2002 pointed out that the lead concentration in samples taken from an e-waste recycling facility in Guiyu was

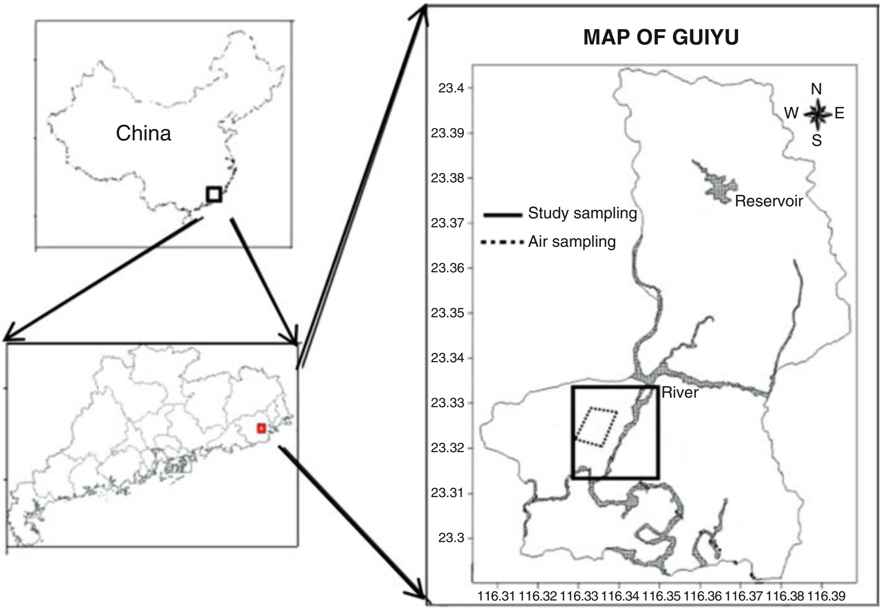

Fig. 1 Map of Guiyu Town. The rectangles show the sampling area for determination of Pb in air and water as pointed out by Leung et al. [2] and Guo et al. [3]

2,400 times higher than what is prescribed in the World Health Organization's (WHO) Drinking Water Guidelines [4]. In December 2001, the levels at the same site were found to be 190 times the threshold WHO level. Furthermore, Leung et al. [5] conducted a detailed study of the Guiyu area to quantify the pollution levels generated from e-waste, and found PBDE levels up to 1.169 mg kg^{-1} (dry weight) in soils near the recycling areas, which were 10–60 times higher than PBDE contamination reported at other locations in the world. In 2007, this study was extended [6] to surface soils and combusted residue in the Guiyu area. Leung et al. found that total PBDE concentrations were highest in the combustion residue of plastic chips and cables collected from a residential area (33–97.4 mg kg^{-1}, dry wt); in soils from an acid leaching site (2.72–4.25 mg kg^{-1}, dry wt); and at a printer roller dump site (0.59–2.89 mg kg^{-1}, dry wt). The authors also found that DeBDE was the dominant congener (35–82%) among the study sites.

2.2 Modeled Substances

The models were run for two different electronic additives, one metal – lead (Pb) and one organic compound – decabrominated diphenyl ether (DeBDE).

The importance of assessing human and environmental impacts caused by emissions of metals and brominated flame retardants (BFRs) has been growing in recent years [7, 8]. Metals are known for their high toxicity and capacity of accumulation in the environment and in the human body. Long-term exposure to even low levels of metal contamination can lead to significant impacts on human health. Impacts resulting from chronic lead exposure have been extensively studied and demonstrated; for example, the lowered cognitive and learning abilities in children exposed to Pb during infancy [9, 10]. Concerning the BFRs, which is the chemical class that DeBDE belongs to, their impact on health and their environmental characteristics are generally not well known. However, the acute toxicity of most of the BFRs has proven to be fairly low, but some BFRs have shown similar toxic effects as PCBs and PCDDs and furans [11]. The available data suggest, for example, that the lower PBDE congeners (tetra to hexa) are likely to be carcinogens, endocrine disrupters, and/or neurodevelopment toxicants [12]. DeBDE, which is the major commercial product, is presumed to be a less active congener than the lower BDEs because of its lower bioavailability and poor gastrointestinal adsorption [13].

3 Environmental and Human Health Modeling

3.1 Description of Models

A detailed description of the four models involved in this study has been provided in the Chapters "Environmental Fate Models" and "A Revision of Current Models for Environmental and Human Health Impact and Risk Assessment for Application to Emerging Chemicals." Models were run preferably for Pb and DeBDE on different geographical scales:

USEtox (Rosenbaum et al. 2008 [42]) was used to address the continental scale. It can be applied to assess either ecotoxicity or human toxicity from different pollutants. It calculates characterization factors for human toxicity and freshwater ecotoxicity, taking into account the environmental fate, exposure and effects of the substance.

For regional scale, EUSES, a European Union multimedia environmental model for risk assessment of new and existing substances was applied considering the region where the e-waste recycling sites are.

QWASI, the Quantitative Water, Air Sediment Interaction model by Mackay et al. [14] is a fugacity III model (Version 3.10, 2007) and it describes the fate of chemicals in aquatic systems, depending on direct discharge, inflow in rivers, and atmospheric deposition. Hence, this model addresses the local scale, as does the 2-FUN Tool.

The 2-FUN Tool is a new integrated software based on an environmental multimedia model (comprising several environmental compartments), PBPK models (to simulate the body burden of toxic chemicals), and associated databases.

Table 1 Characteristics summary of the applied models

	USEtox	EUSES	QWASI	2-FUN
Geographical scale addressed in this chapter	Global (results obtained for China)	Regional (results obtained for Guiyu region)	Local (results obtained for Guiyu town)	Local (results obtained for Guiyu town)
Environmental compartments addressed	Air Freshwater Coastal water Natural soil Agricultural soil	Air Freshwater Sediment Natural soil Agricultural soil Industrial soil Vegetables, Animal products Fish	Air Sediment Water	Air Water Soil Vegetables Animal products (milk and beef) Fish
Human health-related output	Human intake doses	Human and ecosystems risk	–	Arterial blood concentrations in workers/children
Substances addressed in this chapter	DeBDE Pb	DeBDE	DeBDE Pb	Pb

In Table 1 a characteristics summary of the applied models is presented. The listed parameters are selected with regard to relevance to this chapter and do not assume completeness.

In the following subsections, the inputs required and outputs obtained by these models are presented.

3.2 *Inputs to Models*

Each model requires inputs, some of them are common but there are others that differ, in the following subsections these inputs are explained in more detail.

3.2.1 Background Data

USEtox™. In order to determine the environmental risk characterization for DeBDEs and Pb in China, USEtox™ requires that different scales are defined. Since China is such a big country, the whole country has been considered as a continent. Therefore, the continental landscape data are defined by parameters describing this target country. Moreover, due to the nature of the model, two additional scales have to be defined, Global and Urban. To solve this issue, the world is defined as the global scale and Guiyu is taken into account as the urban one. However, although two other scales are defined, the final results are obtained for China. More details on the landscape data is provided in the annex section.

EUSES. The present model requires, as the USEtox model, the definition of different scales. In this study the regional scale environment is calibrated for Guiyu region (10^3 km^2), and the continental scale for the country of China. Concerning the data sources, the information for the continental scale has been extracted from GLOBACK (Globack 2.0 [15]). It seems important to highlight that the parameter sets contain the spatially differentiated parameters for the GLOBOX (Globack 2.0 [15]) model. Monte Carlo simulation was run using Crystal Ball 2000.2.2, Standard Edition software. Detailed input data, used for the present case study, are available in the Annex 1.

QWASI. Lacking more detailed knowledge on the actual Guiyu site, it was assumed that emissions take place to a river that is 5 m deep, 60 m wide, and 5 km long. Its sediment has an active layer of 0.05 m, and an organic content of 3%. The burial rate of solids equals the resuspension rate and is assumed to be 0.6 g m^{-2} day^{-1}. The flow rate of the river was estimated using the data in Italian rivers, because of the scarcity of data from Chinese rivers. Therefore, based on the previously settled Guiyu river characteristic and the slope of the Guiyu surface (data available from Google Earth) and comparing with the Italian rivers, a flow rate of 40 m^3 s^{-1} was considered. An average rain rate of 2.2 m year^{-1} is used. Further assumptions are specified in the appendix.

2 FUN Tool. For the development of the scenario, it was only considered the Guiyu area where the e-waste recycling facilities are located, near the main rivers Lianjiang and Nianyang, 10 km^2. Due to the fact that the two rivers are connected, it has been considered as one main river. This approach was previously adopted by Leung et al. [2] and Guo et al. [3] (Fig. 1). The river geometry data, necessary for the scenario development, have been derived based on Google Earth distance measurements using the ruler tool, and was used when running QWASI model as well. The depth of the river was settled at 5 m based on the data reported by Chen et al. [16], which presented the velocity profile of rivers in China. Water flow has been estimated to be 40 m^3 s^{-1}. The weather data of the region, necessary for the development of the scenario (air temperature, wind speed, precipitation), were available from online databases[1] whereas the soil temperature was calculated based on air temperature using the approach described by D. L Nofziger[2] Monitoring data for Pb concentration in water and air found in literature were scarce; therefore, maximum and minimum values were selected, based on two main climatic seasons. A sinusoidal function was applied using the maximum and minimum values in order to create the essential model inputs. The inputs for Pb concentration in air were created based on the data reported by Leung et al. [2] and Wong et al. [17] whereas

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[1] http://www.tutiempo.net/en/Climate/Shantou/05-2010/593160.htm (last online check 24/04/2012).

[2] http://soilphysics.okstate.edu/software/SoilTemperature/document.pdf.

the inputs for Pb concentration in surface water were taken from Guo et al. [3]. Additional regional data as total suspended particles in the atmosphere and global solar radiation were set based on information available in literature [18, 19]. All the input data, used for the present case study, are available in the Annex 1.

3.2.2 Substance Data

The substance data required by the models (e.g., physicochemical parameters and toxicological data) have been normally extracted from different databases depending on the substance. In the present case, the information for both substances, lead and PBDE, were taken from the full Riskcycle Database is included in the CD not only the informations for the Pb and deBDE.

3.2.3 Emissions

USEtox™. In order to make sure that the results provided by USEtox™ are referred to China, the predicted emissions into the environmental compartments have been calculated using as a basis the information on the e-waste flow and presented in the chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China." Therefore these emissions are taken as inputs. Table 2 presents a summary with the main values extracted from the aforementioned chapter and used to run the USEtox™ model.

EUSES. The annual tonnage of e-waste treated in China was assumed to be 2.5×10^6, the percentage treated in Guiyu was assumed to be 50% (with a uniform probability distribution between 40 and 60%). The emission to air is calculated as the sum of three emission sources (emission to air during burning, migration to dust and air, and loss during the process of dismantling) (see chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China"). Soil emission takes into account the concentration of DeBDE in ashes after open burning operation (see chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China"). Finally, water emission takes into account the leaching from open dumps (see chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China"). The values of the emission to air, industrial soil, and surface water are presented in Table 3. Whereas in air and soil normal distributions were considered for probabilistic analysis, a uniform probability function in surface water emission was assumed due to the scarcity of data regarding concentrations of DeBDE in leachate.

QWASI. As QWASI focuses on aquatic systems, either one or more of the following input data is needed in order to calculate the partitioning of substances between air, water, and sediment: Emissions to water, concentration in effluents, or concentration in (emitted) air. For lead, the SFA-study estimated that approximately 9,020 kg of Pb is being emitted to water each year (0.02 kg year^{-1} from

Table 2 Emission (to China) input entered to the USEtox™ model

Emission to: (t year^{-1})	Air	Soil	Water
Pb	0.179	28.6	2.437
DBDE	2.72×10^{-2}	0.736	9.38×10^{-2}

Table 3 Emission to different environmental compartments used by Usetox

Emission to: (t year^{-1})	Air	Industrial soil	Surface water
DeBDE	$8.7 \times 10^{-3} \pm 1.7 \times 10^{-3}$	$2.4 \times 10^{-1} \pm 5.7 \times 10^{-2}$	(Min 5.6×10^{-3}; max 5.6×10^{-2})

dumped plastics; 0.19 kg year^{-1} from dumped metals, 9019.68 kg year^{-1} from CRT glass), while 46 kg year^{-1}were emitted to air from burned plastic, applying emission factors from von Oers (2011) [46] and Thomas et al. (1998) [47]. For the Pb distribution, the input via atmospheric deposition is assumed to have a significant impact on the distribution of the heavy metal. The derivation of average concentration of Pb in air from the SFA results for burned plastics, however, is difficult. Instead, the sensitivity of Pb partitioning to water and sediment for different air concentrations was investigated (low: 0.44×10^{-3} mg m^{-3} [18]; high: 7.47×10^{-3} mg m^{-3}, Leung et al. [2] and rain rates 0.021–4.38 m year^{-1}), assuming the emission to water of 9,020 kg year^{-1} to remain constant.

With regard to DeBDE, the SFA suggested 186 t is deposited around Guiyu as waste every year. Due to the fact that concentrations of DeBDE in leachate are scarce, the same methodology for estimating emissions from leachate as for the Pb case could not be used. Instead, a range of emission values to water (0–30 kg year^{-1}) were used as input data. Resulting concentrations for sediment and water were then compiled from the different simulations.

3.2.4 Human Exposure

2-FUN tool and EUSES. The main pathways of human exposure considered in the scenario were inhalation of contaminated air, ingestion of fish from the river, ingestion of several crops (potato, root, leaf) considered as being cultivated in the area and irrigated with the water from the river, and the ingestion of beef and milk of habitant's cows (Fig. 2). For the 2 FUN Tool, the concentration of Pb in the grass used for cows nutrition was necessary and was calculated considering the Pb concentration in the Guiyu soil and grass uptake [20]. The drinking water was not considered as exposure pathway due to the fact that the levels of toxicity of the water bodies in the Guiyu region were high and the local authorities decide to import the drinking water from other regions, as reported in the literature [1]. The values for the ingestion rates by humans of fish and potato were taken from Xing et al. [21] and FAO [22], respectively. The values for the ingestion rates for root and

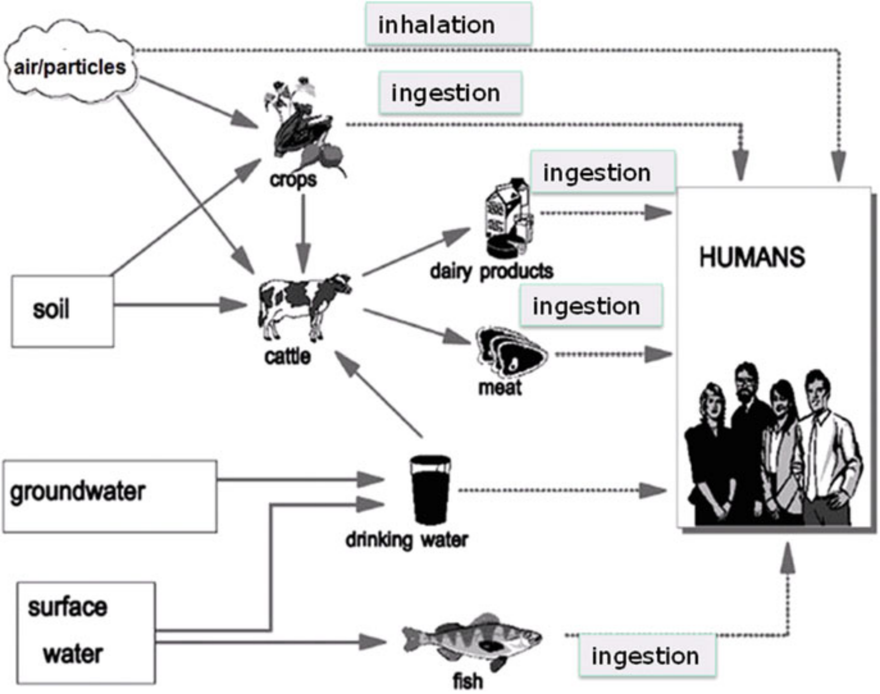

Fig. 2 Lead and PBDE pathways into humans

leaf crops, beef and milk were derived based on literature values [23] or taken from GLOBOX. Parameters from GLOBOX were obtained from FAO Statistical Databases. All the values are presented in the Annex 1.

The key input parameters used in the 2 FUN model were given in the form of probability density function (PDF) to allow the exhaustive probabilistic analysis and sensitivity analysis in terms of simulation outcomes.

As a general comment related to the input data, it is interesting to mention that all the considered models not only allow a wide modification of the input data but also provide default values when there exists a lack of input data. Furthermore, there has been a consensus to select the data used as a basis for all the four applied models from a set of different databases. These data can be consulted in the Annex 1.

3.3 Models Outputs

In this section a brief definition of the main outputs of each model is presented. Again, these outputs can be either common or different. In any case, the outputs provided by each model are detailed below.

3.3.1 Concentration in the Environmental Compartments

USEtox™. Environmental concentrations can be obtained for the theoretical case of 1 kg emitted into the urban air (default USEtox™) or considering the emissions obtained with the developed scenarios (Chap. 1) [51]. It is important to highlight that these concentration values are calculated by the model considering processes such as advection, transportation, and degradation among the different scales implemented by USEtox™.

EUSES. In EUSES 2.0 steady-state exposure concentrations at the regional, continental, and global scales are calculated for all environmental compartments (air, water, soil, sediment, and air) using the multi-media fate model SimpleBox 3.0.

QWASI. QWASI is a fugacity model and has mainly been developed for substances that have a vapor pressure which drives their distribution in the environment. However also inorganic substances such as lead have been modeled, even though they are not volatile and do not partition significantly into air. A modification of the model, requiring partition coefficients for the different interfaces and calculating the partitioning from water concentration, has been used here for lead. Even though speciation is not considered, data are compiled for resulting concentration of additives in sediment, water and air, as well as on their sensitivity regarding emission pathways. The output data are then compared with literature data and provide one basis for human health risk assessment and the environmental risk assessment.

2 FUN Tool. Depending on the complexity of the scenario, the 2FUN Tool calculates the concentration in soil, water, vegetables (leaf and root), cereals, fruits, animal products (milk and beef), and fish.

3.3.2 Human Intake Fractions

USEtox™. The USEtox™ model provides outputs such as human intake fraction of a certain substance ($\text{kg}_{\text{intake}} \cdot \text{kg}_{\text{emitted}}{}^{-1}$) for different exposure pathways.

EUSES. As in the case of USEtox model, the present model provides outputs such as human intake fraction of a certain substance for different exposure pathways. In the present case study, estimation of the human intake doses for Guiyu was calculated. These results were compared with the incidence and severity of the effects (dose–response assessment).

3.3.3 Human and Ecosystem Risk Evaluation

EUSES. The assessment of potential adverse effects induced by DeBDE exposure in both human and environmental targets has been evaluated by means of the EUSES model. Toxicological and ecotoxicological values for this contaminant were included as input values and then compared with the results of the exposure for humans and environmental receptors.

Chronic daily intake (CDI), Hazard Index (HI), and Cancer Risk (CR) for carcinogenic effects were calculated and exposures associated with $HI<1$ and $CR<1E-6$ were considered negligible.

For the ecological assessment, risk analysis was based on PEC/PNEC ratio (Hazard Quotient) where PEC is the predicted environmental concentration (resulting from EUSES results) and PNEC the predicted no-effect concentration. Exposures associated with $HQ<1$ were considered negligible.

2 FUN Tool. The 2FUN Tool provides outputs such as bioaccumulation of the substances in the target organs or concentrations in the human blood. In the present study the Pb concentration in the arterial blood of children/workers has been assessed.

4 Results

Once the main outputs of each model have been explained, the results of the application of the models to the present case study are presented in this section.

4.1 USEtox™

The outputs provided by the model can be used to perform a risk assessment if they are compared with reference limit values and literature data in order to determine whether the situation is risky or not. The values obtained by USEtox™ and used for the characterization of the risk in China are presented in the following tables. Table 4 presents the values for the concentration into the environmental compartments of the concerning additives (Pb and DeBDE).

Comparing these results with the literature values on maximum concentration permitted (MCP) of additives for different environmental compartments, the following statements can be done:

- The Pb concentration obtained in air with USEtox is much lower (8.47×10^{-11} mg m^{-3}) than the MCP values found in literature (5×10^{-2} mg m^{-3}, OSHA [24]).
- The Pb concentration obtained in water with USEtox is lower (9.24×10^{-4} mg m^{-3}) than the MCP values found in literature (50 mg m^{-3}, [25]).
- The DeBDE concentration obtained in air with USEtox is much lower (1.29×10^{-11} mg m^{-3}) than other concentration values (1.24×10^{-5} – 9.89×10^{-8} – 1.24×10^{-5} mg m^{-3}) found in literature [26].
- The DeBDE concentration obtained in water with USEtox is lower (2.20×10^{-5} mg m^{-3}) than concentration values (3.35×10^{-4} – 6.52×10^{-2} mg m^{-3}) found in literature [27].

Table 4 Additive concentration in the environmental compartments calculated by USEtox™

Concentration in: (mg m^{-3})	Air	Freshwater	Coastal water	Nat. soil	Agr. soil
Pb	8.47×10^{-11}	9.24×10^{-4}	4.54×10^{-6}	1.99×10	1.99×10
DeBDE	1.29×10^{-11}	2.20×10^{-5}	5.06×10^{-8}	1.12×10^{-3}	1.12×10^{-3}

Although China is one of the countries with more informal recycling facilities and therefore with a high release of selected additives (Pb and DeBDE) into the environment, the results obtained are lower than the expected ones. This is due to the fact that even if the amount of additives released is high, since China is such a big country, the resulting concentration is diluted. Moreover, there could be an underestimation of the treated e-waste volume in China.

On the other hand, values of intake doses obtained with USEtox for human beings are presented in Table 5.

After an intensive research on maximum intake dose permitted for human beings through different pathways, it has been observed that the most reliable was to consider the total intake since the particular intake pathway data were not clear enough. After comparing these values, the following statements can be made:

- The total intake dose for Pb obtained by USEtox (2.99×10^{-6} mg (kg day)$^{-1}$) is much lower than the intake limit (25×10^{-3} mg (kg day)$^{-1}$, JEFCA [28]).
- The total intake dose for DeBDE obtained by USEtox (1.41×10^{-9} mg (kg day)$^{-1}$) is much lower than the intake limit (0.1 mg (kg day)$^{-4}$, EPA [29]).

In this case, a similar situation to the previous one of the environmental compartments occurs. The fact that the intake dose is calculated for the whole China population supposes that these intake doses are lower than the expected again. They are calculated taking into account the emissions coming mainly from the polluted spots but considering all the Chinese population as a potential receptor. However, not all the citizens are affected by these intake doses. In addition, as mentioned before the potential underestimation of the treated e-waste volume in China could be the cause of these low values.

4.2 EUSES Model

In EUSES 2.0, steady-state exposure concentrations at regional scale are calculated for all environmental compartments using the multi-media fate model SimpleBox 3.0.

Table 6 shows the result of predicted environmental concentration in air, soil (natural, agricultural, and industrial), freshwater, and sediment for regional scale (Guiyu region).

These PECs fit well with data from Guiyu town obtained from a literature review (see Annex 1). It can be observed that the most impacted compartments are soil and sediments. The value of total regional intake doses of DeBDE for human beings is

Table 5 Intake doses for human beings provided by the USEtox™ model

Intake dose through: (mg (kg day)$^{-1}$)	Air	Drinking water	Exposed produce	Unexposed produce	Meat	Dairy products	Fish	Total
Pb	3.91×10^{-11}	4.25×10^{-8}	2.74×10^{-6}	2.33×10^{-7}	5.95×10^{-10}	1.65×10^{-9}	8.34×10^{-8}	2.99×10^{-6}
DeBDE	5.94×10^{-12}	7.02×10^{-11}	2.29×10^{-10}	3.64×10^{-11}	1.47×10^{-10}	3.27×10^{-11}	8.86×10^{-10}	1.41×10^{-9}

Table 6 Predicted environmental concentration (PEC) of DeBDE (mean ± standard deviation)

	Air (mg m^{-3})	Nat. soil (mg kg^{-1})	Agr. soil (mg kg^{-1})	Ind. soil (mg kg^{-1})	Fresh waterwater (mg L^{-1})	Sediment (mg kg^{-1})
PEC regional	1.4×10^{-8} $\pm 2.8 \times 10^{-9}$	1.9×10^{-2} $\pm 4.0 \times 10^{-3}$	1.6×10^{-2} $\pm 3.2 \times 10^{-3}$	1.3×10^{1} ± 3.4	4.9×10^{-6} $\pm 1.2 \times 10^{-6}$	7.6×10^{-3} $\pm 1.8 \times 10^{-3}$

29.7 mg $(\text{kg day})^{-1}$ with a range from 7.8 to 72.5 mg $(\text{kg day})^{-1}$. The main regional pathway of exposure with more than 99.9% of the total contribution is daily intake of root crop due to the high levels in soils. Other regional daily intake pathways are drinking water, fish intake, meat intake, inhalation intake with values 8.0×10^{-8}, 1.2×10^{-6}, 1.1×10^{-6}, and 4.2×10^{-9} mg $(\text{kg day})^{-1}$, respectively.

In order to assess the risk for the population living in Guiyu, the daily intake was compared with the oral reference value for DeBDE. According to EPA (US EPA [30]), the DeBDE daily oral reference and oral slope factor are 7.0E-03 mg $(\text{kg day})^{-1}$ and 7.0×10^{-4} mg^{-1} kg day. Inhalatory reference concentration and inhalatory unit risk have not been established.

Results of the daily intake (oral exposure) in Guiyu are much higher than the oral reference value. Therefore, the hazard quotient is higher than one. That means that there is a risk of developing other effects than carcinogenic ones due to the dietary exposure. The carcinogenic risk resulted to be 8.9×10^{-3} (8.9 cancer cases in 1,000 inhabitants) higher than the acceptable value. On the other hand, the risk for the soil ecosystem (worm-eating predators) is high due to the elevated concentrations found in soil.

4.3 QWASI

On the basis of the above-mentioned assumptions, atmospheric concentrations, used as inflows to the model, in the range of 9.37×10^{-9} to 2×10^{-6} mg m^{-3} (data not shown) did not have a significant influence on the partitioning of DeBDE. A strong impact could be assigned to the direct discharge and to chemical concentration in inflow waters. There is, however, no information available on concentration of DeBDE in emitted waters. Consequently, different direct discharges from the e-waste sites were used as emission data and the subsequent concentrations for sediment and water concentrations in the river were calculated (Fig. 3).

Applying emission data in the range of 1–30 kg year^{-1}, sediment concentrations ranged from 1.4×10^{-2} to 4.32×10^{-1} mg kg^{-1}, water concentrations were calculated to be in the range 0.7×10^{-6} and 2.37×10^{-5} mg L^{-1}.

Comparing the result from the EUSES model for the concentration of DeBDE in water (4.43×10^{-6} mg L^{-1}), this would refer to approximately 6 kg DeBDE·year^{-1} emitted to water and a concentration in sediment of below 0.1 mg kg^{-1}. With regard to sediment concentration, this is in the same range of magnitude as data published by Luo et al. 2007 [48], who measured DeBDE concentrations at 3 different sites in Guiyu of between 1.4×10^{-2} and 6.2×10^{-2} mg kg^{-1}.

Comparing the results on direct discharges with the results of the SFA for Guiyu of 186 t of DeBDE accumulating over 1 year in a land disposal, the emission of 6 kg would account for 3×10^{-3}% leached material within one year, which is in the range of 3×10^{-3} to 3×10^{-2}% that have been calculated by Choi et al. (2009) [41] for leaching of DeBDE in contact with dissolved humic substances from TV housing plastics.

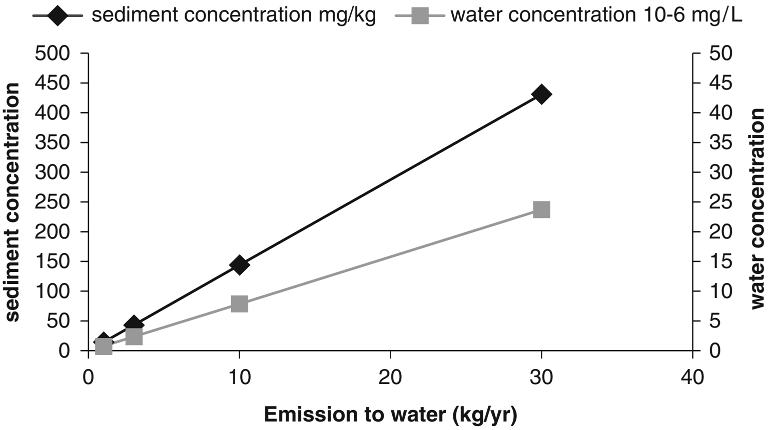

Fig. 3 Relationship between direct discharges of DeBDE to water in kg/year from a hypothetical e-waste side and the partitioning of the substance between sediment and water phase

Table 7 Pb concentrations in water (upper table) and sediment (lower table) as calculated by QWASI

Pb WATER concentration (mg L^{-1})				
		Rain rate in m $year^{-1}$		
		Low 0.021	Average 2.2	High 4.38
Concentration in air	Low (0.44×10^{-3} mg m^{-3})	7×10^{-3}	2.5×10^{-2}	4.4×10^{-2}
	High (7.44×10^{-3} mg m^{-3})	9×10^{-3}	3.2×10^{-1}	6.3×10^{-1}

Pb SEDIMENT concentration (mg kg^{-1})				
		Rain rate in m $year^{-1}$		
		Low 0.021	Average 2.2	High 4.38
Concentration in air	Low (0.44×10^{-3} mg m^{-3})	0.4×10^{-3}	1.6×10^{-3}	2.7×10^{-3}
	High (7.44×10^{-3} mg m^{-3})	0.5×10^{-3}	1.9×10^{-2}	3.8×10^{-2}

4.3.1 Lead

Table 7 lists Pb concentrations in water (upper table) and sediment (lower table) for different air concentrations and rain rates, using a constant emission of lead to water of 9,019 kg/year. Resulting sediment concentrations vary between 0.4×10^3 mg kg^{-1} (low rain rate, low air concentration) and 38×10^3 mg kg^{-1}

(high rain rate, high air concentration). Water concentrations under the same conditions range from 7×10^{-3} to 63×10^{-2} mg L^{-1}.

According to Guo et al. [3], lead concentrations of 6×10^{-3} to 6.1×10^{-2} mg L^{-1} have been measured in water in Guiyu. This would be in the range of our results assuming a low concentration in air and low to high rain rates, or a high concentration in air and low rain rate. The combination of high air concentration and high rain rate, resulting in as much as 3.8×10^{-2} mg kg^{-1} in sediment, is highly unlikely, as increased precipitation would quickly reduce the lead content in air.

4.4 2 FUN

Figure 4 presents Pb concentrations in the arterial blood over the simulation period, with values at mean, 5th and 95th percentiles. The input data for Pb concentration in air and water for the region, used for the simulations, were created based on monitoring data available in literature. Simulations were performed for 10 years, setting the initial age of population at 2 years (Fig. 4a), 10 years (Fig. 4b), and 20 years (Fig. 4c) respectively. This distribution comes from the fact that many articles report that young children spent a long time in e-waste recycling sites, sometimes to help their parents. It can be assumed that the values at 95th percentile represent "pessimistic" scenarios in the context of health risk assessment. It was found that the Pb concentration in blood is much higher in very young children than in more grown-up children whereas the general trend is to find the lowest concentration in adults' blood. Looking at the values at mean and 95th percentile for all the cases considered, the values of Pb in the arterial blood were higher than the limit established by the Centre of Disease, Control and Prevention, 10 μg dL^{-1} [31]. For the very young children in the first six simulated years even the values at 5% were higher than the limit of 10 μg dL^{-1}. These results are in agreement with the monitoring results reported by Huo et al. [32], who observed that the levels of Pb in blood in 165 children of Guiyu ranged from 4.40 to 32.67 μg dL^{-1} with a mean of 15.3 μg dL^{-1}.

Furthermore, the higher concentration of Pb was observed in fish and leaf when comparing with the beef, milk and the other considered crops (Fig. 5). By multiplying the Pb concentrations in each compartment by the respective ingestion rates, the intake of Pb was obtained. The results showed that the Pb exposed to humans is mostly influenced by fish ingestion followed by leaf ingestion (Fig. 6).

Concerning the results, using the concentration of Pb in the river water calculated with the QWASI model as inputs, significant differences on the concentrations of Pb in the arterial blood of children/adults were not observed when these results were compared with the obtained using the literature values for lead concentration in the river water as inputs (data not showed). This was somehow expected considering that the results of QWASI model were in the range as the

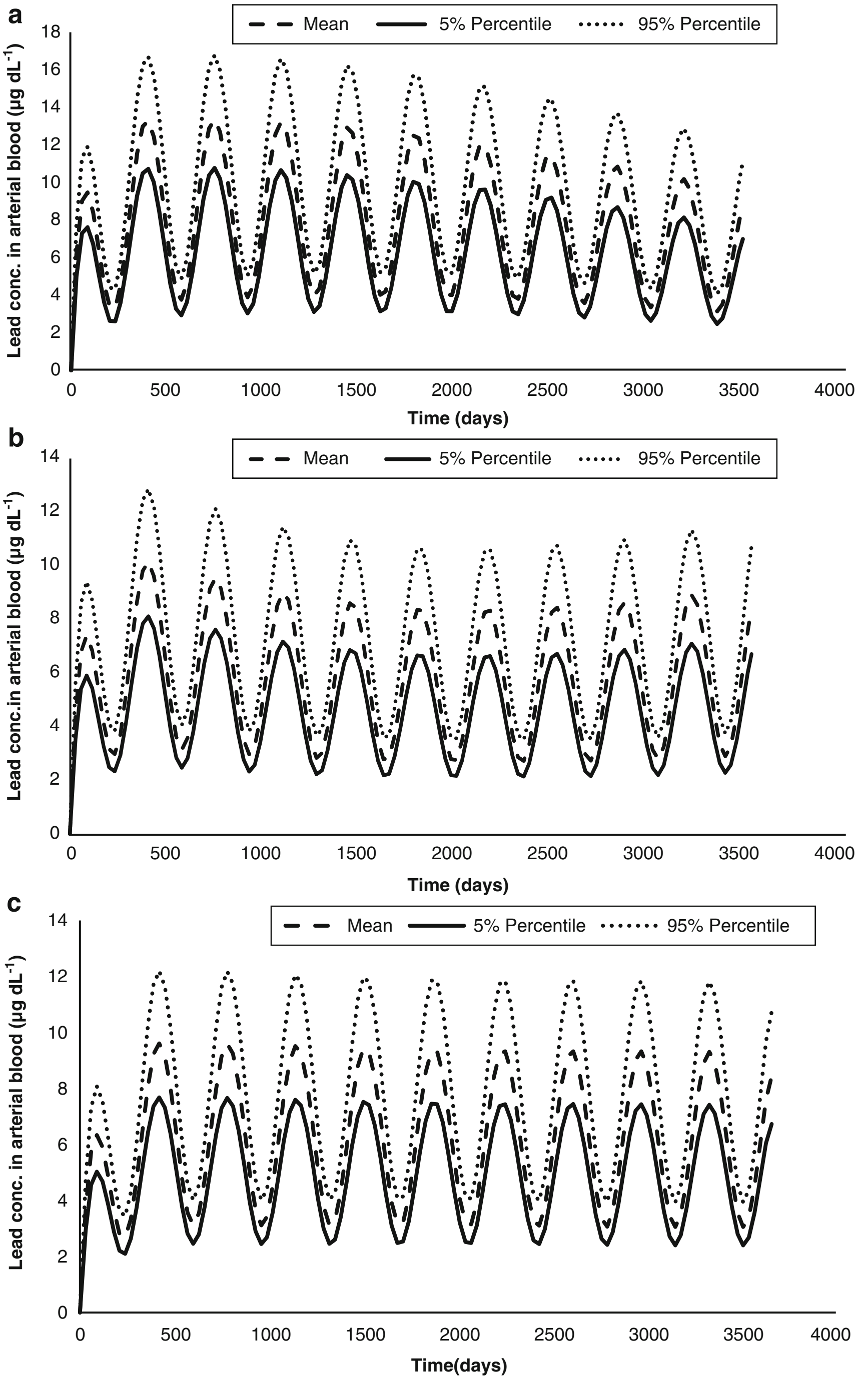

Fig. 4 Lead concentrations in arterial blood (µg dL^{-1}) over 10 years simulation; (**a**) initial age 2 years, (**b**) initial age 10 years, (**c**) initial age 20 years

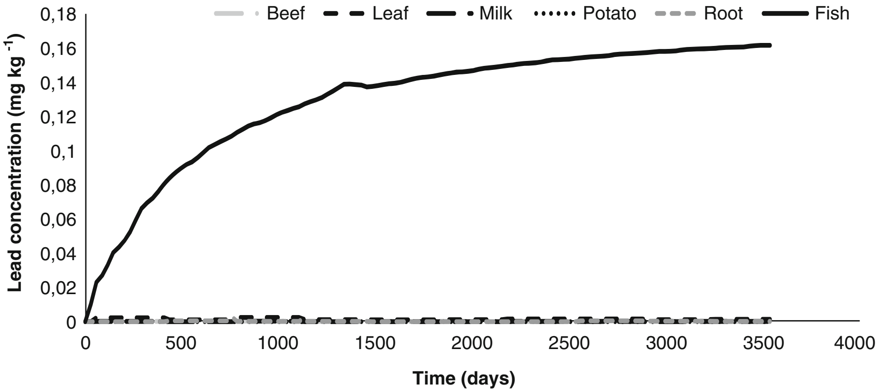

Fig. 5 Lead concentration in the considered crops, fish, milk, and beef (mg kg^{-1})

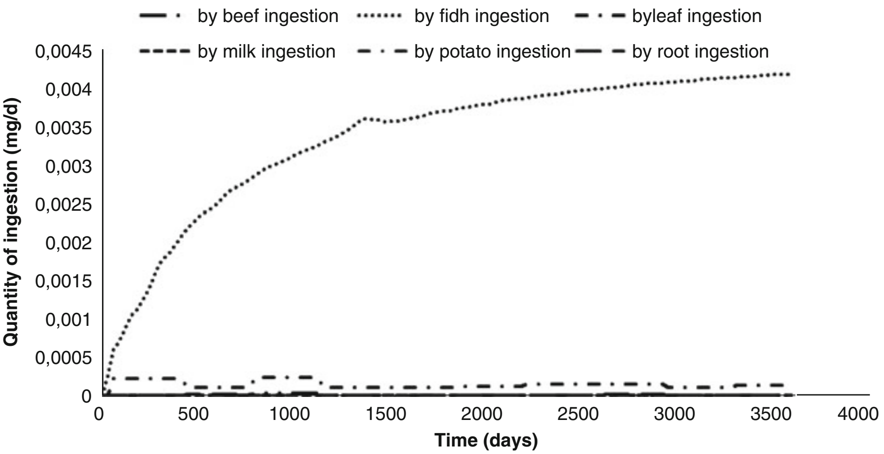

Fig. 6 Time-dependent quantity of Pb entering humans through the ingestions of different food and drink items (mg day^{-1})

measurements reported in literature. Furthermore, significant differences were not observed for lead concentrations in leaf, root, fish, beef, milk, and potato either.

4.4.1 Global Sensitivity Analysis

A global sensitivity analysis was performed for the lead concentration in the arterial blood model (Fig. 7) over the simulation period for each parameter. Parameters considered for the sensitivity analysis are listed in Table 8 (Annex 1). The magnitude of sensitivity is shown by relative sensitivity index. It was observed that the most influential parameter is the porosity of the sediment of the river (phi_sed)

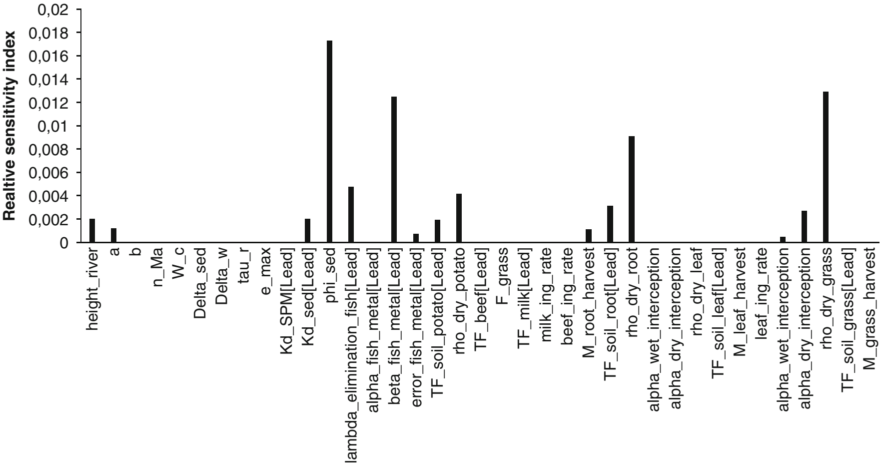

Fig. 7 A global sensitivity analysis for lead concentration in arterial blood

followed by the density of the dry grass, the second regression coefficient of the relationship expressed by log(fish_BCF) = $\alpha + \beta \times$ log(C_dis_water) and the density of the dry root.

5 Discussion

After presenting the results obtained by each model, an integration of all them is done in this section going from the general background information (China) to the most specific case scenario (Guiyu).

The results obtained with USEtox™ for China show that the situation is not risky concerning the hazards caused by the selected additives in this country. However, this is due to the fact that all the areas of land and fresh water in China have been taken into account whereas there is only a fraction of this area that is really affected, as well as that not all the population intakes the obtained fractions.

Obviously, when focusing on the source of pollution, for example the Guiyu Region, these results are higher since, according to the present research (Zoeteman et al. 2010 [44]; Lee 2002 [45]), this region deals with practically half of the China e-waste.

It is interesting to mention that USEtox™ is mainly a tool for LCIA studies where characterization factors are obtained for a wide list of substances. However, the model also provides intermediate output parameters (e.g., intake doses, concentrations in environmental compartments, substance exposure) that can be used for risk assessment studies. This was the case in the present study comparing the values from USEtox with reference limit values.

Moreover, this model counts with a substance database for both organic and inorganic substances as well as default values when a parameter is unknown. In addition, the model can conduct calculations for different substances at the same time. However, the model is more developed for the organic compounds than for the inorganic ones.

The results obtained with the EUSES model for the region of Guiyu are in some cases concerning. In particular, it was observed that the daily intake (oral exposure) is much higher than the oral reference value. On the other hand, the carcinogenic risk (8.9 cancer cases in 1,000 inhabitants) is higher than the acceptable value. Because the higher dietary levels come from root vegetables, especially from those that grow up in contaminated soil, population should be informed about this potential risk. Regarding environmental risk, there is a high risk situation for soil ecosystem and especially in the case of worm-eating predators (1.2×10^2) (PEC/PNEC ratio).

EUSES is a useful model for chemicals outside the domain of the persistent, non-dissociating substances of intermediate lipophilicity. Due to the high complexity of the model, it is lacking in transparency on the other hand, the performance of the model is characterized as a good compromise between complexity and practicability. In order to adapt the model to different assumptions or assess the uncertainty, it is necessary to use the EU TGD2003 Spreadsheet version 1.24 of April 2008. This spreadsheet aims to represent the algorithms described in the 2003-version of the EU Technical Guidance Document, as implemented in EUSES 2.0.3.

Under the applied QWASI model assumptions, the QWASI results are in the range of measured data reported in literature and thus support that the strongest impact to sediment and water concentrations of DeBDE are from direct emission to water as opposed to atmospheric concentrations. This result points out the high importance of DeBDE-leaching from deposited waste material and a lower meaning of the fraction that is transferred to the atmosphere.

Pb concentration in the environment, on the other hand, is strongly influenced by air concentration and rain rate, in addition to direct emissions to water. For this metal the exposure pathway via burning gains a high importance among the different informal recycling processes.

While QWASI is an easy to use multimedia fate modeling tool, it has been originally designed as a fugacity model. Even though an adaptation to ionic substances exists and it has been applied to lead before, it needs to be recognized that it does not take speciation of metals into account. This adds to the overall uncertainty of results.

If the results of the EUSES model show a certain concern for human risk and ecosystems due to DeBDE released during the e-waste recycling operations in the region of Guiyu, the results of the 2 FUN Tool show a real health risk for workers/habitants of the Guiyu town due to the release of Pb. A higher risk was observed for very young children, with values of Pb in the arterial blood at 5%, mean and 95% higher than 10 $\mu g\ dL^{-1}$. The U.S. Centre for Disease Control and Prevention (CDC) defined elevated blood lead levels as those $\geq 10\ \mu g\ dL^{-1}$ in children ≤ 6 years of age [31]. Nevertheless, studies have increasingly shown that low blood Pb concentrations, even <10 μg/dL, were inversely associated with children's IQ (Intelligent coefficient) scores and academic skills [9, 33, 34]. Therefore, no safety margin at existing exposures was identified [35].

Average range between Pb concentrations at 5th and 95th percentiles over the 10-year simulation period, for very young children (i.e., 2 years), children (i.e., 10 years), and adults (i.e., 20 years) was 1.3 orders of magnitude. It indicates that the parametric uncertainties and variability contained in input parameter contribute significantly to propagation of such gaps in outputs.

Regarding the global sensitivity analysis, the results indicate that the variation of the model output is highly sensitive to the variations of parameters used in fish and root compartments. The higher concentration of Pb in fish than in potato, leaf, root, milk, and beef (Fig. 6) reflects that the variation of the model output is more sensitive to variations of fish parameters than of potato, leaf, root, milk, and beef parameters.

However, as a general observation, this study demonstrated the feasibility of the integrated modeling approach to couple an environmental multimedia and a PBPK models, considering multi-exposure pathways, and thus the potential applicability of the 2-FUN tool for health risk assessment. The global sensitivity analysis effectively discovered which input parameters and exposure pathways were the key drivers of Pb concentrations in the arterial blood of adults and children. This information allows us to focus on predominant input parameters and exposure pathways, and then to improve more efficiently the performance of the modeling tool for the risk assessment.

6 Conclusions

During the development of this study, the uncertainty has been present in many occasions, especially when gathering data concerning the e-waste amounts, the content of additives in the e-waste inflow, and the percentages of additives going to the different environmental compartments. This has implied that some assumptions have to be made. However, due to the capability of the selected models of treating uncertain values, the results obtained after the models calculations were quite acceptable. Through the comparison of the results of each model with values extracted from literature, in most of the cases it was observed that the predicted values were at the same order of magnitude as the monitored values. This fact reinforces the suitability of the selected models and the validity of the obtained results.

Concerning the risk characterization of the selected additives, a clear increase of the risk for the environment and human health when reducing the scale of the study has been observed. Therefore when analyzing Guiyu city, the most worrying results are obtained. This statement could seem obvious but there exists a strong belief that the whole country of China is suffering the hazard of the e-waste pollution, even if when running the USEtoxTM, to assess the environmental distribution of additives for the country of China, low concentrations of e-waste additives were found.

Nevertheless, at a regional scale, the results provided by EUSES model were higher and quite similar to the monitoring data found in literature for the region of Guiyu. Therefore, since the monitored values from literature are pointed out to be higher than the reference limit values, it can be stated that, as expected, the region of Guiyu present a high level of risk for both environment and human health. When analyzing the local scale results, a similar situation was observed looking at the data obtained by the QWASI model for the aquatic environment; values on the same range that the monitored values extracted from literature were observed coming up with similar conclusions than the ones obtained for the regional scale. Finally, with the PBPK model of the 2-FUN tool generated values for lead concentration in the arterial blood at a higher range than the limit of concern established by the CDP, above all for the very young children. These results were, as in the previous cases, in agreement with the monitoring data reported in the literature. With all this, it seems clear to state that the potential risk caused by the e-waste additives due to the informal recycling in Guiyu is significant.

As a final objective of this study, an assessment of the strengths and weaknesses of the selected models for this type of studies was undertaken. Despite the fact that the USEtoxTM model is actually a tool for LCIA assessment, a risk characterization has been performed with this model in order to provide some background information to the present case study. The EUSES model has presented results quite similar to the monitoring data of the literature; therefore, it can be stated that the model can be considered a suitable tool for this type of studies. As aforementioned, application of the QWASI model resulted in an estimation of the most important pathways to water and sediment, which were the emissions to water and, in the case of lead, also to air. As this model is focusing on local scale and the distribution of substances between the compartments, air, water, and sediment, its results could be more accurate, depending on the database, but are also limited to the aquatic scenario. Finally, the 2-FUN model provided data (lead level in blood) useful to perform a detailed risk assessment, by linking the environmental concentrations to the human body. Bearing in mind the foresaid advantages and drawbacks, it is strongly believed that the combination of all the strengths of the selected models has provided an interesting picture of the case study situation.

Annex

USEtox Data Input

Euses Input Parameters

Continental and Regional Parameters

In Table 9, the parameters of the continental area and regional area are shown.

Table 8 Landscape data required by USEtox^{TM}

Name	Units	Value	Reference
Continental scale			
Area land	km^2	9.596.960	GLOBOX
Area sea	km^2	3.500.000	GLOBOX
Areafrac fresh water	[−]	0.02	GLOBOX
Areafrac nat soil	[−]	0.37	GLOBOX
Areafrac agr soil	[−]	0.52	GLOBOX
Areafrac other soil	km	0.09	GLOBOX
Temp	°C	11.8	GLOBOX
Wind speed	$m\ s^{-1}$	2.5	GLOBOX
Rain rate	$mm\ year^{-1}$	627	GLOBOX
Depth fresh water	m	5.9	GLOBOX
RiverFlow reg-cont	[−]	0	GLOBOX
Fraction run off	[−]	0.25	Default USEtox^{TM}
Fraction infiltration	[−]	0.25	Default USEtox^{TM}
Soil erosion	$mm\ year^{-1}$	0.03	Default USEtox^{TM}
Global scale			
Area land	km^2	141.000.000	Default USEtox^{TM}
Area sea	km^2	329.000.000	Default USEtox^{TM}
Areafrac fresh water	[−]	0.03	Default USEtox^{TM}
Areafrac nat soil	[−]	0.485	Default USEtox^{TM}
Areafrac agr soil	[−]	0.485	Default USEtox^{TM}
Areafrac other soil	[−]	1×10^{-20}	Default USEtox^{TM}
Temp	oC	12	Default USEtox^{TM}
Wind speed	$m.s^{-1}$	3	Default USEtox^{TM}
Rain rate	$mm\ year^{-1}$	700	Default USEtox^{TM}
Depth fresh water	m	2.5	Default USEtox^{TM}
RiverFlow reg-cont	[−]	0	Default USEtox^{TM}
Fraction run off	[−]	0.25	Default USEtox^{TM}
Fraction infiltration	[−]	0.25	Default USEtox^{TM}
Soil erosion	$mm\ year^{-1}$	0.03	Default USEtox^{TM}
Urban scale			
Area land	km^2	100	GLOBOX
Areafrac nat soil	[−]	0.667	Default USEtox^{TM}
Areafrac other soil	[−]	0.333	Default USEtox^{TM}
Human population			
Human pop world	[−]	6.852.252.823	Default USEtox^{TM}
Human pop continent	[−]	1.337.798.957	GLOBOX
Human pop urban	[−]	150.000	GLOBOX
Exposure			
Human breathing rate (world + cont + urban)	m^3/(person day)	18	GLOBOX
Water ingestion (world + cont)	l/(person day)	1.8	GLOBOX

(continued)

Table 8 (continued)

Name	Units	Value	Reference
Production-based intake rates			
Exposed produce world	kg/(day capita)	0.753	Default USEtox^{TM}
Exposed produce continent	kg/(day capita)	0.753	Default USEtox^{TM}
Unexposed produce world	kg/(day capita)	0.235	Default USEtox^{TM}
Unexposed produce continent	kg/(day capita)	0.235	Default USEtox^{TM}
Meat world	kg/(day capita)	0.084	Default USEtox^{TM}
Meat continent	kg/(day capita)	0.088	GLOBOX
Dairy products world	kg/(day capita)	0.250	Default USEtox^{TM}
Dairy products continent	kg/(day capita)	0.018	GLOBOX
Fish freshwater world	kg/(day capita)	0.013	Default USEtox^{TM}
Fish freshwater Continent	kg/(day capita)	0.009	GLOBOX
Fish coastal marine water world	kg/(day capita)	0.036	Default USEtox^{TM}
Fish coastal marine water continent	kg/(day capita)	0.018	GLOBOX

Table 9 Continental parameters

Continental	Value	Units	Reference
Total area China + Seas (continent + region, incl. sea)	9.60×10^{6}	km^2	GLOBOX
Area (land + rivers) of continental system (excl. regional system)	6.37×10^{6}	km^2	
Area fraction fresh water in continental system (excl. sea)	1.35×10^{-2}	–	GLOBOX
Area fraction natural soil in continental system (excl. sea)	3.68×10^{-1}	–	GLOBOX
Area fraction agricultural soil in continental system (excl. sea)	5.15×10^{-1}	–	GLOBOX
Area fraction urban/industrial soil in continental system (excl. sea)	8.90×10^{-2}	–	GLOBOX
Area fraction fresh water in continental system (total)	8.96×10^{-3}	–	GLOBOX
Area fraction sea water in continental system (total)	3.36×10^{-1}	–	GLOBOX
Area fraction natural soil in continental system (total)	2.44×10^{-1}	–	GLOBOX
Area fraction agricultural soil in continental system (total)	3.42×10^{-1}	–	GLOBOX
Area fraction urban/industrial soil in continental system (total)	5.91×10^{-2}	–	GLOBOX
Moderate	**Value**	**Units**	**Reference**
Area of total moderate system (incl. continent, region)	8.50×10^{13}	m^2	Default
Area of moderate system (excl. continent, region)	7.80×10^{13}	m^2	Default
Area fraction sea water moderate system	5.00×10^{-1}	–	Default
Arctic	**Value**	**Units**	**Reference**
Area arctic system	4.25×10^{13}	m^2	Default
Area fraction sea water arctic system	6.00×10^{-1}	–	Default
Tropic	–	–	–
Area tropical system	1.28×10^{14}	m^2	Default
Area fraction sea water tropical system	7.00×10^{-1}	–	Default

Meteorological Data

Population Parameters

Population parameters were shown in Table 11. Guiyu was considered Coastal Region to obtain the Daily intake from Li et al. [23]. If no data of distribution was found, normal distribution with standard deviation equal to the 10% of the mean was assumed (Table 10).

Table 10 Meteorological data

Temperature	Value	Units	Reference
Temperature regional scale	2.96×10^2	K	Wong et al. [36]
Temperature continental scale	2.85×10^2	K	GLOBOX
Temperature moderate zone	2.85×10^2	K	Default
Temperature arctic zone	2.63×10^2	K	Default
Temperature tropical zone	2.98×10^2	K	Default
Air	Value	Units	Reference
General			
Atmospheric mixing height	1.00×10^3	m	Default
Wind speed regional	2.16×10^5	m day^{-1}	Default
Wind speed continental	2.33×10^5	m day^{-1}	GLOBOX
Rain			
Average precipitation regional	1.72×10^3	mm year^{-1}	Wong et al. [36]
Average precipitation continental	6.27×10^2	mm year^{-1}	GLOBOX
Average precipitation moderate	7.00×10^2	mm year^{-1}	Default
Average precipitation arctic	2.50×10^2	mm year^{-1}	Default
Average precipitation tropical	1.30×10^3	mm year^{-1}	Default

Table 11 Population parameters

Human parameters	Value	Probability density function	Units	Reference
Daily intake of drinking water	1.43	N(1.43; 0.64)	L day^{-1}	Wu et al. [37]
Daily intake of fish	4.23×10^{-2}	N(0.04228;0.00423)	kg day^{-1}	Li et al. [23]
Daily intake of leaf crops	7.47×10^{-1}	N(0.747;0.075)	kg day^{-1}	GLOBOX
Daily intake of root crops	1.16×10^{-1}	N(0.116;0.012)	kg day^{-1}	GLOBOX
Daily intake of meat	1.06×10^{-1}	N(0.1055;0.0106)	kg day^{-1}	Li et al. [23]
Daily intake of dairy products	1.77×10^{-2}	N(0.0177; 0.0018)	kg day^{-1}	GLOBOX
Inhalation rate humans (consumers, environment)	0.75	N(0.75;0.08)	$m^3\ h^{-1}$	GLOBOX
Body weight of the human considered	57.3	N(5.,3; 5.59)	kg	Wu et al. [37]
Inhabitants				
Number of inhabitants of region	299000	–	–	Wu et al. [38]
Number of inhabitants of China	1.34×10^9	–	–	NBSC [39]

Emissions

In Table 12, the EUSES inputs regarding emissions parameters are shown.

Table 12 Emission parameters in EU TGD2003 Spreadsheet

Tonnages	Value	Units	Reference
Tonnage in China	2.50×10^6	Tonnes year^{-1}	Assumption
Fraction of China production volume in Region	0.50 U (0.40;0.60)	–	Assumption
Release fractions	**Value**	**Units**	**Reference**
Fraction of tonnage released to air	8.36×10^{-9} N(8.36×10^{-9}; 1.78×10^{-9})	–	Chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China"
Fraction of tonnage released to surface water	3.13×10^{-8} U(5.69×10^{-9}; 5.69×10^{-8})	–	
Fraction of tonnage released to industrial soil	2.42×10^{-7} N(2.42×10^{-7}; 5.79×10^{-8})	–	
Emission days	**Value**	**Units**	**Reference**
Fraction of the main local source	1.0	–	
Number of emission days per year	365	day year^{-1}	Assumption
Local release rates	**Value**	**Units**	**Reference**
Local emission to air during episode	2.02×10^{-3} N(0.00202;0.00032)	kg day^{-1}	Chapter "Tracking Global Flows of E-Waste Additives by Using Substance Flow Analysis, With a Case Study in China"
Local emission to wastewater during episode	U(0.0153;0.153)	kg day^{-1}	

QWASI Data Input/Creation

Climate data concerning the average rain rate were obtained from Hong et al. [40]. Table 13 shows the input parameters for the QWASI approach

Table 13 The parameter used as input data for the QWASI approach

Parameter	Unit	Data
River depth	m	5.00
Active layer of sediment	m	0.05
Organic content of sediment	%	3
Water flow in waterbody	$m^3\ s^{-1}$	40
Average rainrate	$m\ y^{-1}$	2.2
Lead emission to water	$kg\ y^{-1}$	9020 (0.02 from dumped plastics, 0.19 from dumped metals, 9019.68 from CRT glass
Air concentration lead	$mg\ m^{-3}$	Low: 0.44×10^{-3} High 7.74×10^{-3}
DeBDE deposited around Guiyu	$t\ y^{-1}$	0–30
Bulk desity of sediment	$kg\ m^{-3}$	1.23×10^3
Area of local system	km^2	52
Water surface total	km^2	1.00
Water volume	m^3	5.00×10^6
Mixed height air compartment	m	1.00×10^4
Density of solids in water	$kg\ m^{-3}$	1.00×10^3
Total suspended particles in atmosphere	$g\ m^{-3}$	1.24×10^2
Deposition velocity of aerosol particles	$m\ s^{-1}$	1.00×10^{-3}
Rainfall scavenging ratio for particles	$m^3\ m^{-3}$	1.00×10^2
Average monthly precipitation	$m\ day^{-1}$	3.45×10^{-5} to 1.2×10^{-2}
PARTIAL MASS TRANSFER COEFFICIENT air side of air/soil interface	$m\ s^{-1}$	1.05×10^{-3}
PARTIAL MASS TRANSFER COEFFICIENT water side of water/sediment interface	$m\ s^{-1}$	2.78×10^{-6}
PARTIAL MASS TRANSFER COEFFICIENT sediment side of water/sedidment interface	$m\ s^{-1}$	2.78×10^{-6}
CONCENTRATION suspended matter in fresh water	$mg\ L^{-1}$	1.50×10^1
Mass FRACTION organic carbon in suspended matter	(–)	1.00×10^{-1}
Mass Fraction of organic carbon in resuspended matter	(–)	5.00×10^{-2}
Mass FRACTION organic carbon freshwater sediment	(–)	5.00×10^{-2}

FUN Data Input/Creation

Air temperature, precipitation, and wind speed data were considered for the Shantou Province, representing the climatic conditions of the year 2010 (Figs. 8, 9, and 10) and were obtained from: http://www.tutiempo.net/en/Climate/Shantou/

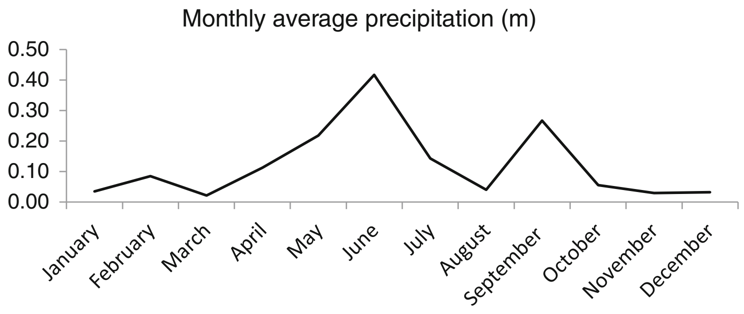

Fig. 8 Monthly average precipitation

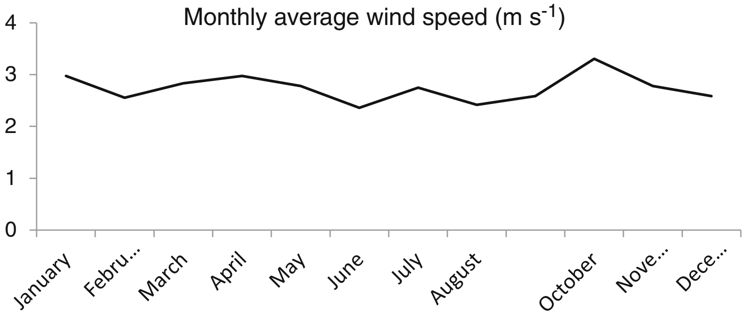

Fig. 9 Monthly average wind speed

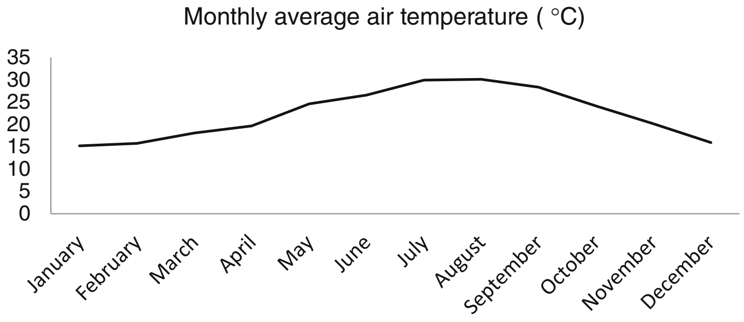

Fig. 10 Monthly average air temperature

05-2010/593160.htm. Finally the data were created for a 10-year period repeating for 10 times the 2010 data.

The soil temperature was created based on air temperature and the data are presented in the Fig. 11.

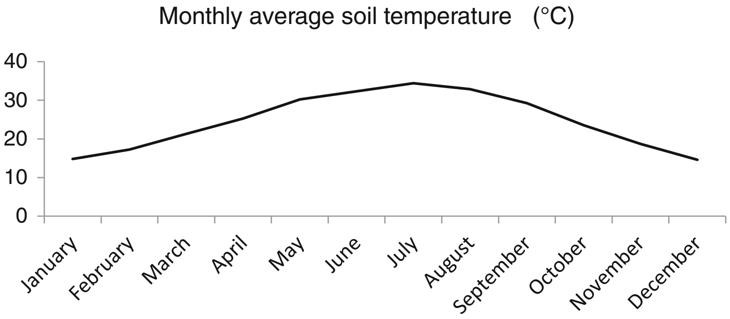

Fig. 11 Monthly average soil temperature

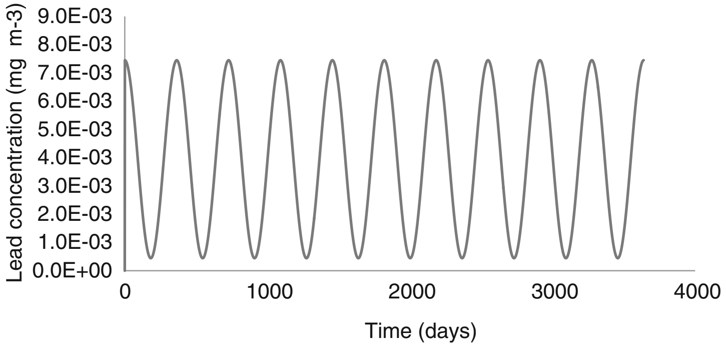

Fig. 12 Pb concentration in air entering the target region

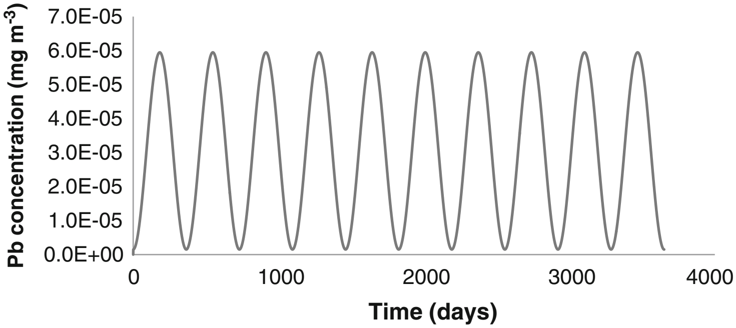

Fig. 13 Pb concentration in surface water at upstream zone

Pb concentration in air and surface water (SW) data used as inputs are presented in the Figs. 12 and 13 and were created by applying the following sinusoidal functions:

Table 14 The parameters used for the sensitivity and uncertainty analyses for the model outputs

Parameter	Unit	PDF
River depth	m	N(3.0,1.0,0.0)
1st empirical parameter for the rating curve relating suspended particulate matter (SPM) and flow rate in river (log(a))	–	N(−4.19, 0.33)
2nd empirical parameter for the rating curve relating SPM and flow rate in river (b)	–	N(0.99, 0.13)
Manning's coefficient	$m^{1/3}\ s^{-1}$	unif(0.02,0.07)
Settling velocity of particles Wc	m/d	LN2(18.9, 3.0)
Boundary layer thickness above sediment δ_{sed}	m	unif(0.0,0.03)
Layer thickness below sediment δ_w (2.0×10^{-4},7.0×10^{-4})	m	unif
Critical shear stress for resuspension	Pa	N2(1.71,1.33)
Maximum erosion rate	$g\ m^{-2}\ day^{-1}$	N2(7.891,1.69)
Partition coefficient of metal at the water–SPM interface	m^3/g	N2(−0.69,0.92)
Partition coefficient of metal at the sediment–pore water interface	m^3/g	N2(−3.2,4.4)
Porosity of sediment ϕ_{sed}	–	unif(0.33,0.41)
Elimination rate constant in fish $\lambda_{elimination\_fish}$	day^{-1}	N2(−4.79,1.42)
1st regression coefficient of the relationship log (BCF) = f(log(C_dis_water)) α_{fish_metal}	$log(m^3/g)$	norm(5.2,0.38)
2nd regression coefficient of the relationship log (BCF) = f(log(C_dis_water)) β_{fish_metal}	–	norm(−0.85,0.073)
Random error of the regression of the relationship log (BCF) = f(log(C_dis_water)) ε_{fish_metal}	–	norm(0.0,1.11)
Transfer factor from soil to potato $TF_{soil,potato}$	$kg_{dw}\ kg_{dw}^{-1}$	N(0.0020,0.91)
Density of dry potato $\rho_{dry,potato}$	$kg_{dw}\ L^{-1}$	Triang (0.163,0.233,0.195)
Transfer factor from soil to root $TF_{soil,root}$	$kg_{dw}\ kg_{dw}^{-1}$	LN(0.011,0.67)
Density of dry root $\rho_{dry,root}$	$kg_{dw}\ L^{-1}$	Triang (0.077,0.115,0.101)
Mass of root per field area in root compartment M_{root}	kg_{fw}/m^2	LN(1.0, 0.017)
Mass of leaf per field area in leaf compartment M_{leaf}	kg_{fw}/m^2	LN(1.0, 0.017)
Alpha_wet_interception	$m^2\ kg_{dw}^{-1}$	LogT(0.25,11.5,1.68)
Alpha_dry_interception	$m^2\ kg_{dw}^{-1}$	LogT(0.16,14.0,1.51)
Density of dry grass $\rho_{dry,grass}$	$kg_{dw}\ L^{-1}$	Triang(0.034,0.06,0.048)

$$Cair_{\text{flow}(t)} = \frac{c_{\max} + C_{\min}}{2} + \frac{C_{\max} + C_{\min}}{2} \times \sin\left(2\pi \frac{t}{365} + \frac{\pi}{2}\right)$$

$$Csw_{\text{flow}(t)} = \frac{c_{\max} + C_{\min}}{2} + \frac{C_{\max} + C_{\min}}{2} \times \sin\left(2\pi \frac{t}{365} - \frac{\pi}{2}\right)$$

The minimum and maximum values used were:

- Air: min Pb concentration (summer) – 7.4×10^{-3} mg m^{-3}
- Air: max Pb concentration (winter) – 4.4×10^{-4} mg m^{-3}
- SW: min Pb concentration (winter) – 6.1×10^{-5} mg m^{-3}
- SW: max Pb concentration (summer) – 3×10^{-6} mg m^{-3}

The total suspended particles value considered as input was 1.24×10^{-4} g m^{-3} whereas the global solar radiation was set at 158.95. Table 14 shows the input parameters used in the form of probability density function(PDF) and which allow the probabilistic analysis and sensitivity analysis in terms of simulation outcomes.

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In Search of Zero Waste: An Experiment in Progress

C.F. Mahler, A.S. Schueler, and Z. Fonseca

Abstract In Cantagalo, a city located in the mountain region of the state of Rio de Janeiro (Brazil), a pioneering experiment in solid waste management has been under way in recent years, in which the aim is to avoid having to rely on landfills for final disposal of waste by instead recycling or otherwise reusing all the solid waste generated.

The experiment dates to 2006 when the cement maker Lafarge, with a plant located in the city, requested COPPE/Federal University of Rio de Janeiro to conduct a study of the use of solid waste in its industrial activities through coprocessing. The study involved joint work among the Waste Treatment Study Group of COPPE, the company, and the municipal government in order to provide better knowledge of the solid waste materials produced in the city and their possible uses. The resulting findings led to improvements in the process of collecting and sorting waste by the municipal government, with the recycling or use of a significant portion of the solid waste for the production of compost for soil improvement. Most of the material left-over from these two processes (waste not suitable for recycling or use as compost) started to be sent to the cement plant to be burned together with coke as fuel in the industrial process, thus taking advantage of the calorific energy of this material. The ash left from this burning was removed periodically from the furnaces, and a part was used as a cement ingredient. The rest was either used in civil construction or other activities or sent for burial in a landfill for inert substances. Cantagalo is perhaps the first "zero

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waste" city in Brazil that can be said to have truly sustainable waste processing. This chapter presents the results of the studies and laboratory tests for determination of the calorific power, ash percentage, and chlorides concentration of the city's solid waste and other important information regarding the implementation of the process.

Keywords Coprocessing, Recycling, Urban solid waste management, Waste incineration, Waste-to-energy

Contents

1 Introduction

The treatment and disposal of urban solid waste in Brazil fall under municipal responsibility. Although some municipalities collaborate for joint waste collection, treatment and disposal in many smaller ones (especially with populations under 50,000 people) are poorly handled. Of the more than 3,000 Brazilian municipalities of this size, virtually none provide adequate treatment and final disposal of their solid waste. While waste collection tends to be reasonable, particularly in the urban centers, very few municipalities have systems of waste separation implemented, much less systems that are working correctly. Cantagalo stands out as an oasis in this otherwise dismal picture. The joint action of the municipal government, the Lafarge cement plant, and researchers from COPPE led to a program seeking to achieve "zero waste," by which all waste that cannot be recycled or reused is rendered inert and adequately disposed of. The presence of the cement plant was a key in this respect because of the opportunity of coprocessing through the use of the collected waste to generate the heat necessary to make cement. This chapter describes this pioneering and proactive initiative, at least in Brazil, which involves collection, separation, recycling, compositing, and coprocessing of municipal solid waste (MSW). This program in Cantagalo can serve as an example to other cities in Brazil and other countries as well.

2 Cantagalo

Cantagalo has existed as a separate political unit for 214 years. In recent years, it has matured economically, becoming an important center for cement manufacturing in the state of Rio de Janeiro. It has a population of almost 21,000 inhabitants and an area of 749 km^2, for a population density of 27.4 inhabitants/km^2. It is located in the mountain region of the north-central part of the state (latitude 21°58′52″, longitude 42°22′05″, and altitude of 391 m). More than 80% of the rainfall occurs in the summer, and the average temperature ranges from 19°C to 26°C. The main source of wealth is the extraction of limestone, used to make lime for manufacture of cement and for use as a soil corrective. The limestone reserves are estimated at more than 220 million tonnes (metric tons). The municipality suffers from environmental problems such as, among others, soil erosion, deforestation, air pollution, deficient sewage treatment, degradation of natural areas, precarious living conditions for the poor, and contamination by pesticide.

2.1 Cantagalo Waste Separation and Composting Center

The Cantagalo Waste Separation and Composting Center receives an average of 280 tonnes of solid urban waste per month, besides Class 2A residues (according to the NBR 1004/2004 standard), the latter wastes generated by factories [1].

The municipal government uses two trucks with capacity of 8 m^3 to collect the solid waste. They unload the material on average twice a day (morning and afternoon) at the center.

There are 37 scavengers who work at the center from Monday through Saturday. Of these people, 13 are responsible for sorting the waste on a conveyor belt. Figures 2 and 3 show the sorting belt and the grinder used to prepare the organic waste, which will be sent to the composting silos. The other workers perform the baling of recyclable material (Fig. 4), the formation of the compost heaps (Fig. 5) or the screening of the compost (Fig. 6).

One drawback is the small amount of space along the sorting conveyor, which can reduce the efficiency of separating the material (Fig. 1).

The conveyor belt is automatic, and its speed is constant. What is controlled is its length, which is adjusted depending on the quantity of material to be taken to the grinder. The maximum length is 7 m.

The sorting is carried out as follows: upon arrival at the center, the waste is placed in a hopper located at the start of the conveyor belt. Two workers place the material on the belt with the help of rakes.

When passing along the conveyor belt, the recyclable materials are retrieved (paper, plastic, and glass bottles/jars) and deposited in 200-l barrels, holding an average weight of 62.34 kg of material. This recyclable material is stored for later sale, in bales when necessary.

Fig. 1 Workers along the sorting belt

Fig. 2 Entrance of waste on the sorting conveyor belt

Fig. 3 Grinder for organic waste located at the end of the conveyor belt

Fig. 4 Baler for recyclable material

Fig. 5 Silo with composting pile

Fig. 6 Screen for organic compost

Fig. 7 Incinerator

After removal of the recyclable materials, the remaining wastes on the conveyor belt – the organic material and waste unsuitable for recycling – has two destinations: the organic material passes through the grinder and then goes to the aerobic compositing silos, while the rejected material (not recyclable) is placed in 200-l barrels (with empty weight of 12 kg) and stored for disposal at the city's landfill.

In the silos, the organic material is biodegraded and becomes raw organic compost. Roughly 117 tonnes per month of material is placed in the silos. To conclude the compositing process, the material is placed in maturing piles after being removed from the silos to produce mature compost. This process takes about 180 days, which guarantees a good level of inertization.

Characterization of the fraction that is recyclable is one of the subjects of this study. Some components of healthcare waste collected is incinerated (Fig. 7).

3 Coprocessing

Coprocessing is a technique that has been used in Europe, Japan, and the United States. It consists of transforming waste materials into alternative fuels and/or substitutes for raw materials. This enables reducing consumption of fossil fuels and helps preserve the environment.

Worldwide, approximately 300 million tonnes of wastes per year are sent in blended form to cement plants to replace fossil fuels (up to 20%) and for use as inputs (up to 6%), thus contributing to reduce CO_2 emissions [2]. This demonstrates its importance in saving natural resources.

The materials normally used as fuels to produce heat energy are plastics, leather, paper, paint, sludge, and emulsions. The materials commonly used as substitute inputs are the ashes from waste incineration [waste-to-energy (WTE)], as well as

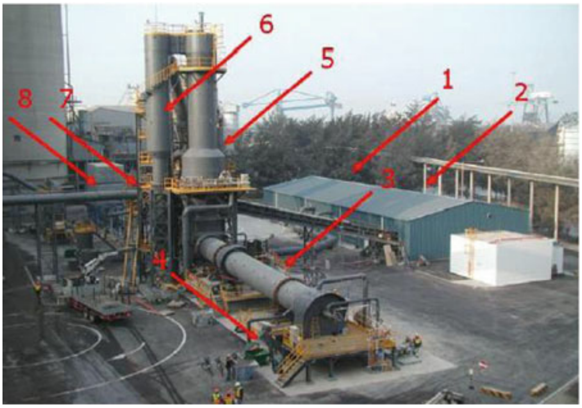

Fig. 8 Pilot plant (*source*: www.apjChemEng.com)

acid residues and sludge. These materials can only be used in cement plants after pretreatment and mixture with other materials to form a blend with the correct specifications.

The coincineration of solid urban waste in Brazil has received a good deal of study to harmonize the process with the existing technology at the country's cement plants, which are located in many states (Rio de Janeiro, São Paulo, Paraná, Minas Gerais, Pernambuco, Ceará, and Piauí).

In the international context, the development of a pilot cement plant in Hong Kong (Fig. 8) using incineration of wastes from a waste recycling separation facility it was reported [3], which includes:

- Receiving area (1)
- Separation area (2)
- Rotating furnace (3)
- Cooling tank (4)
- Secondary combustion chamber (5)
- Pre-calcinator (6)
- NO_x system (7)
- Recovery of materials for energy purposes (8)

The separation process is in harmony with Brazil's National Solid Waste Policy, established by Law 12,305 of 2010. The residual material is sent to the cement plant.

The system for this purpose is composed of the following machines:

- Rotating screens
- Ballistic separator (plastic and paper material)
- Magnetic separator (ferrous material)
- Eddy current separator (nonferrous material)

Coincineration presents some advantages over the WTE process (incineration for energy generation). Table 1 compares the two processes.

Table 1 Comparison of coincineration and WTE

	Coincineration (cement plant)	WTE (waste incineration)
Recyclable materials	Waste from separation	Waste from separation
Combustion residence time	Up to 4 s at about 1,200°C	2 s up to 850°C
Heat treatment	Integrated process	Only incineration
Stability of the process	Without caloric restriction	Minimum CP of 1,400–1,600 kcal/kg
Atmospheric emissions	Much less than the legal limits	Within the legal limits
Solid wastes from the process	Cement furnaces	Sanitary landfills

Adapted from [3]

The waste from the separation is called waste-derived fuel (WDF) or solid recovered fuel (SRF). It is normally composed of materials with good calorific power, such as paper, plastics, fabrics, and wood. These materials are only the rejects that cannot be recycled, due mainly to the level of contaminants they contain.

According to [4], two coincineration routes can be utilized with good energy recovery: coincineration in coal-fired thermoelectric plants and coincineration in cement furnaces to replace fossil fuels, which in the Brazilian case is generally petroleum coke (petcoke). The substitution in power plants is up to 10% and in cement plants up to 30% by weight. The calorific power of the SRF in the study by [4] is 18 MJ/kg or 4,300 kcal/kg, which corresponds to 6% of the calorific power of coal.

There are three cement plants in Cantagalo engaging in coprocessing, but only the Lafarge facility uses treated solid urban waste obtained from the municipal sanitation authority, a practice that started in 2007. This plant is one of the largest producers of construction materials in Brazil, with a product line consisting of cement, concrete, aggregates (sand and gravel), and plaster (gypsum).

4 Technological Aspects

Brazilian cement plants are relatively modern due to the country's more recent industrialization in comparison with many other countries. For example, the average energy consumption per tons of cement produced in Brazil is 112 kWh/t, while in the United States this is around 140 kWh/t. The efforts of companies in the sector have achieved significant progress in terms of more efficient production systems with lower energy consumption. At the same time, the use of additives mixed with clinker, such as blast furnace slag, also has helped reduce CO_2 emissions per tonne of cement, because this pollutant is formed during the production of clinker.

Due to the implementation of energy efficiency measures in Brazil, the country has a carbon dioxide emission factor of approximately 610 kg CO_2/t of cement, lower than countries like Spain (698 kg CO_2/t), England (839 kg CO_2/t), and China (848 kg CO_2/t) [5].

One potential energy-saving measure not yet widely exploited is cogeneration, with the use of flue gases to generate steam to drive turbines and generate electricity, helping to reduce greenhouse gas emissions.

Coprocessing basically started in the 1980s as a consequence of the two oil price shocks in the preceding decade. Initially, the fuel used was industrial waste, posing a significant environmental hazard. Today, the trend is to shift to SRF obtained from urban waste, which is generated in huge quantities in the country's large urban centers. This shift is also driven by the increasingly strict limits on disposal of waste in sanitary landfills and dumps. According to the National Solid Waste Policy (established by Law 12,305/2010), only material that is not recyclable or reusable can be buried in landfills. However, the necessary enabling regulations of this law are only being phased in gradually, so the policy's effects will only be felt fully in the future. Another hindrance to the use of solid urban waste is the long distance between sources of waste and cement plants and coal-fired thermoelectric plants.

5 Characteristics of the Waste Materials for Coprocessing

The waste materials from the separation process are prepared for coprocessing by a contracted firm. Different tests are carried out on the waste material at the Lafarge laboratories to control the calorific power, ash production, and presence of chlorides. These characteristics are extremely important for successful coprocessing [6]. An example of the trends of the results of these tests is shown in Fig. 9.

The average calorific power of the material received for coprocessing, which in August 2010 was 3,898 kcal/kg, increased to 5,495 kcal/kg in September that year. The average ash content fell from 14.09% in August 2010 to 8.46% in the following month, while the concentration of chlorides fell from 1.02% to 0.37% in the same period.

Since the concentration of chlorides is associated with the presence of plastics, it can be concluded that in August there was more plastic material from the separation process, which also led to a lower calorific power and higher ash content after burning. In this respect, according to [6], the level of chlorides also depends on the type of plastic.

Table 2 presents the results of tests to measure the calorific power, ash content, and chlorides concentration of some of the materials obtained from the separation process, such as polystyrene, aluminum foil, plastic foam, and other plastics (general, clear, colored, black, and vinyl). Polystyrene and clear plastic have very high calorific power and low levels of chlorides, but polystyrene has very high ash content. Figures 10–17 present the samples of waste components from the separation and composting plant of Cantagalo.

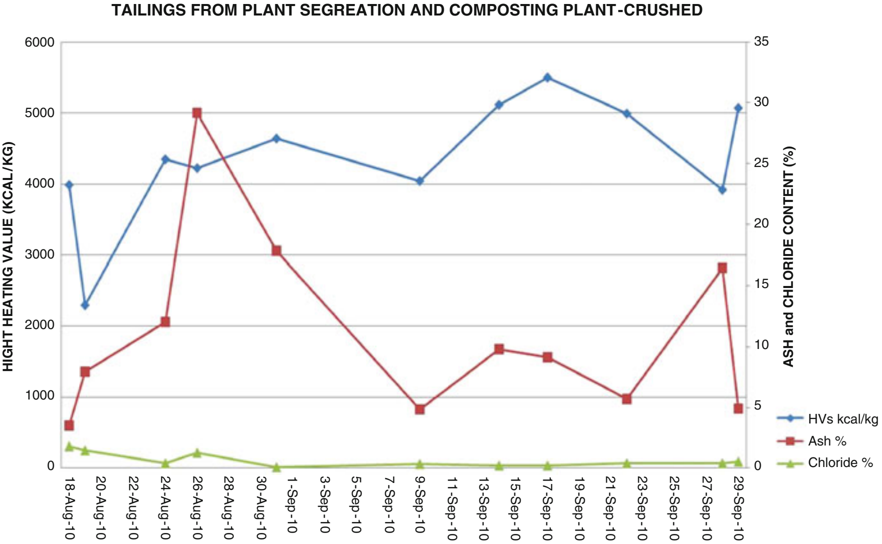

Fig. 9 Chemical analyses of the samples of materials for coprocessing from the waste separation and composting center

Table 2 Chemical analyses of the waste components from the separation and composting plant

Component	Superior heating value (kcal/kg)	Ash content (%)	Chloride content (%)
Polystyrene	9,014	9.15	0.21
Aluminum foil	3,440	64.55	0.03
Plastic foam	6,390	7.26	0.07
Plastic (general)	7,435	7.33	17.87
Clear plastic	10,564	0.26	0.00
Colored plastic	10,103	6.79	0.28
Vinyl	5,411	21.72	12.99
Black plastic	6,385	2.38	29.79

Fig. 10 Sample of polystyrene from Cantagalo Waste Separation and Composting Center

Fig. 11 Sample of aluminum foil from Cantagalo Waste Separation and Composting Center

Fig. 12 Sample of plastic foam from Cantagalo Waste Separation and Composting Center

Fig. 13 Sample of general plastic from Cantagalo Waste Separation and Composting Center

Fig. 14 Sample of clear plastic from Cantagalo Waste Separation and Composting Center

Fig. 15 Sample of colored plastic from Cantagalo Waste Separation and Composting Center

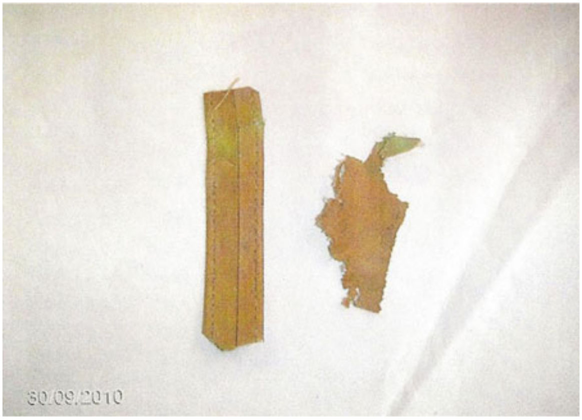

Fig. 16 Sample of unusable vinyl from Cantagalo Waste Separation and Composting Center

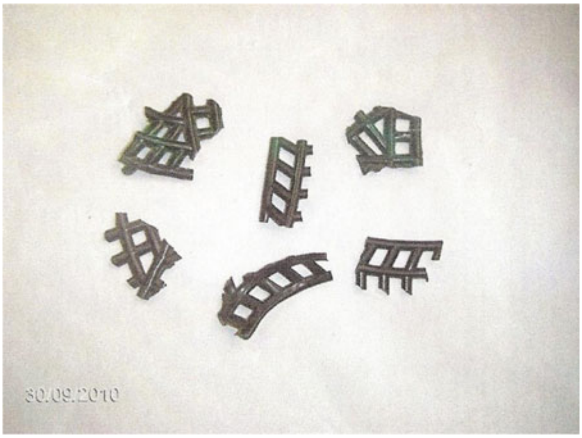

Fig. 17 Sample of black plastic from Cantagalo Waste Separation and Composting Center

6 Final Observation

The city of Cantagalo is one of the first in Brazil to establish organized separation and treatment of solid wastes for reuse, to avoid the need for disposal in landfills. The separation with proper allocation for coprocessing of the portion of the waste not suitable for recycling or composting is a laudable solution from both an environmental and economic standpoint. The process is being improved, with the preparation of increasing portions of the waste materials for use to generate heat energy to make cement.

The results of the tests to determine the calorific power show satisfactory values for coprocessing, be it for mixed materials, otherwise unusable material from separation or plastics in general. As observed by [6], the level of chlorides is closely related to the quantity of plastics in the mixture, and also depends on the type of plastic.

There is a need for further studies of the calorific power, ash content, and level of chlorides in waste materials for coprocessing in the cement industry or for incineration to generate energy (WTE), considering the variability of the wastes produced at different times of the year and by different populations, as shown by the test results.

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Mineral Oil in Board and Paper Recycling

Antje Kersten, Hans-Joachim Putz, and Samuel Schabel

Abstract Paper for recycling is the most important fibre raw material of the German paper industry. 16.3 Mio t of paper for recycling was utilised in 2010 corresponding to 72% of the total fibre raw material input for paper and board production. In comparison to the used virgin fibre-based chemical and mechanical pulp, the utilised amount of paper for recycling is about 2.6 times higher.

The utilisation of paper for recycling in the four major paper product categories is developed differently and reaches its highest utilisation rates traditionally in the production of packaging paper and board (100%). In absolute figures, the yearly usage of paper for recycling in this area is with 10.2 Mio t about twice as high as for the production of graphic papers (4.9 Mio t).

Recycling creates places of employment and saves the resources raw material, energy and water. Wood is a very important renewable raw material which is used in many fields of application. Also, the paper industry requires wood for the production of virgin fibres to ensure the multiple use of the construction material paper. It is necessary to upright the paper recycling loop to cover the tremendous demand of paper in Europe.

In the final consequence, it means that the problem of mineral oil migration from board to foodstuff – mainly discussed in Germany – has to be treated and solved on a European level. The possible solutions and drawbacks for the folding boxboard production as packaging material discussed in this chapter include:

- The substitution of paper for recycling by virgin fibres.
- The utilisation of paper grades for recycling with lower newspaper content in comparison to the typically used mixed paper grades for recycling.
- The usage of mineral oil-free chemical additives in virgin fibre and paper production.

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- The opportunities to remove mineral oil in processing of paper for recycling.
- The use of barrier coatings and bags in box systems.
- The conversion of the offset printing process for newspapers to other print systems.
- The substitution of mineral oil by vegetable oil in offset coldset inks.

Keywords Corrugated board, Folding boxboard, Food packaging, Mineral oil, Recovered paper, Recycling

Contents

1 Introduction

Recovered paper (RCP) is the most important fibre raw material of the German paper industry. In total, 16.3 Mio t of RCP was utilised in Germany for paper and board production in 2010, corresponding to 72% of the total fibre consumption for the production of paper and board. In comparison to the sum of virgin fibres as chemical and mechanical pulp, the used amount of RCP is about 2.6 times higher. Typically, the utilisation ratio of RCP is calculated by the mass relation between used RCP and total paper and board production. In 2010, the German average was 70%. The utilisation of RCP is very different in the four major paper product categories and achieves traditionally for the production of packaging papers and board a much higher utilisation rate (100%) than for the production of sanitary papers (50%), graphic papers (49%) or special paper and board (42%) [1]. The yearly consumption of RCP is in absolute figures, 10.2 Mio t for the production for packaging paper and board, about twice as high as for the production of graphic papers (4.9 Mio t RCP) and roughly eight times higher as for the total production of sanitary and special paper grades (1.2 Mio t RCP).

2 Board Packaging and the Problem of Mineral Oil

In the context with the utilisation of recycled fibres for the production of food packaging material, the possible input of harmful substances has to be considered. During the last two years, an intensive discussion between representatives from authorities, paper manufacturers and researchers about mineral oil in foodstuff and packaging material has taken place. The fact that traces of mineral oils are detectable in board for food packaging cannot be ignored [2] and is well known as mineral oil hump since a long time by the experts. In the production of packaging material for foodstuff, paragraphs 30 et seq. of the German Food and Feed Code have to be considered. For routine checks during production of board for foodstuff, it is common to use Recommendation XXXVI [3] of the Federal Institute for Risk Assessment which does not contain any explicit specifications regarding mineral oils until now.

Mineral oil compounds can be found in virgin fibre-based board as well as in recycled fibre-based packaging materials. Nevertheless, the contamination of recycled board grades is typically 300–1,000 mg/kg mineral oil with a relative low molar mass (C18–C22) and an aromatic proportion of 15–20% significantly higher [4]. The mineral oil components consist of saturated open-chained mostly branched and cyclic hydrocarbons (“mineral oil saturated hydrocarbons” – MOSH) as well as aromatic hydrocarbons (“mineral oil aromatic hydrocarbons” – MOAH), often with alkylated side chains. From the JECFA (Joint FAO/WHO Expert Committee on Food Additives), a temporary acceptable daily intake (ADI) value of 0.01 mg/kg body weight per day was recommended in 2002 for mineral oils with low and medium viscosity (class II, class III). By considering the daily food consumption and an average body weight of 60 kg, the maximum acceptable concentration was calculated with 0.6 mg/kg foodstuff [2]. But this critical limit value is valid only for the MOSH fraction. Little is known about the toxicity of the MOAH fraction, to which hundreds of individual substances belong. Based on their structural similarity to polycyclic aromatic hydrocarbons, a carcinogenic impact of at least some of these substances is possible, and for some few compounds, this effect has already been proved [5]. For carcinogenic compounds, a limit value in foodstuff does not exist. They should be not at all detectable. The occurrence of aromatic hydrocarbons in the mineral oil can be reduced significantly by hydrogenation and further process engineering measures, resulting in so-called white oils. These oils are toxicologically less critical; aromatic-free white oils with high viscosity are approved with an ADI value of 12 mg/kg body weight a day and even admitted as food additive [4].

Offset printed newspapers were identified as the basic source of mineral oil in recycled board. Due to the fact that the short-chained mineral oil compounds with a chain length below 24 carbon atoms (C24) may migrate, they are in principle able to pass from the board via the gas phase into the foodstuff – the experts name it migration. Inner bags from paper or polyethylene are no effective barriers in food packaging, resulting also in a general mineral oil migration from transport packages (e.g. corrugated boxes) into foodstuff. By the way, this is not only true for foodstuff in board packaging but also for foodstuff in other packaging materials such as plastic bags, which are stored and/or transported in secondary packaging made from corrugated board [6]. Up to now, little is known about the influencing factors (storage period, temperature, three-dimensional distance, use of shrinking foil, etc.) of the mineral oil migration from the board for food packaging, the corrugated board packaging or a secondary packaging into the foodstuff.

Of course, foodstuff should be free of harmful or potential harmful substances – and so also free of mineral oil. Which measures could be taken and are reasonable to avoid the transfer of mineral oil from paper and board packaging material into foodstuff is scrutinised critically in the following chapters.

3 Possible Solutions for Solving the Mineral Oil Problem

To solve the problem of the mineral oil contamination of board packaging materials, the different following measures are conceivable:

- Substitution of recycled fibre-based board by virgin fibre-based board.
- Utilisation of selected RCP grades for the board production.
- Reduction of the mineral oil input during recycled board production by using alternative chemical additives.
- Utilisation of barriers either directly as coating layer on the board or as separate inner bags in the packaging.
- Avoiding the mineral oil input by modifications of printing inks or by the substitution of printing processes.

In the following chapters, the above-named measures are described and benchmarked. The substitution of recycled board packaging for foodstuff by other packaging systems from glass, metal or plastics will not be considered here.

3.1 Substitution by Virgin Fibre-Based Packaging Material

Obviously, the first measure to think about could be the substitution of recycled fibre-based boxboard for foodstuff by virgin fibre-based material. The required amount of recycled fibre-based boxboard for foodstuff equals to 700,000 t/year in Germany [7]. For the substitution of the recycled fibre-based boxboard, it is simply assumed that the required virgin fibre-based board is produced totally from mechanical spruce pulp with a process yield of 97%. This would require in total additionally about 1.68 Mio m^3 wood per year. The inventory study of the carbon balance of the German forests [8] indicates an average yearly wood growth of 11.1 m^3 per hectare (ha). To cover the additional wood demand, a forest area of

151,194 ha would be required, corresponding to the total area of the federal states Berlin and Hamburg in Germany.

Additionally, due to the migration problem of mineral oil, substitution not only for foodstuff packing but also for all secondary packaging has to be considered. Even board packaging not used for foodstuff has to be taken into account because those packages may stand beside foodstuff in the racks of the supermarket or during storage. The boxboard and corrugated board would sum up in 2009 in Germany to the total national sales of 1.3 Mio t machine board and 3.6 Mio t corrugated base papers [1].

In case that corrugated base papers are not any more produced from recycled paper, as it is typical for testliner and medium in Germany, virgin fibres would have to be used. The corresponding paper grades as kraftliner would be produced from kraft pulp and fluting from semi-chemical pulp. For the simplified calculation of the required wood demand for the fibres, an average process yield of 60% (kraft pulp = 50%, semi-chemical pulp = 70%) is used. The substitution of the 3.6 Mio t corrugated base papers requires about 6 Mio t of wood corresponding to 14 Mio m^3 wood.

For the mechanical pulp containing boxboard substitution about 1.3 Mio t of wood, respectively, 3.1 Mio m^3 wood would be required, summing up to a yearly additional softwood demand of roughly 17.1 Mio m^3. Divided by the German yearly average wood growth of 11.1 m^3/ha, the calculated additional wood demand would require an area of 1.54 Mio ha, roughly corresponding to the area of the German federal state of Schleswig-Holstein. Performing the same calculation for total virgin fibre demand of Europe, it becomes evident that the required area becomes as large Hungary and Poland together.

The additional wood demand of 17.1 Mio m^3 corresponds to 27% of the total German wood harvest in 2006 (62.3 Mio m^3). The wood harvest of 2007 of 76.7 Mio m^3 cannot be used as typical reference due to the windfall of the storm “Kyrill”. The harvested wood volume in 2006 has already doubled in comparison to the long-term average of the 1990s (approximately 34 Mio m^3) [9].

Kraftliner as well as fluting are not manufactured in Germany. Corresponding paper grades would have to be imported or at least the necessary raw materials. The required pulp volume for the production of 3.6 Mio t corrugated base papers would exceed the current total chemical pulp import of 3.4 Mio t of the German paper industry.

The production of the virgin fibre-based papers (boxboard and corrugating base paper) needs, in comparison to recycled fibre-based papers, more resources. Based on data from the report of IPPC (Integrated Pollution Prevention and Control) and calculations according to Table 1, the additional yearly consumptions equal for water 63.1 Mio m^3, for electricity 3.9 Mio MWh and for thermal energy 34.2 Mio GJ in terms of steam.

The equivalent calculation of the environmental impact on the European level for substituting recycled fibre-based packaging material by virgin fibre-based material results in the required amount of 47 Mio t of wood or an equivalent of 110 million m^3 of standing timber, an additional annual consumption of 400 Mio m^3 of water, 17.6 Mio MWh of electrical power and 237 Mio GJ of thermal energy.

Table 1 Water, energy and steam demand for virgin and recycled fibre-based paper production according to BAT [10]

	Kraftliner	Testliner/ corrugated medium	Difference to kraftliner	Virgin fibre-based board	Recycled board	Difference to virgin fibre-based
Water demand (m^3/t)	15–25	0–9	15	8–15	0–9	7
Electrical energy (MWh/t)	1.0–1.5	0.7–0.8	0.5	2.3–2.8	0.9–1.0	1.6
Steam demand (GJ/t)	14.0–17.5	6.0–6.5	9.5	3.5–13.0	8.0–9.0	0.0

Savings	Corrugated papers	Board	Total
Production (Mio t/a)	3,600,000	1,300,000	4,900,000
Water demand (m^3/a)	54,000,000	9,100,000	63,100,000
Electrical energy (MWh/a)	1,800,000	2,080,000	3,880,000
Steam demand (GJ/a)	34,200,000	0	34,200,000

Therefore, we conclude that a significantly higher demand on resources (wood, water, energy) would result by the replacement of recycled packaging material with virgin fibre-based packaging material. Additionally, paper mills producing today recycled fibre-based papers and board could not switch to virgin fibre-based production without investments. For these production units, the additional yearly wood demand of 17.1 Mio m^3 stays in competition to the subsidised burning of wood for heating purposes and corresponds to about 24% of the yearly German wood growth [8] (70.5 Mio m^3) or is roughly the double volume of the yearly wood growth surplus of 7.7 Mio m^3 [11].

A total import of all required virgin fibre-based paper and board grades from other European countries to cover the German demand or from outside Europe to cover the European demand would currently fail due to unavailable capacities.

3.2 *Supply with Mineral Oil-Reduced RCP Grades*

Producers of board try to manufacture board for foodstuff packaging with other, less mineral oil-contaminated RCP grades. Major sources of mineral oil in paper for recycling are offset coldset inks preferably used in newspapers and which contain typically 20–30% mineral oil as solvent [12]. By appropriate sorting of the RCP, the theoretical possibility exists to remove newspapers from collected household paper mixtures, so-called household collections, so that a mixed RCP grade without newspaper is generated especially for board production.

Unfortunately, the RCP sorting plants today are arranged in a way to remove from collected household paper mixtures non-paper components and the packaging materials which are sold as supermarket corrugated paper and board grade. The target of sorting is the generation of a white RCP mixture for deinking purposes – sorted graphic paper for deinking, which allows a particular high added value. Sorted graphic paper for deinking should not contain any packaging material because brown unbleached fibres after deinking will visually contaminate the bright deinked pulp as so-called mottled fibres. Bleaching as performed in RCP processing cannot brighten the brown fibres effectively.

The reason to arrange the RCP sorting plants with so-called negative sorting by removing unsuitable components from the incoming collected paper stream is based on the composition of the collected papers from the households. In this paper mixture, the amount of print products (newspapers, magazines, catalogues) dominates with 78% in total, whereas the share of packaging material is only 19% on average [13]. A rearrangement of the sorting targets to remove the average newspaper content of 23% would require from the plant operators in general additional measures which would lead to rebuilds and extension investments. Technology today with optical sensors and blowing out technology could handle the targets but with the consequence of a price increase of this new RCP grade “mixed paper for recycling without newspapers”.

RCP mixtures with lower mineral oil content could also generated by a separate collection of graphic papers (newspaper and magazines) on the one hand side and packaging material on the other hand directly from the private households. Sorting is then performed by the citizens, and sorting at the waste disposal companies has control and correction functions only. Due to the fact that such kind of consumer-oriented collection system does practically not exist in Germany, nationwide installations would certainly take several years to complete. In addition, it is doubtful if such concepts will be accepted especially in city regions because the floor space for the collection containers would have to be doubled. Furthermore, the additional efforts for the collection of the used paper and board materials will lead to a cost increase, accompanied possibly by reduced costs for sorting.

3.3 Reduction of the Mineral Oil Input During Paper Production

In general, the sorting of collected paper costs money. Manufacturers of paper and board grades which are not designed for food packaging will still use in the future those RCP grades which are most cost-efficient for the paper grades to be manufactured. This would be a mixed RCP grade containing an average newspaper content of 11% according to the newest examinations [13]. Packaging material produced with these RCP grades will come during its next lifetime into the recycling circuit for food packaging material because it will not be removed from this packaging material flow.

Therefore, the use of mineral oil-reduced RCP grades, e.g. free of newspapers, for food packaging will lead of course to a reduction of the mineral oil contamination and in consequence of the migration problem into foodstuff. However, in general, there will still exist a permanent input of mineral oil from the packaging material production not intended to be used for non-food packaging. The mineral oil content of packaging materials for foodstuff produced from mineral oil-reduced RCP grades will therefore not tend towards zero but will decrease to a lower level.

These estimations can be documented by the well-known example with the diisopropylnaphthalene (DIPN) contamination in mixed RCP (RCP grade 1.02). This chemical substance comes from NCR carbonless copy paper and is in this mentioned RCP grade on an average level of 23 mg/kg TS [13], despite the fact that since several years those papers tried to be separated in the RCP grade “sorted office paper”, “coloured letters” and “carbonless copy paper” to reduce the DIPN concentration in mixed papers and board.

In a presentation [14] on the occasion of a FPT workshop organised by PTS in 2010 the subject “Migration of mineral oils in the paper circuit”, model calculations showed how any separation of the RCP cycles to avoid in medium term the input of newspapers as raw material for board manufacturing for food packaging affected the mineral oil contamination of the board. However, the authors concluded that “under economic, qualitative and ecological aspects a reasonable solution of the problem can lie only in the reduction of the mineral oil load at the source”.

One measure of the manufacturers of board and corrugated papers to reduce the mineral oil contamination could be the implementation of additional process steps in the RCP processing lines. For this, suitable process stages are these which are able to remove ink particles, e.g. flotation or washing. Both technologies are available in industrial scale but typically used for processing graphic RCP grades for manufacturing “white” papers such as newsprint, magazine papers or sanitary papers. Previous laboratory trials show that mineral oil reduction rates by single-stage flotation reach scarcely 50% [15]. Unfortunately, these results require significant investment costs and increase strongly the fibre losses.

Unpublished laboratory results of PMV about high temperature treatment of RCP with suitable exhaust air and duration time showed a significant reduction of the volatile mineral oil constitutions of a magnitude of up to 98%. An up-scaling of those process stages or even an industrial implementation is not yet realised because the laboratory conditions cannot be transferred in an economical way.

From the experience with graphic RCP processing, it is known that the losses in the production of standard newsprint with one-loop flotation deinking are in a range between 13% and 20% [16]. With two-loop flotation for improved newsprint, it is 15–24% [16, 17, 18], and for high-quality graphic papers, the losses are between 18% and 35% [16–18]. Based on the special quality requirements of tissue papers, the losses result in a range between 28% and 42% by combination of flotation and washing [16–18].

Considering these additional losses, the paper mills producing packaging paper and board would have to buy larger amounts of RCP and would have to calculate increased costs for the disposal of the resulting rejects. Disposal costs depend on the particular mill situation, e.g. amount and type of rejects, and can vary significantly as the last disposal enquiry of VDP and PTS showed [19]. They determined average disposal costs of 50 €/t for rejects from RCP processing with a dryness of 50% (incl. sludges from deinking and effluent treatment). With an assumed additional yield loss of 15% and costs for the mixed RCP (1.02) of 70 €/t [20], the additional

Table 2 Model calculation of extra costs for a RCP process with additional 15% losses

	Basic situation	+15% rejects	Additional demand	Costs (€/t)	Additional costs (€/day)
Production (t/day)	900	900			
Process losses (%)	10	25			
Rejects (t/day)	100	300			
RCP utilisation (t/day)	1,000	1,200	200	70	14,000
Reject dryness (t/day)	50	50			
Reject mass to be disposed (t/day)	200	600	400	50	20,000
Total					34,000
Additional costs per year for 350 working days in €					11,900,000

costs add up according to Table 2 to a yearly amount of 11.9 Mio € for a production unit of 900 t/day with 350 working days per year. Related to an average selling price of 700 €/t [20] for GD II board, the additional costs correspond to 5.4% of the selling price. Simultaneously, the average MOSH contamination of board with 265 mg/kg is reduced by a single flotation process by about 50%. This contamination level is still above the discussed limit value of 0.6 mg/kg for MOSH in foodstuff given by an expert commission [4].

By control and substitution of chemicals used in the paper mills, manufacturers of packaging papers and board can contribute themselves directly to a small mineral oil reduction in their products. Some additives contain mineral oil as solvent such as flocculation or retention aids based on polyacrylamide (PAA), resin sizing agents or defoamers. A change of such products to mineral oil-free additives removes their own mineral oil input and reduces the contamination of packaging material. In the area of retention aids based on PAA, this conversion has already mostly taken place.

Defoamers and deaeration additives contained in the past mineral oils as active component but they are not anymore used in Europe. In emulsions, mineral oil can amount up to 10% mass content maximum. If defoamers and deaeration additives are used at a maximum of 0.1% in paper production [22], per each ton of paper, a maximum of 1,000 g defoamers and deaeration additives are used which contain 100 g mineral oil. In consideration of a 50% retention on the fibres, a theoretical content of 50 mg mineral oil per kilogramme final paper would result. By using further mineral oil-containing additives, the concentration in the paper can increase. However, only some chemical additives contain mineral oil constituents, and in most cases their proportion is in a range between 1% and 3% maximum related on the additive mass.

A review of the chemical additives used is recommended not only for the manufacturer of recycled fibre-based packaging material but also for the producers of virgin fibre-based paper products. This should close this input pathway to avoid the contamination of their own products by chemical additives. Manufacturers of print products and packaging material not intended to be used in the foodstuff area should also close this input pathway due to the fact that the used papers and packages with their mineral oil content come back by recycling in the circuit for food packaging material. Exception should be only accepted for such paper products which are not intended for material recycling after its use such as sanitary papers, decor paper or cigarette papers.

A further measure which can be used by paper manufacturers is a single-sided coating of their products in a way that it contributes as barrier against mineral oil. This would preferably be applied by on-machine coating units. Those functional barriers are already available against water vapour. An oiltight barrier coating on paper is not yet available, but manufacturers of folding boxboard are working on the development of barrier coatings to reduce mineral oil migration. If such coatings can stop oil migration completely cannot be answered yet. Anyhow, barrier coatings should be recyclable. That means that they should not affect negatively a typical RCP process and should not load paper as well as effluent with problematic chemical substances.

3.4 Measures in Paper Converting and Product Filling

Paper converters and foodstuff filling companies are able to take the same measures as paper manufacturers who try to use functional barriers to avoid migration of mineral oil constituents in foodstuff. Paper converters can laminate boxboard or corrugated board with plastic or aluminium foils in a way that the composite material has a lower migration tendency. Foodstuff filling companies can use inner bags of different materials inside the board boxes to reduce the migration potential. It is well known that functional barriers from polyethylene are not suitable to avoid mineral oil migration. Polypropylene is somewhat better, and PET (polyethylenterephthalate) and aluminium foil are good barriers against mineral oils.

For subsequent paper recycling, the use of inner bags might be somewhat more beneficial than composite materials because the inner bag can be separated by the end user and introduced in a separate recycling cycle. In contrast, during paper recycling of composite materials, accompanying plastic or aluminium always results as rejects in general and has to be disposed or introduced into other utilisation processes. The use of functional barriers is combined with higher costs for the packaging in general. Knowledge on the efficiency of different functional barriers, their dependence on applied basis weight (thickness), the mineral oil contamination of the board, the packed foodstuff, time and temperature during storage is not sufficient at the moment. Further research activities are required.

3.5 Modification of Printing Inks

The primary sources for the mineral oil contamination in secondary fibre-based packaging materials are the coldset inks from newspapers because offset printing is the dominating printing process for this type of graphic paper product in Europe. Offset coldset inks consist of up to 30% of mineral oil as solvent. In general, offset inks are available which are based on mineral oil-reduced or mineral oil-free formulations. As basic material, mainly vegetable oils are used for substitution, but there is no clear numeric percentage value defined from which an ink can be called officially as “vegetable oil-based ink”. This means that vegetable oil-based ink can still contain mineral oil components even though on a lower level.

Vegetable oil-based inks today offered in Germany are mainly for the heatset printing colours cyan, magenta, yellow and to a lesser extent black. The use of fatty acid alkyl esters as high-boiling solvents in offset inks as substitution of mineral oils is also practised [23].

In the 1990s, several research projects were performed on the development of mineral oil-free offset inks for newspaper printing primarily to manufacture “green” inks on basis of renewable raw materials. In the frame of an EU project [21], Centre Technique du Papier (CTP), Kao Corporation, Pira International and Trenal, a Belgian ink manufacturer, had developed mineral oil-free inks which did not contain any mineral oil components according to the statement of the former technical director. “The labelling ‘vegetable oil ink’ means for Trenal always, that these printing inks are based on 100% on vegetable oils” [24]. As basic raw material, optionally soybean, oilseed, sunflower, palm or linseed oil was used. The INGEDE (International Association of the Deinking Industry) had tested the deinkability of such test prints and found that it was comparable to mineral oil-based prints [24].

For the determination of the mineral oil content in paper and board, various test methods are available which finally are based on a gas chromatographic separation and quantification. In 2003, for graphic papers, a method for the evaluation of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) was established and standardised. This method was developed for the analysis of recycled copy papers according to RAL-UZ 14 for the award of the German environmental sign “Blue Angel” and is described in detail in annex 4 of this standard [25]. The range of SVOC compounds covers by definition the eluted organic substances between n-hexadecane (hydrocarbons with 16 carbon atoms) and n-docosane (hydrocarbons with 22 carbon atoms) after thermodesorption GC/MS. The SVOC value as sum parameter includes substantial parts of the mineral oils from offset inks (cyclic and branched alkanes up to C24) and in small amounts also phthalates, benzophenones and other organic contaminants.

Results of the PMV on VOC/SVOC analysis from different newspapers according to RAL-UZ 14 annex 4 show that worldwide different ink binders and solvents are used. This is documented in Table 3 by the amount and composition of the purgeable volatile substances from the newspapers. Especially in Asia, increased amounts of

Table 3 SVOC of different printed newspapers (calculated as TSVOC in μg/g)

Newspaper from	Black-printed areas	Coloured-printed areas	Unprinted areas
Germany (offset)	9,204	7,653	1,725
Japan (offset)	6,022	6,349	3,434
Vietnam	3,345	3,737	1,646
China	4,484	3,868	2,802
USA	6,099	6,857	3,203
Great Britain (flexo)	665	651	489

vegetable-based raw materials are used. This reduces the VOC/SVOC concentration and results in different typical peaks in the chromatogram.

In Japan, the standard Eco Mark Product Category No. 102 “Printing Ink Version 2.6” [26] sets on a voluntary basis standards for an environmentally friendly composition of printing inks. Since introduction of this standard in 1997, more than 90% of all offset inks in Japan were reformulated to inks free from aromatic compounds (“white oil”). To fulfil the above-mentioned standard, the inks should be based on vegetable oils. They should not contain more than 1 vol.% of aromatic hydrocarbons (“white oils”). Additionally, sheet-fed offset inks should not contain more than 30% of crude oil-based solvents and not more than 3% VOC. Web offset inks should contain no more than 45% crude oil solvents (which seems not really to be a progress in comparison to typical standard inks). By the way, it is expected from vegetable oil-based inks that the print products are as deinkable as conventional mineral oil-based offset inks.

It is indeed well known from the experiences of the early 1990s that vegetable oil-based offset inks have often a poorer deinkability than inks on mineral oil basis. This is the result of cross-linking reactions of the ink with increasing storage time which can result in a poorer ink detachment from the fibres and reduced deinkability [27]. One reason for the relatively poor laboratory deinking results was the accelerated ageing time of 6 days at that time in comparison to the nowadays applied 3-day ageing. The accelerated ageing at 60°C simulates the cross-linking of oxidative drying printing inks such as offset coldset inks. A rough estimation compares one day of accelerated ageing with about one month of natural ageing. From a 1995 finished INGEDE research project [28], it is known that in Germany the transfer time for newspapers is even shorter because 78% of all newspapers return within one month as RCP back into the paper mills. Therefore, as result of the INGEDE project 6098 IfP/PTS “Development of criteria for the evaluation of print products regarding their recyclability” [29], the first INGEDE standard method of the deinkability test published in 1999 reduced the duration of the accelerated ageing to 3 days which is closer to reality. They are still valid in the current version of INGEDE method 11p [30].

Good deinkable vegetable oil-based printing inks were developed during the already-cited EU project [21] which, however, did not result in subsequent breakthrough on the market. Therefore, it is strongly required to pick up this development work again to optimise printability on the one hand side and to evaluate the deinkability with the new and modified methods and to improve it if necessary on the other hand. The development of printing inks could be pushed first by a reduction of the mineral oil content in the inks before finally mineral oil-free inks are available.

In this context, the question has to be raised about the contribution offset heatset inks make to the mineral oil problem in RCP. The inks themselves can contain a significant mineral oil content even when mineral oil-free inks are available on the market. During the drying process, the majority of the oils evaporate. Nevertheless, in RCP from offset heatset printed magazines, mineral oil constituents will exist even though on a much lower level than in recovered newspapers and despite the fact that the ink application in magazine printing is substantially higher than in newspaper printing.

3.6 Change of Printing Processes

A further chance to solve the problem could exist in the exchange of the printing technologies for newspapers from the offset coldset to the waterborne flexo process. Of course, this significant change in printing technology is combined with large investments for the printing and publishing houses and can only be considered as long-term technology conversion. In flexo printed newspapers, the mineral oil contamination by the applied printing ink is minimised. Small amounts of mineral oil residuals result in fact from the recycling of old offset printed products to manufacture newsprint.

Only by the exchange of mineral oil-containing printing inks with mineral oil-free ink systems (mineral oil-free offset, waterborne flexo, inkjet) will it be possible to stop the continuous introduction of mineral oil into the recycling circuit. So a long-term increase of the mineral oil concentration will be avoided in those production areas where no significant decontamination takes place by the applied process technology, e.g. production of corrugated material or board. Simultaneously, in the long-term, the total RCP will be reduced in mineral oil contamination. In this context, it is necessary to ensure that new ink formulations or printing technologies meet the requirements of recycling-friendly print products. At first, a sufficient deinkability of the print products is required, whether they are printed with vegetable oil-based offset, waterborne flexo or inkjet inks to avoid a massive hazard of the recycling circuit of the graphic paper products. Up to now, there is no sufficient deinkability given for waterborne flexo and inkjet prints [18], resulting in the acceptance of only small amounts of those products in the RCP for deinking. Therefore, the solution has to lie in the development of mineral oil-reduced or even mineral oil-free offset coldset inks and their increasing application for newspaper production.

4 Evaluation of the Proposed Measures Regarding Mineral Oil Reduction

In the following chapter, results are summarised from INFOR project 155 [31] which was performed in collaboration with PTS/Munich and PMV/Darmstadt to evaluate the various measures to reduce the mineral oil content in folding boxboard and corrugating papers. It was the aim of the project to identify and evaluate the technological, economic and environmental effects of various measures on paper recycling and packaging paper and board production in Germany. First, a mass balance of the relevant paper products was built. A mass flow model for the German

Table 4 Model validation

MOSH/MOAH content of paper products (printed)	Newspapers	Magazines (wood containing)	Corrugated board	Folding boxes made from RCP (food packaging)	Folding boxes made from RCP (non-food applications)
Calculated (mg/kg)	4,313	540	270	403	620
Relation calculated vs. measured (=100%)	108%	81%	119%	76%	83%
Measured (avg.) (mg/kg)	3,988	667	226	527	744
Measured (min.) (mg/kg)	1,870	189	64	177	433
Measured (max.) (mg/kg)	7,457	1,090	447	1,826	1,967

paper and board production and the RCP flows was formulated and combined with the relevant mineral oil contents of the various mass flow streams. Therefore, additional mineral oil measurements in paper and pulp samples along paper production and converting processes were necessary. After that, the model was calibrated and different assumptions were made. The major boundary conditions were:

- The mass balance is based on 2008 data, the year before the economic crisis which seems more relevant than newer figures during the crisis.
- The mineral oil data were all new and measured in 2011.
- The modelling is based on the assumption that changes in Germany will occur simultaneously abroad.
- The stated mineral oil concentrations refer to the state of equilibrium.

Table 4 shows that after model validation, the calculated mineral oil content for different paper products (newspaper, magazine, corrugated board, folding boxes from RCP for food and non-food applications) was in the range of the measured average values of about ±20% and fits completely in the measured range of minimum and maximum values.

The considered scenarios are listed in Table 5. They cover the "as it is" status (scenario 1), resulting in an average mineral oil content of recycled fibre folding boxboard and testliner or fluting. The replacement of the mixed RCP grade 1.02 with less mineral oil-contaminated RCP grades or even virgin fibres is considered on three different levels in scenarios 2a, 2b and 2c. The separated RCP collection for graphic paper products and packaging material is investigated in scenario 3a for a realistic assumption and in 3b as a hypothetic scenario for a complete separation. The conversion of mineral oil-containing printing inks by mineral oil-free inks is considered in the scenarios 4a in which 50% of the inks are substituted, 4b with a 100% substitution and 4c in which besides all inks, also all papermaking additives are substituted by the paper manufacturers. In scenario 6, the producers of board for

Table 5 Calculated scenarios

Option	Scenario	
As-is scenario	1	
Replace 1.02 by high-quality fibre stock	2a, b, c	(2a) Virgin fibre in folding box board only (2b) Grades 2.X, 3.X in folding box board only (2c) Virgin fibre in folding boxboard + testliner/fluting
Separate collection of packaging RCP	3a, b	(3a) To the feasible extent (INTECUS/PMV) (3b) 100% separation (theoretical scenario)
Conversion to MOSH/MOAH-free printing inks	4a, b, c	(4a) Reduction by 50% (4b) Reduction by 100% (4c) 4b + replacement of MOSH/MOAH-containing papermaking additives
Protective measures	5a, b	(5a) Bag in box (5b) Barrier coating
Apply flotation in stock prep.	6	(6) Efficiency 47%; losses 10%
"All paper makers could do"	7	(7) 6 + ban of all MOSH/MOAH in papermaking

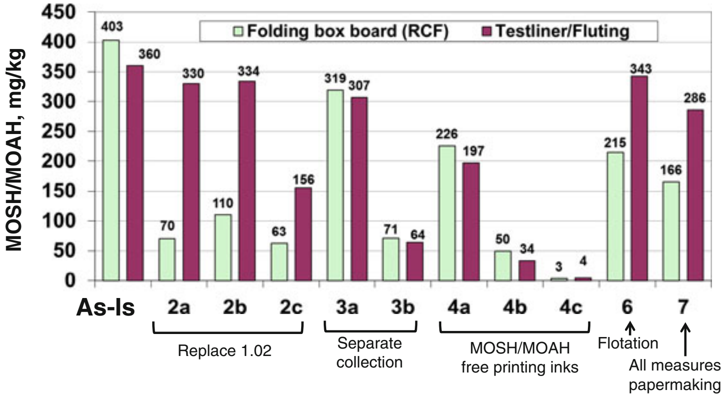

Fig. 1 Calculated MOSH/MOAH concentrations in board and testliner/fluting for different scenarios

food packaging will install a single-stage flotation process to reduce the mineral oil content, and in scenario 7, all paper and board manufacturers ban all MOSH/MOAH-containing additives in their production.

It becomes evident from Fig. 1 that from all the investigated measures, only the substitution of the mineral oil-containing inks by mineral oil-free inks will lead to single-digit MOSH/MOAH concentrations if additionally also papermakers will use mineral oil-free additives. All other measures will lead to such high mineral oil concentrations in the folding boxboard that it is estimated that the currently discussed limit values of MOSH and MOAH in foodstuff will be exceeded several fold by migration.

1: < 10 Mio € (Cost)
2: 11 – 50 Mio €
3: 51 – 100 Mio €
4: 101 – 250 Mio €
5: 251 – 500 Mio €
6: > 501 Mio €

As-Is scenario	1
Replace 1.02 by high quality fibre stock	2 a, b, c
Separate collection of graphical and packaging RCP	3 a, b
Conversion to MOSH/MOAH free printing inks	4 a, b, c
Protective measures	5 a, b
Apply flotation in stock prep.	6
“All papermakers could do”	7

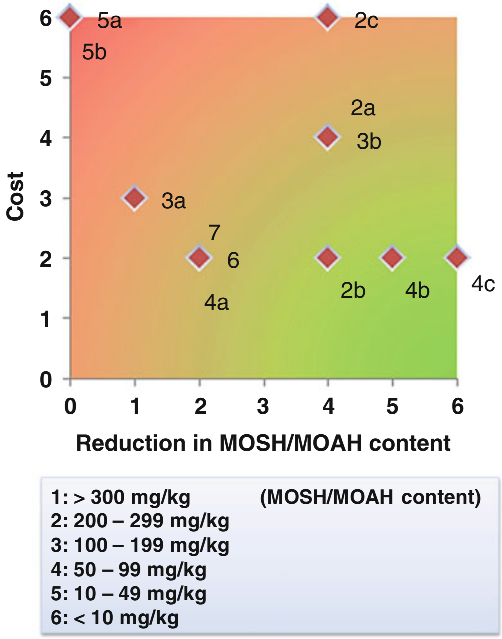

Fig. 2 Cost–benefit consideration of the evaluated measures

In Fig. 2, a consideration on costs and benefits is performed, which covers also the scenarios 5a and 5b of protective measures for the packed foodstuff by usage of inner bags or barrier coatings which do of course not reduce the mineral oil concentration in paper and board. In the diagram, this solution did contribute to the highest estimated costs of more than 500 Mio € without any mineral oil reduction. Similarly ineffective due to the high costs is also scenario 2c with the replacement of mineral oil RCP grades by virgin fibres. Clearly, the most effective in terms of MOSH/MOAH reduction is the substitution of the mineral oil-containing printing inks by mineral oil-free inks supported by the use of mineral oil-free papermaking additives (scenario 4c). Fortunately, this scenario does also belong to the most cost-effective one and should be preferred.

5 Conclusions

Recycling creates jobs and preserves resources such as raw material, energy and water. Wood is an important renewable raw material which is used in various areas of application and which is necessary for the paper industry to provide the required virgin fibres for the multiple use of the construction material paper. To cover the enormous paper demand in Europe, the paper recycling circuits have to be absolutely preserved. This means ultimately that the problem of mineral oil migration in foodstuff, primarily discussed in Germany until now, should be handled and solved on a European level. Thereby, the question to be investigated is what amounts of mineral oil are more or less already widely spread in our environment and to what extent foodstuff can be contaminated [32].

From the pros and cons of the discussed measures to solve the migration problems of mineral oil from packaging material into foodstuff, the following consequences in the opinion of the authors are derived:

- The substitution of recycled fibre-based boxboard for foodstuff and from corrugated boxes as transport packaging to virgin fibre-based products is impossible due to insufficient availability of fibres and of paper and board production capacity.
- The usage of RCP grades with less newspaper content for the production of folding boxboard alleviates the situation and helps to reduce the mineral oil concentration in the board. But it will not be a sufficient solution to decrease the mineral oil load in board by some orders of magnitude.
- The reduction of the mineral oil input during paper production by utilisation of mineral oil-free additives should be the responsibility of each paper manufacturer regardless of the type of the produced paper or board grade. This would be a contribution to keep the recycling loops as much as possible clean.
- Measures in RCP processing to reduce the mineral oil do not obtain the desired success so far. Development work on the finishing of board products with functional barriers is under progress. In both areas, further research needs exist. The use of inner bags as barrier against mineral oil migration is possible but cannot be used for all types of foodstuff. Here also exists research demand.
- The exchange of the printing process for newspaper to waterborne flexo or inkjet is no solution at the moment. A sufficient deinkability of those print products is not in sight. Large volumes of such print products would have significant impact on the recycling circuit of graphic paper products. The mass volume from which such effects occur cannot yet estimated.
- Finally, the conversion of mineral oil-based offset newspaper inks to mineral oil-free inks is the most promising option. In the sense of ecological actions, it is now the time to work seriously on this conversion which requires for sure further research needs. The developments on mineral oil-free inks stopped about 15 years ago have to be adopted on the new generations of offset printing machines. The deinkability of those inks causes promise to find fast industrial solutions eventually via a first step with mineral oil-reduced offset inks. Nevertheless, the deinkability found to be all right at that time has to be tested again.
- The utilisation of RCP as secondary raw material has to find a quantitative risk assessment in the future to establish meaningful limit values as basis for the development of e.g. elimination processes or barrier coatings.

The removal of harmful substances from a printing ink by substitution by another toxicologically less critical substance is not only in the responsibility of the printing ink manufacturers and developers but also in the responsibility of the publishers who have to use such inks for newspaper production. Finally, the conversion to mineral oil-free offset newspaper inks would be consistent with the next-to-last European Declaration on Paper Recycling 2006–2010 [33] which was signed by the whole paper chain. This declaration had the target to maintain and to strengthen Europe as a "global leader in paper recycling – in millions of tonnes and in knowledge". The last European Declaration on Paper Recycling 2011–2015 [34] was not signed anymore by the whole paper chain. The publishers refused the general target to support anything for using waste as a resource to build up a "circular economy". Nevertheless, with view to reduce the amounts of cost-effective available crude oil in the future, the development and the utilisation of inks without significant amounts of mineral oil seems to be a question of time and will bring back publishers to support the targets of the actual European Declaration.

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Proposed Plan for Disposal of Mercury-Bearing Lamps for India

Suneel Pandey, Rakesh Hooda, and Arabinda Mishra

Abstract The mercury-bearing lamps, towards the end-of-life, pose significant hazard potential due to the likely release of mercury. Though, these fluorescent lamps (FLs) release relatively less quantity of mercury when disposed as compared to other mercury-based products, they are still a concern due to the large and further growing number of FLs in service, particularly, in the domestic sector and their fragile nature.

At the end-of-life, compact fluorescent lamps/fluorescent tube lights (CFLs/FTLs) are either disposed in bulk (sold in auction) or disposed individually along with municipal waste. Proper and safe collection of these products would mean its intact collection, transportation, and recovery of different components including mercury. Currently, safe disposal is not practiced in any part of India. Presently, a fraction of the generated end-of-life FLs are being collected by the informal sector (junk dealers), largely from the large-scale consumers (industries and corporate). The lamps are then disassembled by crude methods into useful components such as glass tubes (glass and phosphor powder), aluminum end caps, polypropylene caps, and electronic ballasts (electronic components which contain metal).

An all India primary survey on the lamp users indicates that average replacement rate per household per year for CFLs and FTLs is about 1.26 and 1.05, respectively. The survey also indicated that majority of consumers are not willing to take the direct responsibility in funding system, therefore, a decentralized system of collection should work in Indian conditions. The recovery chain has to be clearly established with incentive-based roles identified for household consumers, retailers, and junk dealers. Further, the onward linkages must be assured so that the collected wastes are recycled and residues adequately disposed of.

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The proposed institutional framework for safe collection and recycling system has three subsystems – the Producer Responsibility Organization (PRO), the Producer Responsibility Fund (PRF), and the system's integrator. Keeping with the principles of extended producer responsibility (EPR), the institutional framework allocates financial responsibility for establishing PRF to the producers, and physical responsibility to the range of actors including the PROs, the collection agents, recyclers, urban local bodies (ULBs), central and state agencies, and finally the consumers. The system integrator works to furnish information at all levels to achieve transparency in the set-up.

The model for collection and recycling of used FLs can be rolled out in phases targeting the first 2 years a 35% recycling rate for waste lamps, 45% recycling rate in next 1 year, and 60% recycling rate in the following years. There are three scenarios discussed for implementation of lamps collection and recycling program at the national level.

A comprehensive public awareness campaign is needed to sensitize the range of actors to their roles and responsibilities. The awareness program should be started before undertaking the pilot so that potential recyclers and technology providers, NGOs, ULBs, private firms, as well as the manufacturers, sellers, and consumers of the FLs are conscious about the elements of the proposed master plan, its implementation, and the need for safe disposal of spent FLs.

Keywords Fluorescent lamps · Mercury dosing · Producer Responsibility Fund · Producer Responsibility Organization

Contents

1 Introduction

The release of mercury into the environment, its introduction in the biogeochemical cycle, and its concentrated propagation along the food chain due to changes in climate are a worldwide concern. The problem of mercury in the society is not new, it has long been considered as toxic element of concern owing to its mobility, volatility, persistence, and potential for bioaccumulation due to a number of environmental incidents related to it [1, 2].

Fluorescent tube lamps, compact fluorescent lamps (CFLs), and high intensity discharge (HID) lamps are the three most common types of lamps that use mercury. HID lamps, which include mercury vapor, metal halide, and high-pressure sodium lamps, are used for streetlights, floodlights, and entertainment, sports, and industrial lighting. The mercury content of spent fluorescent lamps globally has been reported to be between 0.72 and 115 mg/lamp with an average mercury content of about 30 mg/lamp depending on type, producer, and the year of production [3]. In India, the mercury content in the lamps is between 3 and 60 mg. Presently, India has no dosing standards for regulating the amount of mercury in FLs.

The mercury-bearing lamps, towards the end-of-life, pose significant hazard due to the likely release of mercury. As use of fluorescent lamps (FLs), including fluorescent tube lights (FTLs) and CFLs, is increasing due to being more energy efficient as compared to conventional incandescent lamps. Though, these FLs release relatively less quantity of mercury when disposed as compared to other mercury-based products, they are still a matter of concern due to the large and further growing number of FLs in service, particularly, in the domestic sector.

The FLs are fragile, low weight, and generated in a very high volume with comparatively less residual value at the end-of-life. The decentralized usage and involvement of multiple formal and informal actors in manufacturing and collection make the entire process of recycling more complex and challenging. The absence of safe disposal practices, suitable business model, appropriate policy, standard for dosing mercury, and performance standard for lamps exacerbate the nature of the problem. The present set-up of improper mercury management in the country and the ever-increasing number of mercury-bearing lamps justifies the exigency for environmentally sound management of mercury in the fluorescent lamp sector.

The objective of this research was therefore to develop a master plan for the safe management of end-of-life mercury containing lamps for the entire country. It encompasses detailed analysis of the complete system of logistics (collection, transportation, and safe disposal of end-of-life CFLs/FTLs), financing models, institutional mechanisms, policy framework, and issue of public awareness.

2 Present Status of Lighting Sector in India

An estimated 18% of the energy consumption in India is due to lighting. Growing environmental concern and heightened climate change awareness amongst public has prompted a trend of increased use of energy saving alternatives. This has led to a rapid growth in the consumption of fluorescent lights (CFLs/FTLs) relative to regular incandescent lamps. In India, fluorescent lamp sector has grown at a rate of about 26% since year 2005 with sales of CFLs and FTLs reaching 304 and 182 million pieces, respectively, at the end of year 2010 (Table 1).

Table 1 Annual sale of lamps in India (quantity in million pieces) (Electric Lamp and Component Manufacturers Association of India (ELCOMA) 2011)

Category	2005	2006	2007	2008	2009	2010
Incandescent lamps	711	757	779	734	766	797
Fluorescent lamps	180	186	190	186	179	182
Compact fluorescent lamps	67	100	140	199	255	304
Special lamps (HID)	10	14	17	21	18	NA

NA not available, *HID* high intensity discharge

Some of the key drivers responsible for a steady growth in the consumer base of FLs are:

- Government initiatives and programs generating greater awareness
- Rising household demand
- Huge energy-saving potential
- Better luminescence
- Longer life-span
- Lower cost over the life time as compared to incandescent lamps

The major challenges encountered in management of FLs are:

- Quantity of Hg dosing
- Issues with the safe disposal and Hg contaminated waste
- Influx from the informal market – substandard lamps being manufactured and distributed in a growing network
- Absence of regulatory framework for safe collection, recycling, and disposal

3 Current Management Practices in India

The main components of CFLs are glass tube (glass and phosphor powder), wire, aluminum cap, plastic, electronic blasts (electronic components) and in FTLs, it is mainly aluminum cap, glass tube, phosphor powder, LIW (lead-in wire) metal/filament metal. Fluorescent light bulbs contain mercury energized by electrodes to produce ultraviolet energy, which is absorbed by a phosphor coating on the glass tube to emit visible light.

The estimated weight of a typical CFL is 0.04 kg without base, which is expected to contain around 20% of waste (by weight) as mercury-contaminated waste. The typical 1.2-m fluorescent lamps contain approximately 0.26 kg of glass, 0.02 kg of combined metals, and 0.01 kg of phosphor powder. In these waste streams, the concern is waste mercury and the broken parts of the lamps contaminated with mercury.

It is estimated that about 192.7 metric tons (MT) of mercury was imported in year 2006–2007 in India. Lighting and electrical industry consumes only about 4% of total mercury consumed in India. Out of this, mercury used in lamps is only about 2%. The contribution of chlor-alkali industry and mercury-based battery sector is 16% each, thermometer and other measuring instruments (14%), thermostat (12%), and unknown sectors contributes about 38% mercury consumption in India [4]. The mercury released into the environment, from fluorescent lamp sector has been estimated at around 8.8 MT for the year 2009. Out of which approximately 3.5 MT of mercury is estimated to be released into air (with the assumption that all mercury are released as elemental vapor). A study reports that between 17% and 40% of the mercury from the broken FLs is released in the atmosphere during a 2-week period immediately after breakage [5]. Moreover, there are, reportedly, no imports of FTLs into the country, whereas there is an import of CFLs and CFL components to the tune of about 300 million units per annum at present. Thus, the mercury content from these imported lamps has been estimated in the range of 3.0–3.6 MT of Hg/annum, considering that they contain 10–13 mg/CFL [6].

In India, for mercury dosing, generally CFL manufacturing facilities have pill dosing system, whereas most FTL producers have liquid dosing system, which is expected to result in higher (than required) mercury consumption. The FL manufacturing units have varied level of waste generation and management practices. The mercury-bearing waste is either sent to licensed disposal facility or dumped at some site near the unit. There has not been enough thrust given to recovery of mercury due to its low cost.

The used FLs, though containing mercury, are not classified as hazardous wastes, as per the Hazardous Waste (Management, Handling and Transboudary) Rules, 2008. In the E-waste (Management and Handling) rules, 2011, notified by the Ministry of Environment and Forests, mercury is categorized under hazardous substances and the threshold limit for its use has been limited to $\geq 3\%$ to $\leq 0.25\%$ but lighting products are excluded from ambit of E-waste rules due to their fragile nature.

Currently, at consumer level the used lamps are collected by the *kabadiwalas*[1] from households. Metal components are separated and broken glass components are thrown in the garbage bins and finally reaching municipal garbage dumpsites, thus contaminating air, water, and soil. If not broken to recover the aluminum caps, they break either in transit to solid waste bins (provided by local civic authority) or final disposal site. In some cases, the glass component is sold to the glass recyclers. All these operations take place in unorganized sector.

Few recyclers have taken the initiative to collect the spent FLs from bulk consumers along with E-waste material to sustain the relationship with their customers. The crushing practice at the manufacturing or recycling units is performed employing bulb eater/vacuum chambers to reduce the volume of waste and to avoid the breakage of glass during transit phase. These crushing processes virtually capture and neutralize all the mercury vapors released during the controlled crushing of FLs.

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[1] Junk dealers.

4 Market Linkages

At present, a fraction of the generated end-of-life FLs are being collected by the informal sector (*kabadiwalas*), largely from the large-scale consumers (industries and corporate sectors). The lamps are then disassembled by crude methods into useful components such as glass tubes (glass and phosphor powder), aluminum end caps, polypropylene caps, and electronic ballasts (electronic components which contain metal). The major processing hubs for the various components exist as follows:

- Glass: Motinagar in Delhi (collection of glass) and Firozabad in Uttar Pradesh (washing and crushing of glass)
- Metal: Moradabad in Uttar Pradesh (obtaining metal from Printed Circuit Boards)
- Polypropylene: Mundka in Delhi (converting into granules)

After processing, the components are usually sold to the industrial clusters which recycle these components. The existing markets for the various components are the following:

- Glass: Firozabad (Uttar Pradesh)
- Metal: Moradabad (Uttar Pradesh)
- Polypropylene: Bhiwani (Haryana), Khalilabad (Uttar Pradesh)

The various components are usually delivered to the manufacturers in the following form:

- Glass: cleaned (without phosphor powder and mercury) and crushed
- PCB intact: as such (for reuse purpose)
- PCB broken: metal is usually extracted by heating and sold to the manufacturers
- Polypropylene: granulated form

The typical existing costs for the various lamp components in the informal market are:

- Glass: €0.029–0.036 per kg (without washing and crushing), €0.062 per kg (after washing and crushing and including transport from Delhi to Firozabad)
- Polypropylene : €0.175–0.365 per kg
- Metal : €0.014 per PCB from a typical CFL
- PCB intact (for reuse): €0.073–0.145 per piece

5 Review of International Practices

Environmental and health considerations and other perceived risks have led many countries to adopt a policy for safe management of mercury in fluorescent lamps. For example, USA, Germany, Sweden, Finland, Japan, China, Taiwan, Hong Kong are some countries that have initiated programs and achieved varying degree of success in collection and recycling/safe disposal of used fluorescent lamps over the past decade. The roles and responsibilities of different stakeholders (such as the producers, retailers, municipalities, consumers) in the collection and recycling programs and the financial and institutional mechanisms vary from country to country.

European countries follow the policy of EPR for dealing with waste electrical and electronic equipment, as per the WEEE Directive 2002/95/EC. Following the issuance of the Directive in 2003, several countries framed national laws which initially covered equipment such as refrigerators, air conditioners, computers, and were later extended it to the management of used FLs. For example, Germany framed the "Recovery and Disposal Act" under the "Law of Waste Production and Consumption," for recycling used FLs in special lamp recycling facilities. As per the "Waste Ordinance" in Sweden, the responsibility for collection, treatment, recycling, and disposal of used FLs rests with the producers. In Finland, the municipalities have an obligation to arrange collection of FLs and other Hg containing wastes from households, and the waste lamps are treated only by authorized hazardous waste handlers.

The concept of EPR, around which the WEEE Directive is framed, essentially requires that the responsibility of the producers extends beyond manufacturing to environmentally sound management of their end-of-life products. As producers may not always have the capacity to undertake full physical and financial responsibility, models of shared responsibility are most prevalent. Producers may enter into an agreement with the municipalities or enlist distributors and retailers to collect the waste products, and may contract with a recycling firm for their safe disposal. In some countries, Producer Responsibility Organizations (PROs) have been formed as third party organizations to allow producers to collectively manage the take-back (and often arrange for the treatment) of products. Most PROs in operation till date collect a fee directly from the producers based on a specific fee structure, ideally designed to reward those producers who move to achieve EPR policy goals and objectives. Often a trademark is established for the PRO and the producer pays a fee to carry the trademark on the product. PROs can also have various functions extending beyond the management of the take-back, such as education and training of producers and consumers, collection of fees, etc. These models of EPR are being implemented for collection and recycling of a variety of electrical and electronic products, as well as packaging materials in Europe and some other countries like Japan.

In contrast to EU, USA has an independent market-oriented system, where the consumer is required to pay money for deposit, treatment, and disposal at the centers recognized by the concerned regulatory authority. Used FLs are covered under the Universal Waste Rules, which govern hazardous substances that have been commonly thrown by households and businesses into the municipal waste streams. The generators of such universal wastes are allowed less stringent standards for collection, storage, and transportation. However, they must still comply with the full hazardous waste regulatory requirements for recycling, treatment, and disposal.

Some of common approaches for collection and recycling of FLs in the USA include the following:

- Mail-back programs for recycling out-of-service CFLs are being implemented for consumers that do not have access to a collection site, or other recycling service. To facilitate the mail back, manufacturer-sponsored lamp recyclers' kits are sold at a reasonable price to consumers. An advantage of the mail-back system is that in rural areas, where people may be far from a retail collection center, there is access to a post office or mailbox. The United States Postal Service (USPS) is currently piloting a CFL recycling program for consumers. The USPS is working with Osram Sylvania (a lighting manufacturer) and Veolia Environmental Services (a mercury lamp recycler) to help consumers properly recycle spent CFLs through the mail in prepaid packages specifically designed for the product. The USPS has over 37,000 retail outlets, post office locations and over 300,000 drop boxes accessible to residents in the USA. Such widespread convenience could make it easy for consumers to recycle CFLs because they could choose a drop-off location that is convenient for them. The USPS offers homeowners free pick-up and delivery service. Mail carriers pickup and deliver the prepaid packages from the consumer free of charge. The postage is paid by the recycler upon receipt of the item.
- Collection programs at retail and wholesale locations offer consumers the ability to deposit their end of use CFLs at designated locations. Utility-sponsored collection programs may also support collection sites at retail or other locations. These are then sent to recycling centers.
- Publicly sponsored programs, such as household hazardous waste (HHW) collection facilities, municipal collection sites, and curb side recycling services also target CFL recycling for consumers. Depending on the program, these services may or may not include a fee. The programs which are free to consumers generally are funded either by energy saving fund or environment fund (e.g., part of solid waste tipping fee). Long-term sustainability of such programs, however, remains an issue.
- Another interesting development in the USA is the recent passage of a law by the state of Maine for management of mercury in end-of-life CFLs [6]. The law is intended to provide consumers with convenient recycling opportunities, with the costs shared by the lamp manufacturers and others (Box 1).

Box 1: Lamp Recycling Legislation in Maine, USA [6]

The Maine legislature recently enacted a bill, *Legislative Decision* (LD) 973, to require CFL bulb manufacturers to share the costs and responsibility for recycling mercury-added bulbs. The law requires manufacturers that sell or distribute mercury-added lamps in Maine to implement an approved collection and recycling program for mercury-added lamps sold or distributed for household use by January 1, 2011. The approved recycling program(s) will be free to consumers and will encourage recycling of CFLs and other mercury-added lamps by offering convenient collection locations throughout the state (including municipal collection sites). Provisions for providing education and outreach to consumers are also included. Similar legislation has been introduced in other states, including Massachusetts.

Several other countries in the Europe and Asia also have appropriate legislation and programs for managing waste FLs. These initiatives include the following:

- Japan follows the "Law for Effective Utilization of Resources," with the collection of used lamps through local governing bodies and treatment/disposal through common authorized lamp recycling facilities.
- The "Waste Disposal Act" is implemented in Taiwan for the recycling of used FLs. As per the Act, the retailers are responsible for the operation of collection centers, whereas authorized recycling facilities are responsible for the lamp recycling/disposal process.
- Sunshine Lighting Ltd. (a lamp manufacture in Hong Kong and China) piloted a CFL recovery initiative for the general public in November 2007. The program was called the "Save the Earth Energy Saving Lamp Recycling Campaign," and consumers were allowed to bring in their out-of-service CFLs to any Japan Home Centre (a local hardware store chain) for recycling. To encourage people to continue to use more energy efficient CFLs, Sunshine also provided €0.523 cash vouchers for use towards the purchase of new CFLs.
- In Hong Kong, the "Fluorescent Lamp Recycling Programme," was launched in March 2008, providing households with free collection and recycling for all used mercury-containing lamps, including CFLs. The program is a voluntary Product Responsibility Scheme (PRS) that is funded by 15 members of the lighting industry, and is supported by the Government of Hong Kong's Environmental Protection Department (EPD), and other nongovernment environmental organizations. Under this program, manufacturers and suppliers take responsibility for the proper management of their end-of-life products, such as funding and organizing a recycling program.
- The current practices for collection, treatment, and disposal of used FLs, as adopted by various countries, are summarized in Table 2.

The review of international practices has brought out several aspects that are important for designing a collection and recycling program for mercury bearing waste lamps:

- In developed economy, the product flow chain involves a range of actors – manufacturers, distributors, retailers, household, and bulk consumers – all or some of whom could potentially play a role in the return flow of waste lamps to recycling facilities. In Europe, the preferred system for collection and recycling is based on EPR. The used lamps are either collected by a representative of manufacturer or municipal waste collection infrastructure is used for the

Table 2 Summary of existing collection and recycling schemes [7]

#	Country	Collection of used lamps	Disposal/ recycling	Regulation	Benefits/issues
	Developed countries				
1	USA	Generator has to hand over these to the handler/ authorized recycler	Authorized recycling units	In 1999, FLs were included as Universal Waste under 40 CFR Part 273	Increasing numbers of CFLs have been collected; residents prefer retain-based recycling program, if the service is available for free. However, long terms sustainability of the program remains a suspect if the source of funding is government
2	European Union	Producers to set up collection system for households and other end users	Authorized treatment facility	WEEE and RoHS Directives	Designated collection facilities are preferred as per the directives of WEEE
3	Germany	Collection centers	Lamp recycling facilities	Recovery and disposal act	2006 target of recovery rates of 80% for CFLs has been achieved
4	Sweden	Producer's responsibility for the collection, treatment, and disposal	Producer's responsibility for recycling	Waste ordinance	N/A
5	Russia	N/A	N/A	Federal law – waste of production and consumption	N/A
6	Taiwan	Retailers as collection centers	Authorized recycling facilities	Waste Disposal Act	85% recycling has been achieved through mandatory recycling program

(continued)

Table 2 (continued)

#	Country	Collection of used lamps	Disposal/ recycling	Regulation	Benefits/issues
7	Finland	Municipalities have an obligation to arrange collection of CFls and other Hg containing wastes from households	Waste lamps may only be treated by a company authorized for handling hazardous waste	WEEE Directive	N/A
8	Japan	N/A	N/A	Law for Promotion of Effective Utilization of Resources. Some cities insist on bin separation	N/A
9	South Korea	N/A	N/A	No legislation but some cities insist on bin separation	N/A
10	Australia	Used lamps are dropped at designated retailers	Pilot recycling in operation	No legislation or practice of C&R	Currently most of the lamps are disposed in the landfill in Australia
11	Russia	N/A	N/A	No legislation or practice of C&R	N/A
	Developing countries				
12	China	N/A	N/A	Law of Environmental Protection, fluorescent lamp treated as nontoxic	The recycling program is in early stages

purpose. Whereas in USA, local governments have sometimes funded recycling activities by setting up environment fund for the purpose. The long-term sustainability of such activities is however yet to be established especially when funding from such source is gradually withdrawn. Thus in Indian context, a variety of institutional models are possible for a collection and recycling (C&R) program and an appropriate model may be selected based on local conditions and preferences, including stakeholder perceptions and willingness to participate.

- Incentives may be built into the system to enhance the participation of various actors.

- Other than the few voluntary initiatives, C&R programs in various countries are supported by laws specifically mandating recycling of fluorescent lamps. Legislative back up is therefore preferable for an effective program.
- The most successful waste lamp recycling efforts employ a variety of approaches. Countries that offer a variety of recycling opportunities for consumers appear to be able to collect and recycle the greatest numbers of waste fluorescent lamps.

The primary survey also revealed information on rate of replacement (number of CFLs and FTLs replaced in 1 year) shows that mean number of CFLs replaced in the past 1 year is 1.26, varies from less than one CFL in Bangalore to two CFLs in Ahmedabad. The corresponding figure for FTL is 1.05 which varies from less than one in Bangalore to two FTLs in Ahmedabad.

6 Proposed Plan for Safe Disposal

6.1 Suggested Collection and Recycling

The challenge in setting up a country-wide collection and recycling mechanism for spent FLs lies in the highly fragile and dispersed nature of the waste stream. The primary survey conducted by researchers has brought out the fact that the average replacement rate for CFLs and FTLs is about 1.26 and 1.05, respectively, per household per year. Thus, the small amount of waste generated by a large number of households and bulk consumers needs to be collected intact to minimize the risks of mercury pollution. Further, the onward linkages must be assured so that the collected wastes are recycled and adequately disposed of.

Therefore, after due consultation with the experts in the field and review of available C&R systems, it is proposed to tackle the end-of-life FLs in two ways: (1) deploy safe, fixed, and mobile lamp crushing systems to capture the mercury and reduce the waste volumes before transportation; and (2) feed the crushed material and other components into a suitable recycling and recovery system to assure safe management. The review of available technologies has brought out two types of technologies that could be used in the proposed C&R system:

- *Drum Top Crushers* (*DTCs*) are available in the market for crushing the lamps and capturing the mercury in a safe and contained manner. The full and sealed drums along with filters need to be transported onward to a recycling plant. The cost of the DTC is about €7,300, whereas the operational costs (for replacement of filters, drums, etc.) are in the range of €0.01–0.03 per lamp. The DTCs have a capacity of about 3,000 crushed CFLs or 1,000 crushed FTLs per drum.
- In a *recycling plant*, the recyclable materials (glass, metal, plastic, phosphor powder, mercury) can be separated and safely recovered. Recycling plants compatible with the DTC are available in the market for €0.6 million, with a capacity to process 5 drum loads (1,500 + kg) of crushed lamps per hour (in excess of ten million lamps per annum). Indicative operational costs, excluding

logistics and collection, are around €0.007–0.014 per lamp. Some plants fit in an area of 7.5 × 13.5 m and could be sited in an enclosed building with good ventilation.

The use of DTCs would enhance the collection efficiency of spent FLs, reduce the volume of waste (mainly FTLs), avoid releases of mercury to the environment from breakage of glass during transit, allow safe storage, and minimize the transportation costs. The DTCs could be deployed by collection agents to residential locations, placed at dedicated collection centers or retail outlets, or housed in bulk consumer locations. The sealed drums with the crushed materials and mercury filters could be stored until sufficient quantity is reached, and then transported to the nearest recycling facility. The recycling plants would separate the recyclable materials, and as established in this study, these materials could be sold in the market, thus enabling some degree of cost recovery.

The multiple modes of collection are required for achieving the closed-loop flow for lamp recycling. These modes could be site-specific cost-effective blend of various options as shown in Fig. 1a, b. The consumers varied from household ones in urban and rural areas, bulk consumers, and usage in eating joints across the National Highways and also in weekly *hats* (local weekly market). The entire setup of C&R can be accomplished through strong mass public awareness programs to operationalize the system in the region which is mandate of PRO. The collection agents and aggregation and transport system would be physically established by PRO. The collection agents could be the local bodies, NGOs, or private entities, and may engage *kabadiwalas* for door-to-door collection. Alternatively, the household consumers could be incentivised to bring the spent FLs to the mobile van and other dedicated collection centers and eventually to the DTCs, whereas the bulk consumers could be mandated to have their own DTCs. As depicted in Fig. 1a, the proposed C&R mechanism provides the necessary linkages that are crucial for assuring the viability of the FLs recycling facilities.

It is suggested that the recycling plants may be set up at existing Treatment Storage and Disposal Facility (TSDF) sites for hazardous wastes. There are currently 25 such sites in India spread across 11 states. The state-wise distribution is shown in Fig. 2.

6.2 Suggested Institutional Framework

Based on the results of the primary survey and consultations at various levels, one of the findings of this study has been that in order to operationalize a C&R mechanism for spent FLs, there is a need for an entity that would take the direct physical responsibility for such a system.

The proposed institutional framework for the master plan is therefore centered on the concept of a PRO – an entity which is intended to have the physical responsibility for the FLs recycling mechanism by providing forward and backward

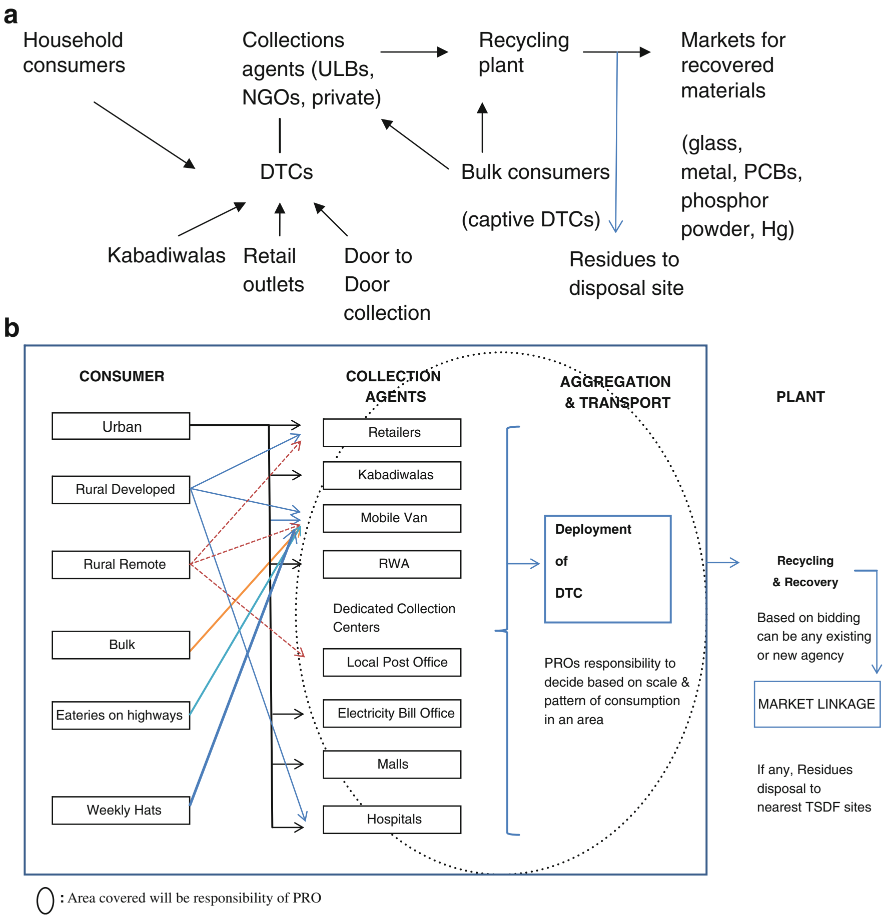

Fig. 1 (**a**) Proposed collection and recycling mechanism. (**b**) Detailed collection and recycling mechanism. The *oval shape* area recovered will be the responsibility of PRO

linkages with all other actors involved in the process. Forward looking manufacturers in the developed countries realizing that their expertise is not in the waste management, have instead facilitated the process. Such PROs have been formed in other countries as third party organizations to manage and collect the end-of-life products in lieu of each producer establishing its own separate system. The establishment of PROs and their functioning may be as follows:

- Any NGO, private firm, or ULB may form a PRO. The selection would be through a bidding process wherein the prospective agencies would be evaluated based on proposals (technical and financial) submitted by them in response to a call for proposals.

Fig. 2 State-wise distribution of TSDFs sites in India (*source*: Central Pollution Control Board, India)

- It is envisaged that there could be several such PROs throughout the country (at least one per region) with in-built flexibility for each PRO to design and operate their C&R mechanism according to the region's needs.
- The PROs would enter into contracts with collection agents and establish a system (financial and physical) for assuring a reliable flow of end-of-life FLs to the recycling facilities.
- The PROs may deploy mobile technology (such as the DTCs) for collection and aggregation of used FLs from dispersed sources. The DTCs may be used in door-to-door collection through mobile van, or placed at dedicated collection centers or retail outlets. Appropriate minimum collection targets may be agreed and written into the contracts of the collection agents. The system may be incentivised to enhance collection beyond the minimum targets. The PRO/collection agents may also integrate the informal sector into their operations.
- The PROs would enter into a contract with a recycling facility for recovering different components of the used FLs (glass, aluminum caps, mercury, phosphor powder, and plastic). The recycler may charge a gate rate to the PRO based on the volume of waste FLs delivered. The gate rate may be fixed to cover the O&M costs, whereas other government measures (such as capital subsidy, land at concessional rates) may be undertaken to assure the viability of the recycling facility. This recycling facility may be incentivised by sale of recovered

materials to prospective buyers on a profit sharing basis between the PRO and the recycler.

- A monitoring system would be put in place at the state level to monitor the functioning and utilization of funds by the PROs, e.g., State Pollution Control Boards (SPCBs).
- PROs may also have various functions extending beyond the management of the C&R mechanism, such as for education and training of producers and consumers.

In order to finance the operation of the C&R system by the PROs, it is suggested that the producers (manufacturers and importers) would bear the part of the financial responsibility by contributing to a *Producer Responsibility Fund* (PRF) that would finance the costs of the establishing and operating PROs. The fund would primarily cover the cost of hardware and O&M. It is expected that like other urban waste management projects, the required land to PROs would be provided by local government under long lease agreement. The Central Government also needs to relax the import duty for the imported equipment to make the project financially attractive to the project developers.

The following steps are suggested for the establishment and operation of the PRF:

- The fund would be managed as Trust Fund for executing the master plan for used lamp recycling and may be rested with a fund managing institute (e.g., State Bank of India or Industrial Finance Corporation of India).
- The Interministerial steering committee can oversee the work of fund managing institute. Members in the apex body named as Interministerial steering committee could be nominated from Ministry of Environment and Forests, Ministry of Power, Ministry of Commerce, Bureau of Energy Efficiency, Central Pollution Control Board, ELCOMA, and a technical consultant.
- The producers would contribute to the fund based on the number of FLs produced.
- Bureau of Energy Efficiency may establish a trademark for the fund, and producers contributing to the fund may be allowed to carry this trademark on their products.
- The fund managing institute, in consultation would approve the disbursement of funds to PROs based on the feasibility of proposals received by the state agencies from prospective organizations.

The third subsystem of this institutional framework is a *System Integrator*, which is envisaged as an IT enabled system for provision of real-time information on the flow of materials. Thus, information on collection agents, recyclers, and buyers and sellers of recovered materials would be fed into a Management Information System by appropriate agencies (service providers) so as to enable identification of the right market opportunities, and for fund managing institute and SPCBs to enable monitoring of PROs functions. The system would:

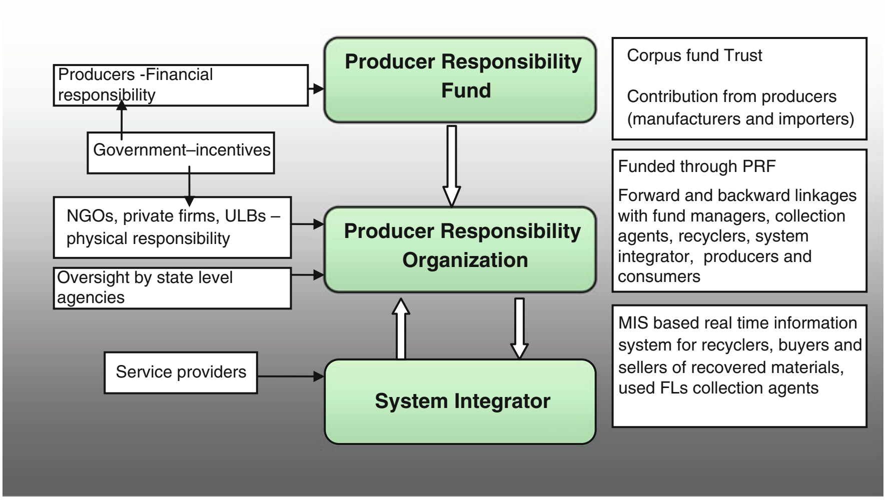

Fig. 3 Institutional frameworks for safe management of end-of-life FLs

- Assist collection agents in identifying potential destinations for the used FLs and necessary transportation requirements.
- Provide information to recyclers on availability of input materials for their facilities and market opportunities for the recovered materials.
- Provide information to buyers and sellers on availability of recovered materials at various lamp recycling facilities.
- Gradually induce development of a market-based system for fluorescent lamp recycling.
- In addition, System Integrator (SI) would also make available the report on environmental performance of PROs to SPCB on regular basis and fund managing institute.

The proposed institutional framework with its three subsystems – the PRO, the PRF, and the SI – is depicted in Fig. 3. In keeping with the principles of EPR, the institutional framework allocates financial responsibility to the producers, and physical responsibility to the range of actors including the PROs, the collection agents, recyclers, ULBs, central and state agencies, and finally the consumers.

To set up and operationalize DTCs, an estimated time of 2–2.5 months would be required by PROs once they are selected. To import the recycling system, erect the commission in India, the estimated time would be around 4–5 months. It is preferred that if DTCs are imported in first instance and made operational as in initial months, there would not be any feed stock available for the recycling unit. Once their operation is stabilized, one can import recycling unit and commission it. These facilities would be required to obtain necessary consent to establish and operate and also to obtain authorization from respective SPCBs in the state where they are commissioned.

The pilot runs would provide further real-time cost inputs for costing activities like collection, setting up of collection centers, and transportation (including investing in infrastructure). These costs would be used to update the proposed financial model. The model may then be rolled out in phases over the rest of the country targeting in the first 2 years a 35% recycling rate for waste lamps, 45% recycling rate in next 1 year, and 60% recycling rate in the following years. There are three scenarios discussed for implementation of lamps collection and recycling program at the National level.

Scenario 1: The first phase of the roll out would be of around 3 years (2013–2016). It would cover mainly the class I cities.[2] It is desired that the collection and recycling program uses the best demonstrated available technology (BDAT) option which are – DTCs to collect and crush lamps without releasing mercury in transit and recycling facility having mercury recovery facility.

To kick-start the process, various government and nongovernment agencies will have to undertake the following functions:

1. Constitution of an interministerial working group with members as stated earlier in the chapter.
2. The Central Government (Ministry of Environment and Forests) will have to come out with enabling legislation to facilitate collection of cess for establishing PRF, its management by nongovernment fund management entity like Industrial Finance Corporation of India (IFCI), layout procedure for environmental performance of PROs and other relevant agencies to undertake collection, transport and recycling of lamps, and spell out roles and responsibilities of Central and State Pollution Control Boards and Committees (SPCBs/PCCs) in monitoring the collection and recycling process. The Government also needs to aggressively start awareness and capacity building of stakeholders, especially the users about the hazards associated with improper handling of fused fluorescent lamps and need to drop at responsible collection centers as mandated by PRO.
3. The State Government to invite bids for establishing collection and recycling facility through involvement of PROs either at the regional level or at city level depending on the penetration of CFLs/FTLs and size of the city. The bid would also be required for establishing recycling unit on regional basis. The PROs would enter in contract, with recycler for recovery of resources and disposal of hazardous waste to nearest TSDF site in a manner prescribed by SPCBs/PCCs.
4. Central Pollution Control Board to issue necessary authorization, as per the enabling legislation.
5. SPCBs to issue consent to establish and operate PROs and recycling units and monitor their environmental performance on regular basis as the mandates of Air, Water, and Environment (Protection) Acts.
6. Any NGO, private firm of ULB will be eligible to bid as PRO, provided it employs the same technologies as specified as BDAT above for collection and

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[2] Cities with more than 50 million population.

recycling. The selection of PRO for a region or a city will be on the basis of bidding process. The PRO would set up collection and recycling system and simultaneously invest in public awareness and capacity building.

The successful roll out of first phase would depend on the following preroll out activities:

1. Constitution of fund handling entity and operationalization of PRF.
2. Notification and enabling legislation and public awareness program.
3. Operationalization of DTCs to facilitate collection of fused fluorescent lamps.

In this phase, the Government has to play more proactive role in the facilitation of above activities.

Scenario 2: The second phase of the roll out would be around 5 years (2016–2020). It is expected that in this phase, the Bachat Lamp Yojana[3] project for distributing CFLs to replace incandescent lamps would have peaked. Collection efficiency for fused lamps which at the start of the project is assumed to be around 35% would increase to around 60% due to enabling legislation support and aggressive public awareness campaigns across the country. The technology deployed for collection and recycling would be well established in this phase and performing to their rated efficiency. It is also expected that the compliance to legislation would also improve.

The Central Government's role in this phase would gradually reduce and shift from regulatory to monitoring and compliance-related functions. The role of State Governments and PROs would increase due to larger number of cities/regions participating in collection and recycling program.

Scenario 3: This phase would roughly comprise of post-2020 period. In this period, the key event expected to happen would be larger penetration of light emitting diode (LED)-based lamps as their prices would become competitive as compared to present prices of CFL. The prices of CFL as a result are expected to fall further. It is thus desirable to implement the master plan in phases, as when the LED lighting becomes affordable at competitive price, the off take of CFLs/FTLs would slow down and plateau out. As LED lamps do not contain mercury, the elaborate recycling system would not be required for the end-of-life LED lamps.

United Nations Environment Programme (UNEP) has also launched an initiative for global phase out of mercury in different products including the lighting and healthcare products. Participating governments have to prepare and implement time-bound action program for reduction and eventual phase out of mercury. This would also have an impact in market for CFLs and FTLs and is likely to hasten the introduction of LED-based lighting products.

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[3] The Central Government's subsidy program to replace incandescent lamps with CFLs.

7 Conclusions and Way Forward

Energy efficient lighting provides significant energy savings in households, and public and commercial facilities. However, the fluorescent lamp sector uses a significant quantity of mercury warranting proper management; therefore policy needs to be in place for safe management of waste fluorescent lamps.

Several countries across the world have adopted policies and programs in this regard. Technologies are also available in the market for crushing waste lamps in a safe and contained manner, and for recovering materials of value such as glass, PCBs, phosphor powder, and mercury. Recycling technologies are considered to provide cheaper and safer alternatives for management of waste lamps, as compared to conventional incineration and landfilling.

The challenge lies in collection of a highly fragile and dispersed waste stream. For recycling facilities to be viable there is a need to assure a reliable inflow of waste lamps to these facilities. The collection of end-of-life lamps in lighting industry, however, is more difficult as compared to other recyclable wastes as the recycling costs are not met by the sale of the recovered materials, resulting in little incentive for the seller (waste generator) and collector (or recycler) to participate in a C&R program. A sound financing mechanism is therefore needed, along with incentives and regulatory measures for various actors to participate and undertake physical responsibility in a C&R program.

The master plan proposed herein suggests setting up of decentralized PROs to undertake physical responsibility for operating flexible and locally suited C&R programs for waste FLs in which a range of other actors may be integrated (e.g., consumers, local bodies, *kabadiwalas*, retailers, etc.) depending on local preferences. The master plan also requires setting up of a centrally placed PRF, with financial contributions from the producers, for financing the costs of the PROs. A third component of the master plan is the System Integrator, which is envisaged as an IT enabled system managed by service providers for provision of real-time information on market opportunities for collection agents, recyclers, and buyers and sellers of recovered materials.

Preliminary cost estimates suggest that a moderate size PRF may be able to finance the recurring costs of the C&R program (at 35%, 45%, and 60% recycling target for the first, second, and third year, respectively, in the initial phase), while also being able to achieve some degree of cost recovery through the sale of recycled materials. The capital and land cost for the recycling plants would, however, need to be financed by the government through subsidies and other means.

It is however, desired to implement the master plan in phases, as when the LED lighting becomes affordable at competitive price, the off take of CFLs/FTLs would slow down and plateau out. As LED lamps do not contain mercury, the elaborate recycling system would not be required for the end-of-life LED lamps.

A comprehensive public awareness campaign would be needed to sensitize the range of actors to their roles and responsibilities, so that potential recyclers and technology providers, NGOs, ULBs, private firms, as well as the manufacturers, sellers, and consumers of the FLs are aware of the proposed master plan, its implementation, and the need for safe disposal of spent FLs.

It should be recognized that while safe management of waste mercury-bearing lamps is a pressing need, supplementary measures to improve technology, reduce mercury content, standardize the mercury dosing methods, and further improving the performance standards (life span) of fluorescent lamps are equally important in managing the environmental risks in this sector.

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Study of the Substitution of Fossil Fuels by RDF Produced from Municipal Solid Waste of Hanoi: A Case Study

Nguyen Thi Diem Trang and N.B. Ngoc

Abstract Looking for the possibility of using Refused Derived Fuels (RDF) in the substitution of fossil fuels is one of the main subjects in the Waste to Energy aspect. Therefore this study has been taken in this direction. The influence of waste composition on RDF quality produced by Dry Stabilization Process (DSP) and the evaluation of CO2 emission of this product were undertaken.

Input material for RDF with different percentage of paper, textile, nylon bag and bio-waste were taken from municipal solid waste of a district in Hanoi. The influence of this input on RDF quality resulted from 3 test samples (R1, R2 and R3). During the composting step stabilization time, temperature, leachate volume and the water content were noticed. As a result, heating value of dry sample and wet waste was determined. Gross heating value of this produced RDF was compared with it of fossil fuel and RDF from other studies. Thereafter, total Green House Gases (GHGs) estimation from both pre-treatment of RDF and RDF utilization steps were calculated.

Keywords Refused Derived Fuels (RDF), Dry Stabilization Process (DSP), Municipal Solid Waste (MSW), Waste composition, Waste amount, Heating value, Emission Factor (EF)

Contents

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1 Introduction

Looking back in the history, energy consumption of the world is constantly increasing. The trend of energy consumption in the world is shown in Fig. 1. In this diagram, oil, coal and natural gas has the largest consumption share of world primary energy, oil, coal, and natural gas are the three main sources.

That is why, since 1969, the global CO_2 emissions from energy use grew at the fastest rate [1]. Therefore, renewable fuels (including biofuels) have been grown fast which are expected to grow at 8.2% p.a. from 2010 to 2030 [2]. One of the new energy sources is fuel from waste.

Therefore, Waste to Energy (WtoE) becomes a hot topic in energy aspect of many countries. WtoE provides not only an energy source but also a contribution to solve the problems of waste management. In this sector, generating quality fuel from waste and controlling environmental impacts during the production process have been the main concerns for developing country such as Vietnam.

This study aims to look for the possibility of producing refuse-derived fuel (RDF) according to dry stabilization process (DSP) and investigates the possibility of substitution of fossil fuels by RDF. With that, this study tried to assess the risk of CO_2 emissions from RDF produced by MSW Hanoi, compared with CO_2 emissions from fossil fuels.

2 Problem Definition

2.1 The Increase of Energy Consumption in Vietnam

In 1990s, electricity consumption per capita in Vietnam increased rapidly since the country changed to market economy. In only 18 years since 1990–2008, electricity consumption per capita in Vietnam increased from 98 to 810 kWh, nearly ten times greater (see Fig. 2).

Moreover, Vietnam population is continuously increasing in the last decade. That situation together with the improvement of living standard pushes more pressure to energy supply. Primary energy consumption, excluding biomass, grew at an annual

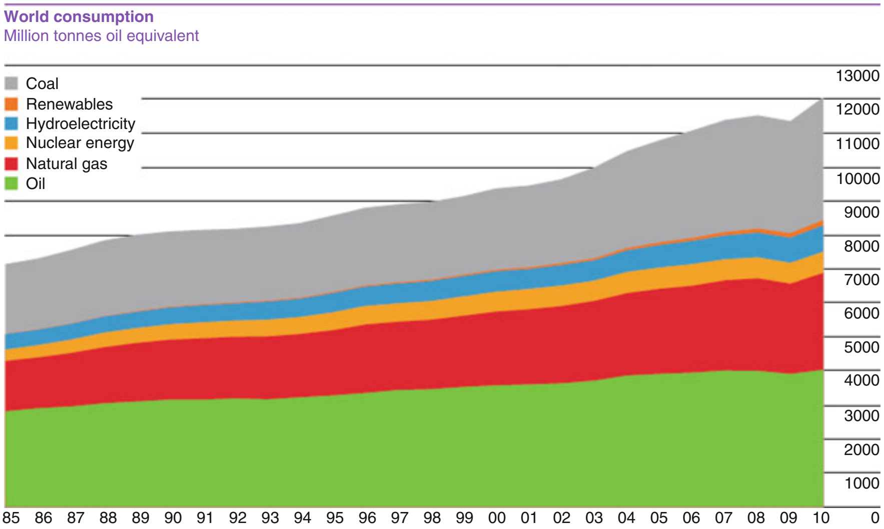

Fig. 1 Global energy consumption from 1985 to 2010 [1]

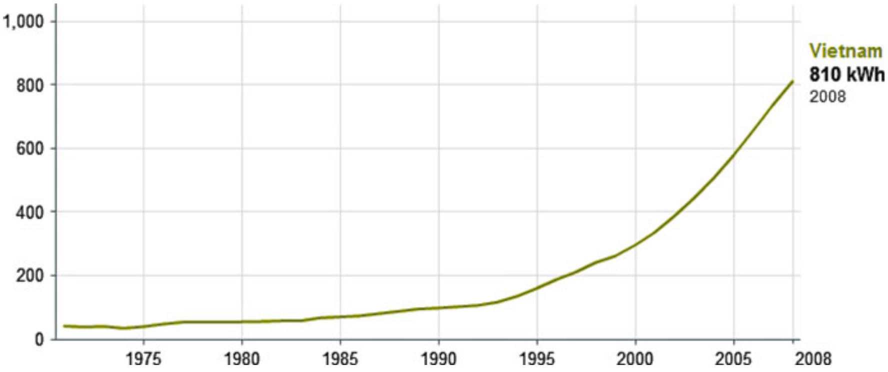

Fig. 2 Electricity consumption per capita in Vietnam [3]

rate of 10.6% in the period 2000–2005. In the total primary energy supply, renewable and waste energy accounts for 42%, main source of it is agricultural waste. In the industrial sector, the main energy source is still fossil fuel (see Fig. 3).

2.2 The Increase of CO_2 Emission by Using Fossil Fuels

The world energy consumption for industrial and human activities has burned more than 10 billion tons of fossil fuels per year (in coal equivalent). This is the major reason for increase CO_2 emission (Fig. 4).

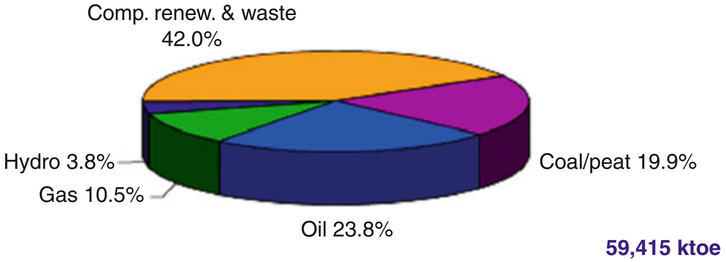

Fig. 3 Share of total primary energy supply in Vietnam 2008 [4]

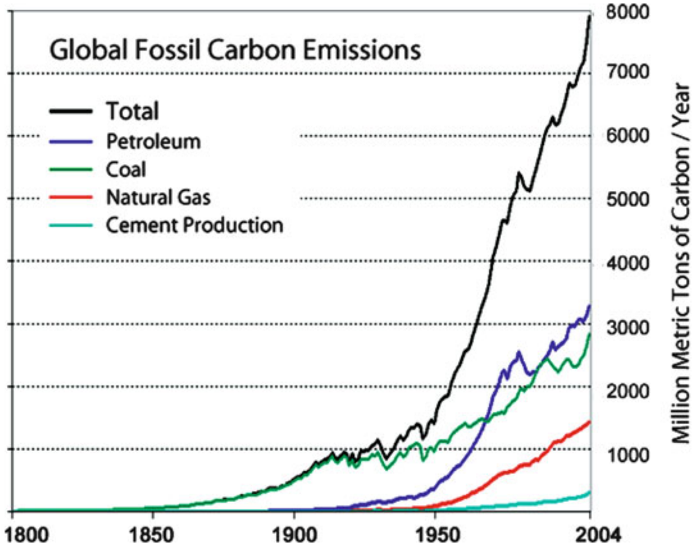

Fig. 4 Global CO_2 emission by using fossil fuel [4]

Table 1 CO_2 emissions of some countries according to World Resources 1990–1991

Country	Scale of emission	% CO_2 emission in total
USA	1	17.8
China	4	6.6
Japan	6	3.9
Indonesia	9	2.4
Philippines	18	1.2
Vietnam	28	0.7
Malaysia	37	0.4

It is estimated that annual burning of fossil fuels released more than 20 billion tons of CO_2. In 2010, there was even 30.6 billion tons of CO_2 emissions, mainly due to fossil fuel burning operations. This factor of some countries has been reported in Table 1 in that USA stays in the first order of scale of emission. USA occupied 17.8% of the total amount of CO_2 emission over the world.

Table 2 Estimated percentage of greenhouse gas emissions per capita (unit: tons of CO_2 equivalent/capita)

	2004	2010
USA[a]	20	21.6
European[a]	11	11
The world average[a]	5	
China[a]	4	
Vietnam[b]	1.5	1.6

Source:

[a] Climate change 101: Understanding and Responding to Global Climate change, 2007

[b] Estimated from the first report of Vietnam for the United Nations about Framework Convention on World Climate Change, 2003

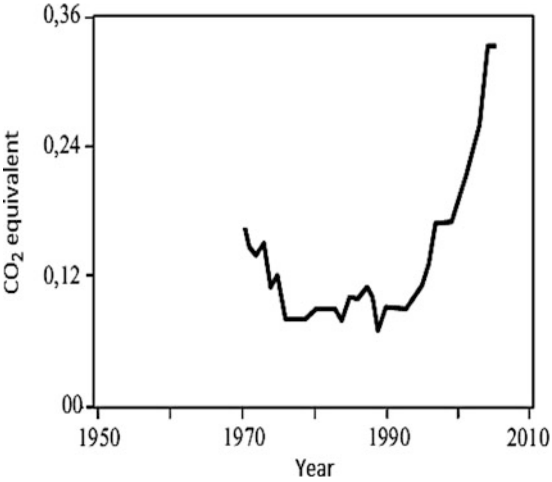

Fig. 5 Level of carbon emissions per capita in Vietnam

In Vietnam, total greenhouse gas emissions in 2000 were 150.9 million tons CO_2 equivalent; thereafter, average per capita was 1.5 million tons. Vietnam's level of CO_2 emissions per capita was rather low compared to world average (Table 2).

In the 1980 and 1990 of the last century, the average CO_2 emissions per capita in Vietnam were 1/10 of the world average, but nowadays is 1/3, while this level in the world is almost stable (Figs. 5 and 6). With increased consumption of fossil fuel at present, it was predicted that in a short time, the level of CO_2 emissions per capita in Vietnam will exceed the world average (Figs. 7 and 8).

In the energy sector, coal-fired power plants contribute 54% of CO_2 emissions, and gas-fired power plants contribute 40%. In 2009, CO_2 emission from fossil fuels is estimated to increase by 113% compared to the year 2000. Each kWh of electricity of Vietnam contributes 0.52 kg CO_2 emission. The contribution of each sector to the total emissions in Vietnam through the years is shown in Fig. 9.

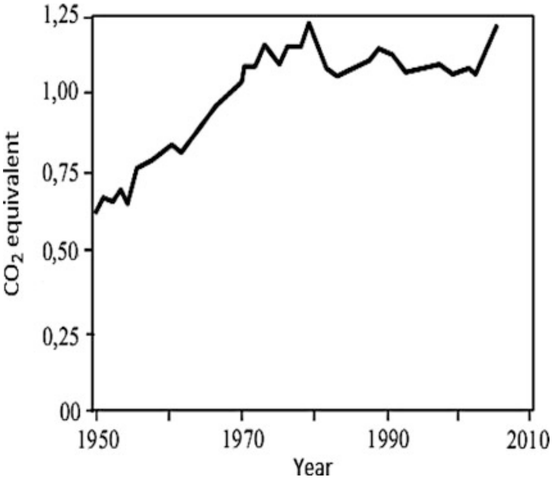

Fig. 6 Level of carbon emissions per capita globally

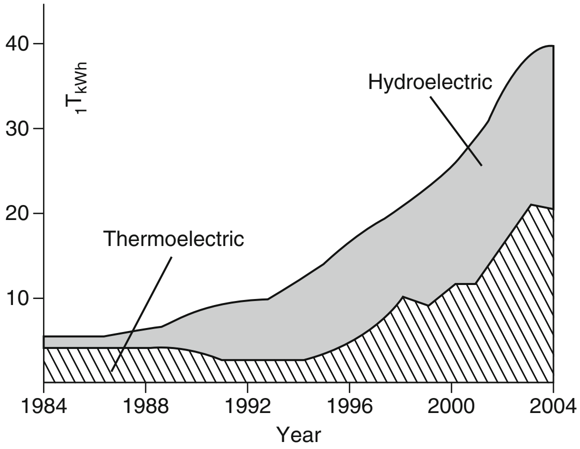

Fig. 7 Electricity production in Vietnam

The inventory results in 2010 showed that agriculture in Vietnam is the largest source of emissions with 65 million tons of CO_2 equivalent (43.1%), followed by energy sector (35%) (Fig. 10) [5].

CO_2 emissions from waste account for a large amount. Waste generation each year is 13 million tons nationwide, of which, 75% was buried mostly in the open dumps. Based on forecast data 2015–2020, municipal waste volume will be two to three times higher than at present. Statistics emissions from not handled organic waste are about 75 million tons of CO_2 – that will be about 113 million tons in 2020 as being forecasted.

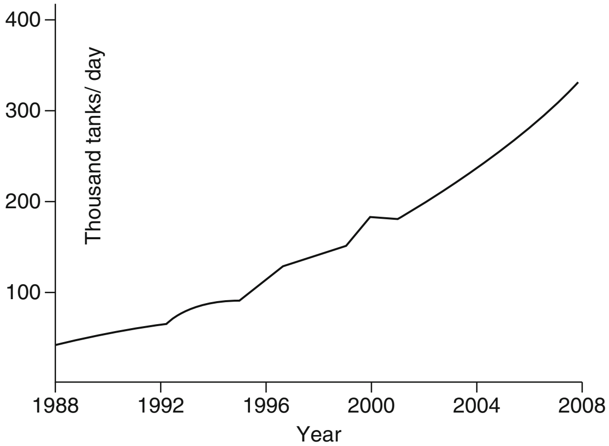

Fig. 8 Oil consumption in Vietnam

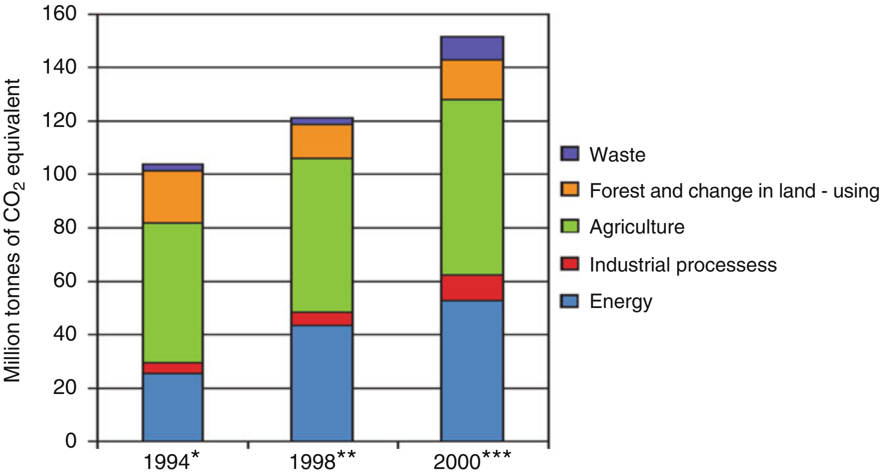

Fig. 9 Evolution of greenhouse gas emissions in Vietnam by each sector in 1994, 1998, and 2000

2.3 The Status of MSW in Hanoi

Hanoi is the capital of Vietnam and the second largest city of the country. Its population in 2009 was estimated at 2.6 million for urban districts and 6.5 million for the metropolitan jurisdiction [6]. Hanoi and Ho Chi Minh City (HCM City) are the main waste generators with 8,000 ton/day (2.92 million ton/a), accounted for 45.24% of total urban MSW, whereby HCM city produces 5,500 tons/day and the left is generated by Hanoi (2006–2007) [7].

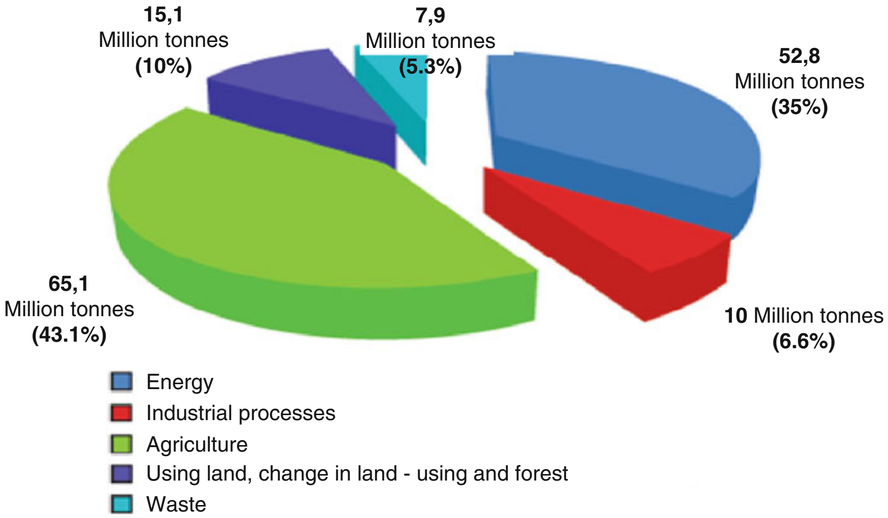

Fig. 10 Emissions inventory for each domain of Vietnam in 2010

Table 3 Waste composition in Hanoi in 1995 and 2003 [8]

Waste component	Percent of total 1995	 2003
Organic	51.9	49.1
Paper and textiles	4.2	1.9
Plastic, rubber, leather, wood, hair, feathers	4.2	16.5 (plastics 15.6)
Metal	0.9	6.0
Glass	0.5	7.2
Inert matter	38.0	18.4
Others	0.2	0.9

Waste composition in Hanoi mainly consists of organic waste (around 50%), and the other half is plastic, paper, textile, metal, glass, and inert matter. However, this characteristic has changed strongly since 1990s with rapid economic growth coupled with fast urbanization. The relative contribution of organic waste is reducing (51.9% → 49.1%), and plastic waste is increasing (4.2% → 15.6%) due to the more affluent lifestyles, larger quantity of commercial activities, and more intense industrialization (Table 3). The proportion of nondegradable waste therefore increases, such as plastic, metal, and glass from 4.3%, 0.9%, and 0.5% in 1995 to 15.6%, 6.0%, and 7.2% in 2003, respectively. It is estimated that the generation rate of plastic increases about 18.3%/year. Therefore, dumping plastic causes not only pollution of the environment with nondegradable materials but also loss of resources. Since in Vietnam incineration techniques are applied only in some special sections of waste treatment, producing RDF in that status is foreseen as a solution for both energy purpose and waste management.

Table 4 Type of RDF

ASTM designation	Description
RDF-1	Waste used as fuel in as-discarded form
RDF-2	Wastes processed to coarse particle size with or without magnetic metals
RDF-3	Shredded fuel derived from MSW has been processed to remove metal, glass, and other inorganic materials (this material has a particle size such that 95 wt.% passes through a 50 mm square mesh)
RDF-4	Combustible waste processed into powder form: 95 wt.% passing 10 mesh screen (2 mm)
RDF-5	Combustible waste densified (compressed) into pellets, slugs, cubettes, or briquettes (this is d-RDF)
RDF-6	Combustible waste processed into liquid fuel
RDF-7	Combustible waste processed into gas fuel

2.4 General in RDF Production

In fact, RDF is a category of the generic class of waste-derived fuel (WDF). RDF has not been given the universe definition; it depends on the technologies and methods of each sector and each country. The American Society for Testing and Materials (ASTM) has defined several forms of RDF as shown in Table 4 [9].

As for ASTM, RDF-1 is the major form of RDF used worldwide; RDF-5 is densified refuse-derived fuel (d-RDF). Waste can be processed to make fuel in solid, liquid, or gas phase. In the frame of this study, only solid RDF will be concerned, and it will be mentioned as RDF from here.

RDF can be produced as fluff or densified forms. As regards fluff RDF, it is not biologically stable and difficult to store, and it must be used within 2 or 3 days. Densified or pelletized RDF has advantages over fluff RDF because it is easier to transport, handle, and store.

RDF produced from MSW with heterogeneous content may give different compositions. Normally, RDF contains plastic (excluding recyclable plastic), paper, cardboard, and textile; however, their proportion changes depending on time, location, and management system.

Quality of RDF can be roughly evaluated by calorific value, ash content, water content, and chlorine and sulfur content. Table 5 presents the quality of RDF depending on several kinds of waste. The table shows that RDF from industrial waste has lower water content and higher heating value than from household or commercial waste. This is because of the low percentage of organic fraction.

For RDF, producing two main methods can be seen:

- Mechanical biological method (MBT) which can be divided to aerobic or anaerobic MBT
- DSP wherein waste can be stabilized by biological or physical process

The main difference between these two methods is that in MBT method, mixed waste is separated into organic, recyclable, metal, inert, and high-caloric

Table 5 Quality of RDF from household and industrial sources [10]

RDF source	Calorific value (MJ/kg)	Ash residue (wt.%)	Chlorine content (wt.%)	Sulfur content (wt.%)	Water content (wt.%)
Household waste[a]	12–16	15–20	0.5–1		10–35
Household waste[b]	13–16	5–10	0.3–1	0.1–0.2	25–35
Commercial waste[b]	16–20	5–7	<0.1–0.2	<0.1	10–20
RDF from industrial waste[a]	18–21	10–15	0.2–1		3–10
Demolition waste[b]	14–15	1–5	<0.1	<0.1	15–25

[a] RDC and Kema 1999
[b] Data reported for Finland

components. Each fraction after that will be treated or reused in different ways. But in DSP method, mixed waste is firstly digested in digestion drums to reduce volume, water content and to stabilize microorganism activities before proceeding into separation step. In this study, DSP method has been applied.

3 RDF Production with DSP Method

3.1 Sampling

This experiment work was done in two phases. The first one was in 2009, samples named E1, E2, and E3 (E1 → E3), and the second was in 2010, named R1, R2, and R3 (R1 → R3). The first phase aimed to look for a possibility of RDF production from MSW in Hanoi by DSP method. And the second tries to determine the influence of waste input on RDF quality.

Samples were taken from MSW in district Hai Ba Trung, Hanoi. Waste sources are mainly from households and small street restaurants without separation at source. In this district, waste composition contains high percentage of biowaste which accounts for 55–69%, and plastic and nylon bag are 4–5% and 1.5–2%, respectively [11, 12].

Following steps were applied for preparing sample R1 → R3 of RDF production (Fig. 11). They firstly separated manually and mixed again to ensure the composition, which will be sent thereafter into digestion barrels.

Figure 12 presented sample composition of R1 → R3 for the three barrels with four high-calorific fractions: biowaste, nylon bag (plastics), paper, and textile in different ratio.

For these three barrels, percentage of paper and textile was kept equally, while shares of nylon bag and biowaste were varied. Details of input material are shown in Table 6.

Samples E1 → E3 were separated to different sizes (<10, 10–40, and >40 mm) and stabilized by DSP method (Table 7) [11].

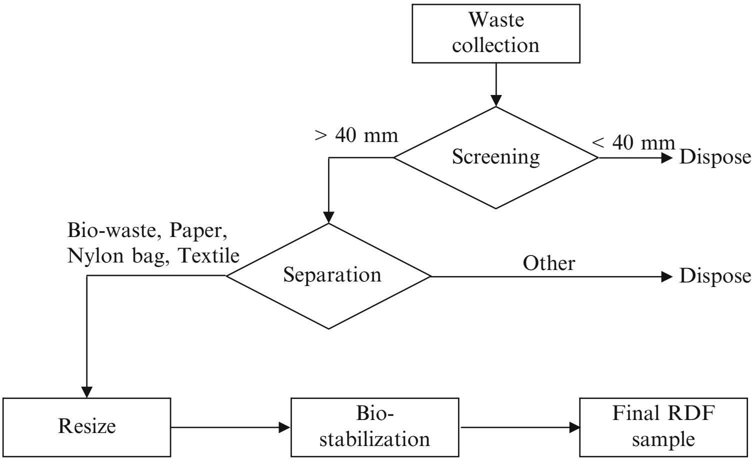

Fig. 11 Preparing steps of RDF sample R1 → R3

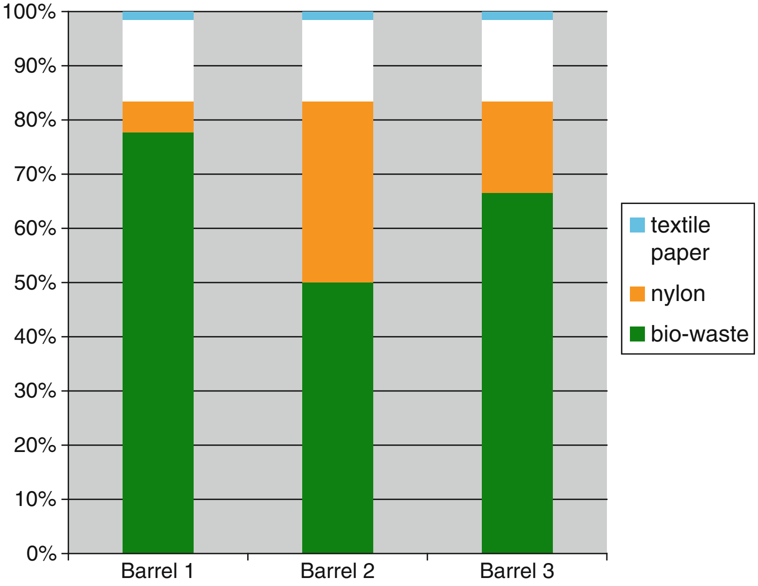

Fig. 12 Sample composition of R1 → R3 for the three barrels

3.2 *Bio-Stabilization Process*

Waste input composition of R1 → R3 was selected from fraction of the size larger than 40 mm. After being resized into 40–100 mm pieces, which were expected to be a good size for the stabilization process, samples were put into barrel (Fig. 13).

Table 6 Waste input composition of R1 → R3

	Barrel 1		Barrel 2		Barrel 3	
	Mass (kg)	%	Mass (kg)	%	Mass (kg)	%
Biowaste	14.0	77.8	9.0	50.0	12.0	66.7
Plastics	1.0	5.6	6.0	33.3	3.0	16.7
Paper	2.7	15.0	2.7	15.0	2.7	15.0
Textile	0.3	1.7	0.3	1.7	0.3	1.7
Total	18.0	100	18.0	100	18.0	100
Biowaste:plastics	14:1		3:2		4:1	
Name of sample	R1		R2		R3	

Table 7 Sample composition of E1 → E3 for RDF product [11]

Sample	E1	E2	E3
Weight	19.08 kg	19.14 kg	19.53 kg
Size	10–40 mm	>40 mm	Mixed
Organic	95%	67%	81%
Plastics	~1%	9%	5%
Paper and cardboard	~3%	13%	8%

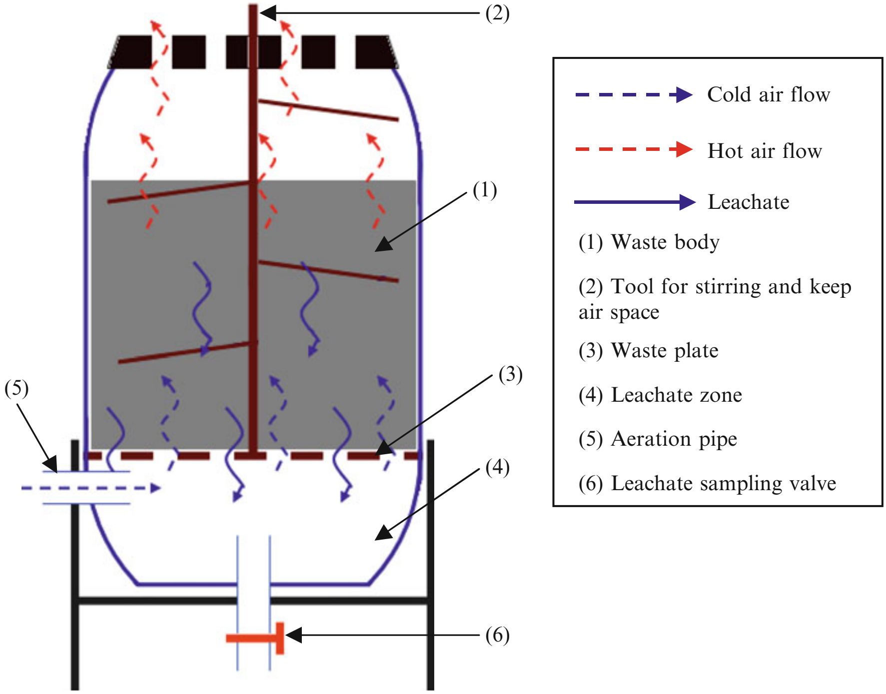

Fig. 13 Waste barrel

Table 8 Bio-stabilization time

Sample	R1	R2	R3	E1 → E3	RDF (Herhof Stabilat Method)
Days	42	42	42	18–51	7

Table 9 Comparison RDF product quality [11, 14]

Parameters	E1	E2	E3 40–100 mm	E3 10–40 mm	RDF in a pilot of Ha Nam province, Vietnam [14]	RDF in German
Heating value (MJ/kg)			17	15	17.5	16.5
TOM (%)	58.992	59.558	64.576	58.516		32.4
WC (%)	13.482	8.562	12.636	9.696	15.56	9.9
Chlorine (%)	0.444	0.732	1.331	1.487	0.288	0.6
Zn	286.880	180.21	193.63	139.57	283.33	400
Cd	0.467	0.829	0.311	0.729	1.786	2.2

In this barrel, air is expected to come naturally. Temperature and leachate volume were measured twice a week. Once a week, waste was taken out to mix with air and then put back into the barrel. At the same time, sample was taken to measure water content. Stabilization step ended when waste body stopped generating water, varied from 18 to 51 days, due to waste input characteristic and environmental temperature. After this time, raw RDF was collected and stored for further analysis. Stabilization time of E1 → E3 and R1 → R3 was compared with that of other study (Table 8).

Table 8 shows large differences in bio-stabilization time. The reason is the thickness and thermo-conduction of the barrel wall which caused heat losing. Ahn's research has proven that the wall conduction accounted to 62% of the heat loss [13]. Two-layer insulation wall is therefore suggested. One more reason is the waste amount which was used, 18 kg/barrel. This weight is maybe not yet in optimal volume with the barrel. It may have resulted in inefficient microorganism activity.

RDF products from E1 → E3 have got high chlorine content in comparison with that of other RDF (see Table 9). In this experiment, digesting time was noticed by the leachate volume. But in R1 → R3, waste was taken out of bio-box when water content was stable in around 6 weeks.

Temperature is an important indicator in RDF producing process. The temperature in these three barrels was higher than atmospheric temperature, but there was not much difference. The barrel was put in the open air; therefore, it might be affected much by the weather changes.

In this study, volume of leachate was monitored twice a week. Once a week, waste was taken out to mix with air with an expectation of raising microorganism activities to enhance the aerobic condition. High amount of leachate in the next days was noticed. As a result, leachate volume of barrels 1 and 3 was higher but not the case for barrel 2 (Fig. 14). Barrel 2 contained lower content of biowaste, which

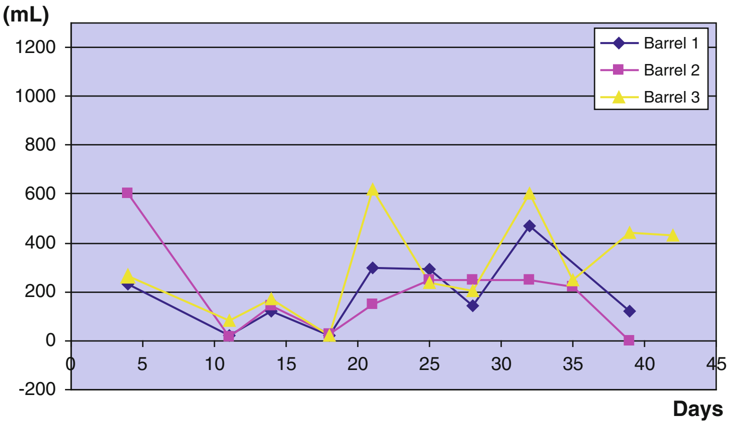

Fig. 14 Leachate volume in the three barrels

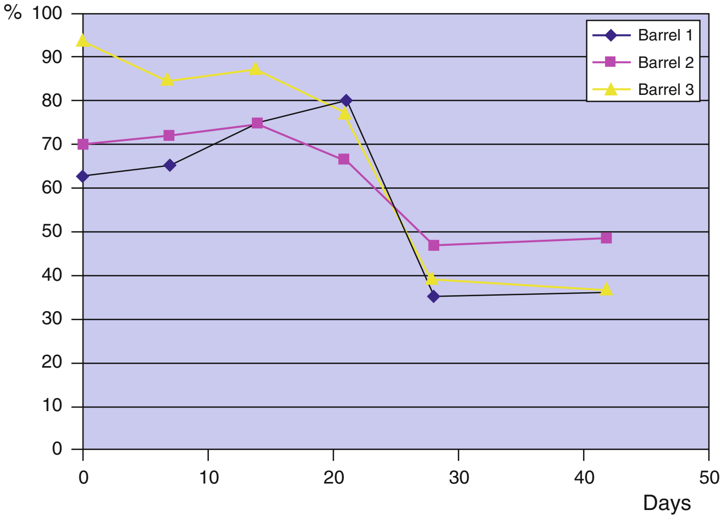

Fig. 15 Water content in digesting process

connected to the low microorganism activities. A relation between biowaste content and microorganism activities resulted in leachate amount therefore must be noticed.

For RDF production, it is important to know the percentage of water in RDF product. This factor is affected very much by water content of waste input. In this study, input material contained more than 60% of water, and sample R3 has got even more (92%) because it was collected after some rainy days in Hanoi.

Water content of the three samples was stable at the range of 35% to nearly 50% in the last 2 weeks before the digesting process ended. It was noticed that water started to drop since the fourth week of experiment work, which is well matched with the temperature curve (Fig. 15).

In drying step, water content from R1 to R3 reduced by 55%, 40%, and 60%, respectively. This phenomenon can be connected to biowaste component in which R1 and R3 have values of 78% and 67%. Therefore, these two samples had higher drying efficiency in comparison with R2 which contained 50% of biowaste. In this case, microorganism working efficiency in R2 may be lower. This may reflect again the relationship between biowaste content and microorganism working efficiency.

In the final product, R2 still had higher water content than that in R1 and R3 in spite of in input material this factor of R2 was lower. May think, the percentage of biowaste plays a key role in reducing the water content. Low biowaste content may result in inefficient drying process, but if this component is high, it will cause low quality of RDF.

The reduction of biowaste content after stabilization time can be identified by the waste composition of input flow (in barrel) and of RDF products of R1 → R3, which is shown in Fig. 16.

In this study, heating value of dry sample [Hu(wf), kJ/kg] and of wet waste [Hu (raw), kJ/kg] was determined with the calculation by formula (1) and (2), respectively. Sample characteristics were also determined by analytic measurement.

$$\mathrm{Hu(wf)} = \sum_{i=1}^{n} \mathrm{TS}_i \cdot \frac{m_i}{m} \cdot \frac{1}{\mathrm{TS}} \cdot \mathrm{Hu(wf)}_i \tag{1}$$

$$\mathrm{Hu(raw)} = \mathrm{Hu(wf)} \cdot \mathrm{TS} - 2441 \cdot (1 - \mathrm{TS}) \tag{2}$$

where Hu(wf): higher heating value of sample (dry RDF kJ/kg); $\mathrm{Hu(wf)}_i$: higher heating value of waste fraction i, dry waste (kJ/kg); Hu(raw): lower heating value of sample, wet RDF (kJ/kg); TS_i: total solid of waste fraction i (%); TS: total solid of RDF (%); m_i: weight of fraction i (kg); m: weight of RDF (kg); and n: number of waste fraction i.

Water content is calculated by the following formula:

$$\mathrm{WC} = \frac{m_0 - m}{m_0} \cdot 100\% \tag{3}$$

And the total solid (TS) was indirectly calculated from WC by formula (4):

$$\mathrm{TS} = 1 - \mathrm{WC} \tag{4}$$

Results about water content and heating value of these three samples R1 → R3 are presented in Table 10.

The higher heating value of R1 → R3 was calculated based on RDF composition when assuming that only biowaste was degradated and the reduction rate was 60%.

R1 has the lowest gross heating value of 16.53 MJ/kg which resulted from the low percentage of nylon bag and the high biowaste content from input material. R2 contained the highest percentage of nylon bag; thereafter, it received the highest

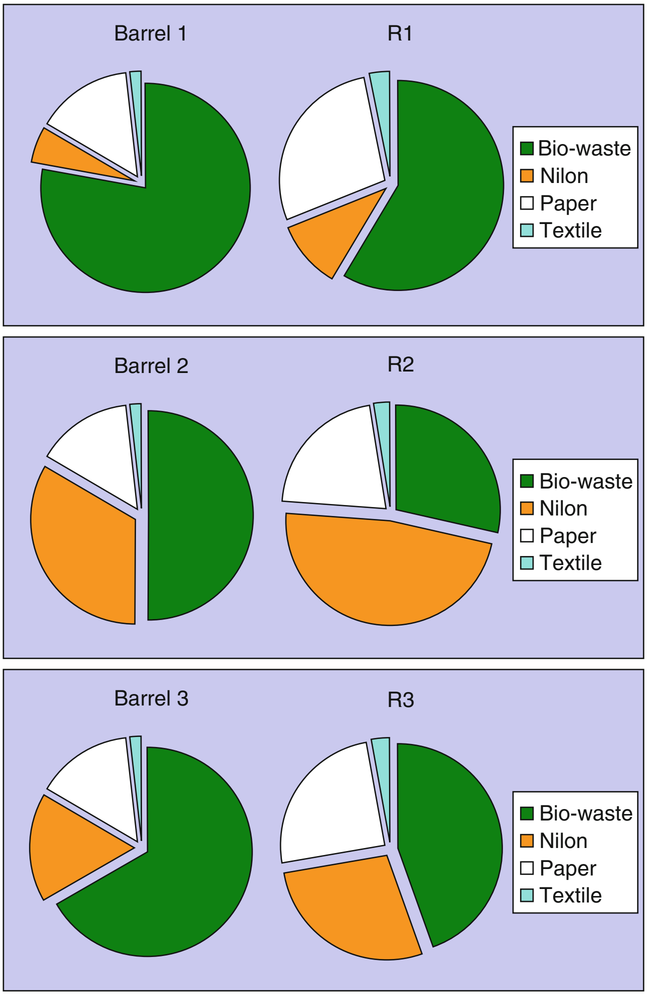

Fig. 16 Input composition (*left*) and output – RDF composition (*right*) of the three samples

Table 10 Heating value of the three RDF samples

		Calculation (MJ/kg)		Measurement (MJ/kg)	
Sample	WC	Hu(wf)	Hu(raw)	Hu(wf)	Hu(raw)
R1	36.21	16.53	9.66	18.10	10.66
R2	48.26	23.54	11.00	31.50	15.12
R3	36.39	20.15	11.86	28.60	17.21

heating value. However, when compared to the net heating value Hu(raw) – heating value of wet RDF – R3 has the higher one than R2, while it contained the lower percentage of nylon bag. The reason may remain in the lower water content of R3 connected to the requirement of energy during combustion step. This result matches with the measurement.

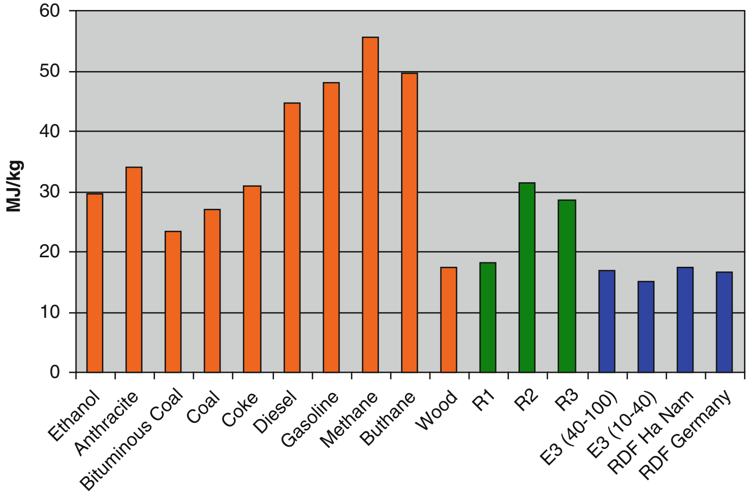

Fig. 17 Gross heating value comparison with fossil fuel and RDF from different studies

All of the measured data are higher than the calculated data. One of the reasons therefore may be the way of calculation – that it was done when assuming biowaste lost 60% – but in fact, it may lost even more.

The figure below presents the comparison between higher heating value Hu(wf)*i* of RDF R1 → R3 and of fossil fuel as well as of some other RDF products (Fig. 17).

In that figure, R1 with the lowest percentage of nylon bag has almost the same heating value with that of other RDF samples and wood. R2 and R3 contained bigger share of nylon bag; therefore, they showed the better result, similar to the one of solid fossil fuel (coal, coke ...). Furthermore, heating value of wet RDF R1 → R3 – Hu(raw) – is higher than 10 MJ/kg, which is high enough to ensure that the combustion does not need support of fossil fuel. Therefore, this RDF product has met the required heating value for one kind of fuel substitutes.

4 Greenhouse Gases Estimation

Energy production and consumption pose nature into pressure and make the energy sector becomes the largest contributor of greenhouse gas (GHG) emission in Vietnam since 2010, accounting for 67%. Several emission sources of GHG could be found in a waste treatment facilities: it came from (1) emission of methane (CH_4, GWP: 25) at landfill of mixed waste, (2) from emission of fossil carbon dioxide through the combustion of plastics and composites or supported fuels (auxiliary), and (3) from emission of nitrous oxide (NOx) during incineration/ pretreatment process, etc.

According to UNEP (2010), waste prevention and materials recovery are the key activities, by which the waste sector can significantly contribute to GHG mitigation.

4.1 GHGs from Pretreatment Step of RDF

Whenever waste is transformed into RDF in the pretreatment step, GHGs can be released from:

- Direct emission of fossil CO_2 by the consumption of energy/auxiliary fuels (i.e., electricity, heat, natural gas/diesel)
- Emission of nitrous oxide (N_2O) in exhausted gas

4.1.1 CO_2 Emission from Consumption of Energy/Auxiliary Fuels

In this study, waste was separated manually and composted without air pumping. Therefore, neither energy nor auxiliary fuels were needed. However, whenever RDF is produced in factory settlement, electricity and diesel are needed together with other supplement activities. For that system by using DSP method, separation, transportation, and other processes are required. Therefore, 93.8 kWh of electricity is needed for 1 ton of input waste operation [15].

Diesel demand for this pretreatment step is estimated between 1.8 and 9.5 kWh/ton input [15–17]. This demand depends on how well the system equipped and on the number of machine using diesel. For calculation, mean value of diesel demand is used 5.6 kWh/ton input waste.

In total, for processing 1 ton of input waste, 99.4 kWh of energy is required. GHGs emission is calculated for energy consumption. It is assumed that electricity is taken from Vietnam electricity grid with an emission factor of 0.5764 ton CO_2/MWh [18].

4.1.2 N_2O Emission

Data for the calculation of N_2O emission in pretreatment process was taken from references. The N_2O emissions are converted to CO_2 equivalents by following formula (5). The average emission of N_2O in RDF plant applying DSP method is considered 5.6 g/ton MSW, which result to the increasing of GHGs emission by 1.62 kg CO_2 eq./ton MSW [15].

$$\mathrm{EF}(\mathrm{CO}_{2,\mathrm{eq.}}) = \mathrm{EF}(\mathrm{N_2O}) \cdot \mathrm{GWP}(\mathrm{N_2O}) \tag{5}$$

where $EF(CO_{2,eq.})$: CO_2 equivalent emission; $EF(N_2O)$: emission factor of nitrous oxide; and $GWP(N_2O)$: global warming potential of N_2O (=298, IPCC).

4.2 GHGs from RDF Utilization Step

GHGs are generated in RDF combustion step from:

- CO_2 emission originated from fossil carbon
- CO_2 eq. emission by auxiliary consumption
- N_2O emission

4.2.1 CO_2 Emission from Combustion Process

Almost carbon (C) in waste is oxidized into CO_2 through combustion process. A small amount is converted into carbon monoxide (CO), but this is often ignored. According to IPCC 2006, only fossil CO_2 is accounted as GHG emission source, while CO_2 which is formed from C bio is considered neutral and not added to total GHGs emission. However, amount of CO_2 bio was still calculated for reference purpose. CO_2 emission in RDF utilization process (burning process) is calculated based on fossil carbon content of waste fractions by the following formula:

$$\mathrm{EF}(\mathrm{CO_2\ fossil}) = \sum_{i=1}^{n} \frac{m_i}{m} \cdot \mathrm{Rfossil}_i \cdot C_i \cdot H_i \cdot \frac{44}{12} \tag{6}$$

$$\mathrm{EF}(\mathrm{CO_2\ bio}) = \sum_{i=1}^{n} \frac{m_i}{m} \cdot \mathrm{Rbio}_i \cdot C_i \cdot H_i \cdot \frac{44}{12} \tag{7}$$

$$\mathrm{EF}(\mathrm{CO_2}) = \mathrm{EF}(\mathrm{CO_2\ fossil}) + \mathrm{EF}(\mathrm{CO_2\ bio}) \tag{8}$$

where $EF(CO_2)$: CO_2 emission factor (kg CO_2/kg RDF); m_i: weight of fraction i in RDF (kg); m: total amount of RDF (kg); $\mathrm{Rfossil}_i$: content of fossil carbon in fraction i (%TC); Rbio_i: content of bio carbon in fraction i (%TC); C_i: total carbon content of waste fraction i (%); H_i: combustion efficiency of waste fraction i (%); and 44/12: conversion from C to CO_2.

The result CO_2 emission from combustion process is shown in Table 11, assuming that average combustion efficiency in all cases is 97.5% [Hu(raw) $>$ 10 MJ/kg RDF].

4.2.2 CO_2-Eq. Emission by Auxiliary Consumption

As mentioned above, LHV of three samples R1 → R3 is higher than 10 MJ/kg fuel; therefore, the combustion does not need auxiliary firing. The small amount of fossil fuels for start-up and shutdown of the procedures is not taken in to account. It means

Table 11 CO_2 emission from combustion process (kg/kg RDF)

	R1			R2			R3		
	CO_2 fossil	CO_2 bio	CO_2 total	CO_2 fossil	CO_2 bio	CO_2 total	CO_2 fossil	CO_2 bio	CO_2 total
Biowaste	0.044	0.266	0.310	0.021	0.130	0.152	0.033	0.203	0.236
Nylon	0.148	0.015	0.163	0.677	0.070	0.747	0.395	0.041	0.436
Paper	0.034	0.216	0.250	0.026	0.165	0.190	0.030	0.192	0.222
Textile	0.027	0.011	0.038	0.020	0.008	0.029	0.024	0.010	0.034
Total	0.252	0.509	0.761	0.744	0.374	1.118	0.482	0.446	0.928

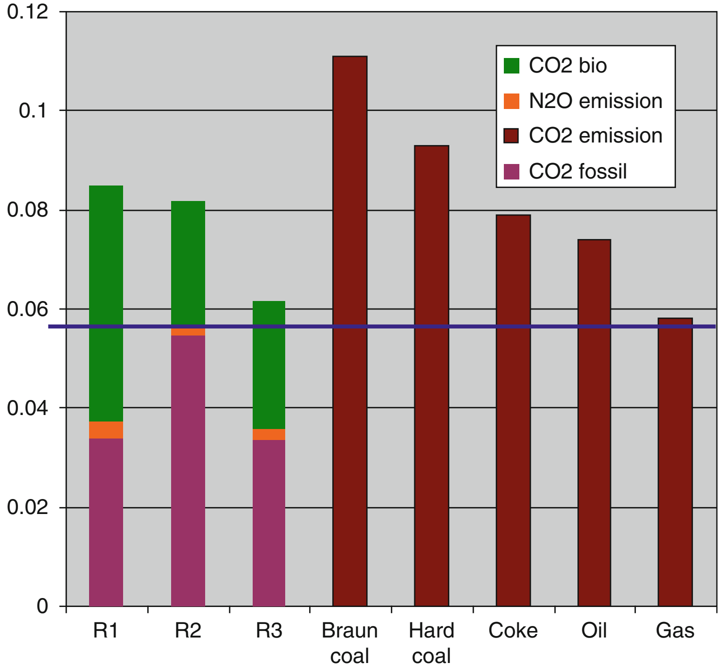

Fig. 18 GHGs emission from RDF sample compare with fossil fuel (kg CO_2 eq./MJ) [15]

that CO_2 emission from consumed fossil fuels for these operation steps is considered to be zero. Therefore, CO_2 emission in this part is 0.

4.2.3 N_2O Emission

In the same way, N_2O emission in pretreatment process was calculated, whereas N_2O emission in this combustion step was taken from references; for German waste, it is estimated to be 3.41 kg CO_2 eq./ton RDF ($GWPN_2O = 298$) [15].

4.3 Total GHGs Emission

The total GHGs emission is the sum of GHGs emission from RDF pretreatment (of 4.1) and utilization step (of 4.2) converted to kg CO_2/MJ. This unit is used to compare GHGs emission from RDF samples and from fossil fuel (Fig. 18).

Emission of CO_2 bio was considered as neutral and did not count for estimating the global warming effect. Therefore, two emission factors are considered for the combustion of 1 MJ of fuel:

- Total GHGs emission factor = CO_2 fossil emission + N_2O emission + CO_2 bio emission
- Emission factor (EF) = CO_2 fossil emission + N_2O emission

It can be seen that total GHGs emission of RDF sample R1 → R3 is lower than that from coal and higher than that from oil and gas (Fig. 18). However, the three RDF samples have lower EF than that of fossil fuel. In this case, the RDF samples have revealed the better result in total GHGs emission factor than that of fossil fuel.

Accordingly, when comparing themselves between samples R1 → R3, EF of R2 was the highest; R1 and R3 have got almost the same value, but based on total GHGs emission, R3 showed the better value. This result may hold promise in MSW treatment toward RDF production by DSP for reduction of GHGs emission.

5 Conclusion

In this study, RDF produced by DSP method from MSW of Hanoi has been reported in details. Results show a potential of producing RDF since the waste amount increases rapidly along with the nondegradable components. For this producing process, the waste amount suitable to the volume of barrel should be taken in consideration.

RDF quality is affected by input component, in that, biowaste content accounted for a remarkable parameter. The three parameters – high heating value, water content (WC), and emission factor (EF) – could be better from sample with medium ratio of biowaste to nylon waste (4:1). The higher or lower value of this ratio has not yet given better result.

In this study, heating value of dry sample and wet waste was determined with the calculation and analytic measurement. Gross heating value comparison between fossil fuel and RDF from different studies has been reported. Accordingly, heating value of wet RDF for the small or bigger scale of production process needs to be noticed.

By calculating the total GHGs emission from pretreatment and utilization step of RDF, converted to kg CO_2/MJ, a figure of GHGs emission from RDF sample compare with fossil fuel has been presented. Result showed an advantage of RDF to fossil fuels because it leads to the less GHG emissions.

Though this study has proven that RDF product has given the required heating value for one kind of fuel substitutes, this was just initial results. Further study to find out suitable ratio between waste components and other technical concern for DSP process in RDF production from MSW in Hanoi still needs to be done.

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Part III
Conclusions

Conclusions

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Abstract Chemical additives are included in numerous products today and a number of these goods have to be handled with care. They need to be monitored and their possible risks need to be considered, investigated and assessed. The results of the investigations presented in this book, focusing on the mentioned issues, will be summarised in this conclusion.

The knowledge of occurrence of pollutants in the environment is essential in order to undertake accurate risk assessment studies. The book "Global Risk-Based Management of Chemical Additives I: Production Usage and Environmental Occurrence" included a review of chemical additives in six industrial sectors in a global context and different case studies all over the world. As logical continuation to this, the book "Global Risk-Based Management of Chemical Additives II: Risk-Based Assessment and Management Strategies" has been published. Within the single chapters, it is described how different methodologies for global management strategies of chemicals could be applied. Further on case studies are presented, which have been exercised under circumstances of different countries and certain industry sectors or focussed on additives in different products.

Keywords Additives, Case studies, Management of chemicals, Properties, Risk-based assessment

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Contents

1 Introduction

Within the EU-funded project RISKCYCLE, several research topics, which are addressed and discussed in Volume I (Global Risk-Based Management of Chemical Additives I: Production, Usage and Environmental Occurrence) and Volume II (Global Risk-Based Management of Chemical Additives II: Risk-Based Assessment and Management Strategies), have been investigated within the last 3 years of the project duration. Within the first book for each of the considered six fractions, a list with five main additives, which have been studied in detail, has been compiled. Using these selected additives, exemplary investigations have been carried out within the single work packages, such as life cycle assessment (LCA) of additives in the plastics and paper industries for the first time or the use of different risk assessment methodologies to investigate the effects of using these additives and their behaviour in various recycling processes.

Volume I primarily provides an outlook at various industrial sectors and the additives applied therein, whereas in the second volume, two risk assessment methods are presented and recommendations for further research activities are discussed.

2 Assessment Methodologies

2.1 *Life Cycle Assessment*

One of the applied assessment methodologies for additives in products is LCA. Within the project it was investigated that huge issues, knowledge gaps and difficulties exist concerning additives. Even so additives are released during the use and recycling phase, they neither are visible in literature nor included in LCA databases for both life cycle inventory (LCI) and life cycle impact assessment (LCIA). Reasons for that might be the missing awareness of this gap or missing data for additives in products and their fate during production, recycling and final disposal. Within the project RISKCYCLE this issue was addressed for plastics and paper only, but the outcome will be certainly adaptable for other industrial sectors as well. The task within RISKCYCLE was to establish a coherent framework for LCA studies on products containing additives. The following recommendations can be stated:

- Additives which are potentially dangerous adding toxic emissions to the environment have to be taken seriously as a part of the life cycle of products.
- LCI databases have to be completed with data on additives (production, emissions, etc.) and expanded with data on various waste treatment processes in a material-specific way.
- LCIA databases should be expanded with standardised characterisation factors on additives.

In case no data exists to be included in the LCI or LCIA, it is recommended to use estimation approaches in combination with sensitivity analysis instead of leaving this issue unmentioned.

The book presents case studies, LCA studies on printed matter, and the additive DEHP in PVC flooring.

The LCA study on printed matter leads to the conclusion that chemical emissions based on additives may play a significant role in the LCA impact profile of printed matter, in contrast to existing studies, which claim that the energy-related impact categories (global warming, acidification and eutrophication) are the most relevant ones. The newly introduced case study includes chemical-related impact categories by making use of knowledge on emissions from ink of the printing industry combined with knowledge about the composition of the printing materials used during the production of offset printing process. The results of the case study clearly revealed that the importance of energy consumption is significantly reduced and less relevant when chemical emission factors combined with toxicity-related impact categories are included in the impact assessment.

The LCA study on DEHP in PVC flooring shows very clearly that this additive on one hand contributes to the toxicity impact and on the other hand to global warming impact. This is caused by the GHG emissions along the cradle-to-grave chain of DEHP and is a more general problem concerning LCA studies regarding chemical additives: the emissions of additives during use and degradation phase are often not included or data are missing at all.

2.2 Chemical Exposure Modelling

Besides the LCA approach, also risk assessment can be performed analysing the chemical compounds or modelling via predictive exposure models. Both types of approaches have their justification: to measure environmental concentrations of chemicals in the environment with laboratory measurement is still the most reliable way for determination. But it goes along with the disadvantage of high investments concerning time and money. Besides that laboratory approaches are limited in terms of space and time, and in consequence, the survey of many micro-pollutants and their interaction among each other are impossible by using analytical chemistry only. A solution of this problem is modelling which becomes more and more of interest to assess the environmental exposure of certain chemicals which might lead to micropollution. Modelling, which means calculation derived from input data and physical–chemical principles, offers the possibility to save time, space and costs in an appropriate way. But the outcome always strongly depends on the kind of model chosen, and due to missing reliable data, there is still an unpredictable certainty. Most of the environmental fate models have been developed based on either the fugacity approach or the Markov Chain principle. Both types of models have in common that they range greatly in complexity. Practitioners of environmental fate models always aim to prefer the simplest model that is able to aim the desired result.

Nowadays, best practice is to combine both modelling and analysis of chemicals for an appropriate assessment of chemical exposure in environmental scenarios. Future research activities should focus on the development of reliable analytical methods at trace level concentrations.

Besides environmental assessment methods, toxicological and ecotoxicological methods are important parts of chemical risk assessment. Concerning animal tests, there is an increasing number of alternative test methods for toxicity prediction, which can be divided into study of toxicity in laboratory tubes on small organisms (in vitro tests) and computational methods (in silico). Both types can be characterised with advantages and disadvantages: in vitro methods, for instance, enable the user to get a result within a few hours or days, require less time and chemicals then other eco-/toxicological methods and are attractive due to causing fewer costs in comparison to animal tests (in vivo methods). But in contrast these in vitro tests have the disadvantage that they only reflect part of the process (e.g. no degradation in the whole organism). In silico models QSAR (quantitative structure–activity relationship) represent a major group and should mimic in vivo experiments.

Obtaining a good quality QSAR model depends on many factors, such as the quality of biological data and the choice of descriptors and statistical methods. As a consequence, the uncertainty of the QSAR predictions is a combination of experimental uncertainties and model uncertainties. QSAR methods have to be applied to individual chemicals, not on mixtures. If the QSAR demands it, the components of the mixture have to be addressed separately and individually – in case of unknown compounds, QSAR cannot identify the toxicity risk and is therefore not useful.

In the end, there are a huge number of available models which cannot be divided into suitable or unsuitable – it is always a case by case decision which approach is the best for the specific problem.

2.3 Socioeconomic Evaluation

In addition to environmental and toxicological assessment of chemical additives in products, the socioeconomic valuation is of high interest, too. Environmental unpredictable degradation with a number of side effects is usually a negative externality of, for example, the use of chemical additives, which causes a market failure, which in turn leads to welfare losses. In the case of health effects, different methods are often used to estimate the impact of externalities and valuating the human health damages. Both productivity losses and costs for hospital admissions or other hospital-related activities are used to monetise health effects. Valuation of environmental impacts can consist of both monetary values and nonmonetary weights to make it easier to estimate total effects from different products and projects. The used tools most often are based on economic assessment tools such as cost–benefit analysis (CBA), in which both cost and benefits are given a monetary value and then compared.

3 Case Studies to Practically Illustrate Methodologies

A topic of a certain concern, which is discussed in several papers in this book, is WEEE (waste from electronic and electric devices) and the informal recycling activities especially in Asian countries. People living near recycling sites in, for example, China, India and Vietnam are definitely threatened by increasing health hazards due to emissions from the recycling activities. Besides that, also the long-range transport of pollutants has to be taken into consideration. Ways to solve these problems are in a first step banning the importation of WEEE from developed countries to developing countries, but nevertheless, the developing countries itself generate a huge amount of WEEE, especially China. Therefore also regulations for the control of national WEEE generation have to be developed. Trying to assess the problems caused by WEEE-recycling activities, a first step would be to trace the e-waste flows and its different amount and number of additives contained in the devices on a global scale. But this is complicated due to missing information, uniform labelling of shipments as well as the trade activities in formal and informal recycling sectors. One possibility to deal with this issue is when trying to trace hazardous substances in the informal e-waste treatment with the substance flow analysis (SFA), which can either follow the single appliance approach or a category approach. The main difference is to focus on single appliances (i.e. TVs, computers) and not on categories (i.e. IT and communication equipment). It may be the case that it is easier to determine concentrations of a certain additive in a single appliance than in a whole category.

The SFA requires the definition of respective substances, a comprehensive analysis of the system (i.e. boundaries), and it is always limited in its extent due to process properties and data availability. Within this chapter the implementation of SFA for tracing hazardous substances in international informal e-waste treatment has been proved to be a useful method. To assess the hazardous consequences and potential risks of the selected chemicals to humans and the environment caused by informal recycling activities in those regions, different models exist, from which four have been chosen according to their specific focus and various pros and cons.

These models have been applied to different scenarios, mainly for two chemicals DeBDE (decabromodiphenyl ether) and Pb (lead). The input data to the models are based on the SFA investigations described above.

Further case studies are included in the book, such as the consequences of mineral oil in board and paper recycling. Mineral oil migration from board to foodstuff has to be treated and solved on a European level. Possible solutions and drawbacks for the folding boxboard production as packaging material for food have been discussed and illustrated. This could be that paper grades for recycling will be utilised with lower newspaper content in comparison to the typically used mixed paper grades for recycling or the usage of mineral oil-free chemical additives in printing ink to have a cleaner secondary fibre.

Furthermore "zero waste" efforts in Brazil to avoid hazardous consequences caused by additives, due to inappropriate handling of waste, are described. The city of Cantagalo is one of the first in Brazil to establish organised separation and treatment of solid wastes for reuse. The separation with proper allocation for coprocessing of the waste not suitable for recycling or composting is a laudable solution from both an environmental and economic standpoint.

Of other concern are mercury-containing lamps. At the end-of-life, compact fluorescent lamps/fluorescent tube lights (CFLs/FTLs) are either disposed in bulk (sold in auction) or disposed individually along with municipal waste. Proper and safe collection of these products would mean its intact collection, transportation and recovery of different components including mercury. The case study outlines the possible hazardous consequences due to improper handling of EoL CFLs and FTLs and proposes a future safe collection, recycling and disposal plan.

Waste to energy (WtoE) becomes a hot topic in respect of energy and safe handling and reduction of waste to a minimum of many countries, such as Brazil, China, India and Vietnam. WtoE provides not only an energy source but also a contribution to solve problems of waste disposal on inadequate landfills. The case study aims at testing the possibility of producing refuse-derived fuel (RDF) to substitute fossil fuels. The results show a potential since the waste amount increases rapidly along with the nondegradable components.

By implementing a well-conceived waste management system, it is possible to contribute to resource conservation, for example, via recycling processes of used products. Chemical additives which have been introduced decades ago may consider being later hazardous substances and should therefore be substituted by non-hazardous chemicals. Within the last years, for example, policy tools have been developed to phase out these goods for special recycling procedures or safe disposal.

To minimise hazardous additives in used goods and to improve their recyclability, it is, for example, required to strictly label appliances containing hazardous substances and to improve safe handling of those goods. For persistent hazardous substances like fluorinated compounds, inventories covering production, trade, transportation, applications and disposal are extremely helpful to identify sources and sinks in the technosphere and in the environment and their impact.

4 RISKCYCLE: Future Outlook

What will be the outcome of the RISKCYCLE project and how is the influence on research policy and legislation? Different ways for implementation are conceivable: the Ecodesign Directive and European Waste Legislation (RoHS, WEEE and REACH).

The Ecodesign Directive is the regulation that sets the standards for products in principle for the preconsume phase so that only those chemical additives may be added that do not cause problems in a sustainable closed material and substance cycle. Currently the directive is being discussed to expand its scope and not only to products related to energy consumption.

Since the implementation of the RoHS Directive, many problems have already been addressed and hazardous components have been limited or banned. The outcome of the RISKCYCLE project and further research initiatives could be a reason to extend the scope of the directive either by a broader scope (not only electrical and electronic equipment) or by extending the catalogue of restricted substances (Annex II of the Directive).

According to the European Chemicals Legislation (REACH), manufacturer and importer have to register chemicals they are bringing on the European market if the sold volume exceeds more than 1 Mg/a. The REACH regulation has the item that after a 5-year period, there should be an evaluation of the regulation itself – this is where the results of the project RISKCYCLE and follow-up research could give more information to the European legislation. As soon as a material or a waste "ceases to be waste", it becomes instead a product and is falling under the REACH regulation. Actually the commission is working on establishing end-of-waste criteria for a number of specific recyclable materials. With regard to the outcome of RISKCYCLE, the obligations for products containing hazardous substances are of great concern; a risk characterisation is mandatory.

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