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Environmental Security

Management of Intentional and Accidental Water Pollution

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Management of Intentional and Accidental Water Pollution

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Management of Intentional and Accidental Water Pollution

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CONTENTS

Preface

Scientists, representing the fields of agriculture, biodiversity, ecology epidemiology, medicine, microbiology, public health, toxicology, risk assessment, environmental protection and bioethics from 15 countries and 3 continents came together in May 8-12 2005, in Sofia, Bulgaria to discuss the future of water safety and security. The goals of the workshop included a discussion of the state of the science in identification of new research and approaches for water pollution events and communication of the management of water pollution and sustainability of water resources.

Critical to management of accidental and intentional pollution events is the assessment of the risk, an understanding of the hazards and lessons learned from events which may lead to preventative management and control strategies. Public health protection will ultimately be improved by the ability to develop management frameworks which are flexible and adaptable to the specific region, country or watershed problems and concerns and allow for prioritization in the decision making.

The integration of scientific information regarding the types of hazards the environmental fate of the chemical/biological, exposure pathways and human and ecosystem impacts may be implemented from both a qualitative or descriptive approach or using a more classical quantitative risk assessment paradigm. Thus the frameworks for assessing the risk and managing the risk may be seen as preventive, early warning and responsive.

The hundreds of biological hazards are as diverse as the list of chemical pollutants and represent groups belonging to algae, bacteria, helminthes, parasites, and viruses. The sources include sewage and animal wastes as well as organisms in the natural water environment that can cause infections or produce toxins. Exposure pathways are complex, recreational waters and drinking waters (at the source, at the treatment plant, in groundwaters and distribution systems) are at risk and these organisms also impact the food chain. In addition, the natural occurring biological integrity of the water is key to ecosystem health and impacts of pollutants can be observed by examining the aquatic microbial populations of a system.

It was emphasized the role of sewage as one of the most important sources of microbial contaminants in water. As for the chemicals the quantitative risk assessment (QRA) framework is used, and while a single fecal indicator system is currently used, better monitoring for a number of indicators, source tracking host-specific markers and pathogens is needed. The toxic algae represent an emerging risk as many of the toxins have not been identified. A tool box of many tests will be necessary and could be developed for evaluation of contamination of drinking and surface water.

The list of agents which could be used to impact drinking waters is limited to chemicals, toxins and biological and the potential and relative risks are influenced by the same set of parameters used in the QRA. Chemicals and toxins were overviewed that may be used as chemical weapons in the intentional pollution of water. A QRA approach is useful for developing priorities associated with acute exposures and influenced by stability in water, susceptibility to treatment and finally toxicity.

An approach which examined the vulnerability of water systems by access, dilution and water treatment demonstrated that the storage reservoirs were at the most risk.

Like the chemical QRA, stability and resistance of biological agents to treatment and potency were the key parameters influencing the vulnerability. The ability to rapidly monitor if a credible threat is identified is a key part of the response plan.

There was much discussion regarding the setting of acceptable (safety) goals. While on the one hand the global guidelines and standards provided by agencies such as WHO and EU lay a minimal level of risk as part of the beginnings of a level playing field, it is clear that part of the society discussion on management needs to include the issue of acceptable risk. While no single target may be set for all safety goals, principals which include shared values and incorporation of the water ethics issues above will guide the costs and benefit analysis that may be undertaken. Recognizing that prevention goals may be more stringent and restoration goals may be time dependent. Geographic and societal characteristics should be considered. Drinking water goals and standards are there also to protect the sensitive and vulnerable populations.

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The editors have to thank the NATO Science Committee for the approval of the workshop, the former Programme Director, Environmental and Earth Science & Technology Dr. Alain Jubier for his continuous help and advices for the organisation of the workshop. and especially to thank for the understanding and support from Mr Deniz Beten, Programme Director Environmental Security.

The organisers of the workshop are convinced on the successfulness of the event and hope that the publication of the results will find its way to the many scientists, regulators and other interested parties in that field.

POTENTIAL WATER QUALITY PROBLEMS POSED BY INTENTIONAL/ACCIDENTAL INTERVENTIONS

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Abstract

Water is an important component supporting human life and the natural environment but also media for transmission of chemical and biological pollutants.

Emergency events like spills of chemicals, industrial or raw sewage discharges, improper treatment practice etc. could pose water quality degradation and subsequently considerable threats to water ecosystems and/or human health. Cases of accidental water pollution are presented with respect to their impact on the chemical and microbiological quality of the drinking water, its aesthetical parameters and possible health implications. Risk factors facilitating water contamination by biological agents are discussed. Actions reducing the impact of the pollution on the drinking water quality are considered in relation to the vulnerability of the water supply chain.

Keywords: water quality/ accidents/ health effects

1. Introduction

The water is one of the most vulnerable environmental compartments to pollution by chemicals and biological agents due to its nature and the hydrological interrelations. As living environment and life securing resources polluted waters may cause serious threats to the integrity of the ecosystems

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 1–10.

and human health. Therefore proper water management is substantially important for the overall human and economic life, and especially significant to avoid water related emergencies.

From regulatory point of view water quality is defined as a complex of chemical, physical, microbiological and radiological properties with respect to its suitability for particular purposes. Following the conventions a significant change of the water characteristics would be associated with loss of any of the actual or potential beneficial uses: for drinking and domestic purposes, production of food and beverages, fishery, livestock watering, crops irrigation etc.

2. Water quality threats associated with chemical releases

A wide range of chemical compounds has been found in the water environment. The fate of the chemicals to the water compartment is influenced by a number of factors including mode, pattern and point of discharge, volume and physicochemical properties of the compound released. The most significant routes of contamination are directly from treated and untreated waste waters, run-off, atmospheric deposition and spray drift or indirectly from leaching (Holt., 2000).

Direct introduction of chemicals and immediate destruction of the water quality is presumed also in cases of intentional/accidental pollution making it non wholesome or unsafe with subsequent acute effects. Accidental contamination and potential water quality problems are difficult but not impossible to be avoided as shown by past events.

Great recall received major chemical accidents causing large-scale effects. A classical example of massive water pollution becomes the fire incident in 1986 at the warehouse of a chemical company in Switzerland. Firefighting water contaminated with mercury- and zinc- based pesticides, organophosphorous (dichlorvos, parathion, etc.) and other pesticides (endosulfan, DNOC etc.) caused pollution of river Rhine and massive fish death. Most of the substances flushed into the river were classified as dangerous to the environment and very toxic or toxic to aquatic organisms. Besides the ecological threat the waterworks along the river had to close due to the pollution and emergency supplies were used (Capel et al., 1988).

Apart of the major chemical emergencies small scale accidents with chemical compounds are not uncommon. They are mainly of a local importance and may affect any link of the water supply.

Relatively high amounts of pesticide residues were found in water samples after incidental pollution events in Bulgaria. In single cases atrazine, simazine and propazine were reported up to 2000, 1120 and 115 μg/l respectively. Trifluralin was found also in high concentrations (700 – 1000 μg/l). Among the detected active substances were also pesticides banned decades ago. DDT (total) was determined in concentrations up to 1.63 μg/l, and lindane up to 0.14 μg/l. The reasons were illegal deposition of pesticides in deserted wells or landfills, destroyed pesticide storehouses or improper storage of banned and obsolete plant protection products (Bratanova and Vassilev, 2001, Kambourova et al., 2005).

In 1991 an accidental spill of phenol into the river Nakdong occurred in Korea. As a consequence the tap water for about two million consumers was contaminated. Gastrointestinal symptoms such as nausea, vomiting, diarrhea, or abdominal pain were reported by the consumers. More than 90 % of the subjects experienced peculiar taste or odor in the tap water during the accident (Kim et al., 1994).

Incidents with water treatment chemicals have been also a reason for changes of the indicator parameters, excessive concentrations of chemicals in the supplied water and even health implications.

Drinking water contamination with large quantity (20 t) of aluminium sulfate was registered in 1988 in Cornwall, England. The extent of the pollution was not immediately realized although acidic water from treatment works entered the distribution system. The water delivered contained high concentration of aluminium with maximum of 620 mg/l. Elevated values of copper, lead, and zinc due to leaching from pipes were also recorded (Owen et al., 2002). No lasting effects but mild and short lived symptoms including nausea, vomiting, diarrhea, mouth and skin ulcers were noted (WHO, 1998).

Accidents due to drinking water hyper-fluoridation have been reported in USA, where water treatment with fluoride compounds is common. Excess hydrofluorosilicic acid was introduced into community water supply with peak fluoride level of 51 mg/l. Due to the water acidification copper leached from the plumbing up to concentrations of 25 - 41 mg/l. 33 % of the consumers developed mild gastroenteritis. Skin contact with hyper-fluoridated water caused itching and skin rashes (Petersen et al., 1988).

Acute fluoride poisoning characterized by nausea, vomiting, diarrhea, abdominal pain, and paresthesias was recorded in 1992 in a village in Alaska. Poisoning of 296 residents and one case with lethal outcome were reported. The fluoride concentration of a water sample was 150 mg/l (Gessner et al., 1994).

During the incident with acute gastrointestinal symptoms registered in 1993 in a small community of Mississippi the water samples contained more than 40 mg/l fluoride. At a point close to the main treatment plant the concentration reached 200 mg/l. Water with high fluoride content had been pumped accidentally into the town system because saturated fluoride solution siphon from the saturator tank into the ground reservoir (Penman et al., 1997).

Accidental contamination of drinking water with styrene occurred in 1999 Castellón, Spain during reparation works with an unsaturated polyester resin based on styrene and fiberglass. Drying was facilitated with a fan and vapors were forced into the drinking water tank. The tap water had a strong solvent-type smell and produced nausea and other gastrointestinal symptoms when consumed. Values of styrene up to 900 μg/l were measured in samples collected three days after the event. The styrene concentration in water declined after the fourth day. Low levels of toluene and other dissolved hydrocarbons were also found. A thin gelatinous layer on the water surface in the tanks due to the poor water solubility of styrene was visible, and nearly all subjects perceived the odor. The reported taste threshold concentration for styrene in water is around 0.7 mg/l (Arnedo-Pena et al., 2003).

The changes in aesthetic properties, fluctuation in water pressure, complaints on disease‘s symptoms and any suspicious activities near water systems are highlighted as first indicators of possible water contamination. Even taste, odor, color and turbidity are considered parameters without direct health threats it is emphasised that due to changes of the organoleptic parameters several true acute health effects have been discovered. Detectable odor is associated to drinking water containing harmful levels of pesticides - diazinon (faint ester-like), malathion (mercaptan, garlic), parathion (rotten onion, garlic), as well as fluoride (sharp, pungent, irritating), cyanogens chloride (pepperish), petroleum products (pungent, hydrocarbon) etc. The analysis of the evidences gained from monitoring the consumer complaints has shown that from a management and public perspective it is important to monitor taste and odor as primary signals of drinking water integrity (Whelton et al., 2004, Watson, 2004).

3. Risky factors and water quality threats associated with biological contamination

In general, pathogenic contamination of drinking water poses the most significant health risk to humans. For the period 1986 - 96, surveillance data from 18 European countries identified a total of more than 2.5 million cases of gastrointestinal and other possibly waterborne diseases, of which 2% were linked to drinking water (Lack, 1999).

The requirement for water free of pathogens and opportunistic microorganisms applies to all kinds of water usage. Water contamination with pathogens is known to occur from a range of sources including municipal wastewater effluents, agricultural wastes, and wildlife. Facilitated by other risky factors they could also be sources of massive accidental water pollution.

Animal waste contains human infectious agents like Salmonella, pathogenic E. coli, parasites etc. that can be 10 to 100 times more concentrated than in human waste. The significance of the animal excreta as a factor contributing to the extent of waterborne diseases is increasing probably due to the difficulties to be controlled. Cattle manure runoff was the most likely source of the E.coli O157:H7 and Campylobacter outbreak in Walkerton, Canada where about 2300 people became ill and seven died from exposure to contaminated drinking water (Hrudey et al., 2003). The outbreak occurred after fife days of heavy rainfall. It is an indication that weather prediction and precipitation forecast have to be considered by water managers and public health authorities as a significant risk factor for water contamination (Auld et al., 2004).

Manure from dairy cows is thought to have contributed to the *Cryptosporidium* contamination of Milwaukee's drinking water in 1993. This and a number of other drinking water related outbreaks have resulted from breaches in treatment facilities. Therefore it is assumed that massively contaminated raw water is associated with greater health risk even when treatment is present.

The zoonose parasites *Giardia lamblia* and *Cryptosporidium spp.* are among the most relevant pathogens of drinking water-associated outbreaks (Exner and Gornik, 2004). The analysis of the registered outbreaks with identified source of contamination caused by *C. parvum* and *G. lamblia* have shown also a relationship with uncommon weather conditions like rainfalls or events as high water and intrusion of surface water or waste water into the wells. In almost all cases the abstracted water was disinfected but not or non-efficiently treated (Schoenen and Kanaris, 2001). It is outlined that disinfection of drinking water cannot replace filtration that is very effective for eliminating pathogens. The disinfection should be used to minimize the residual risk due to the presence of pathogens in the water but cannot be used to recover contaminated water into a sound condition (Schoenen, 2002).

The most common tests used for evaluation of the microbiological water safety are coliforms, E. coli and faecal streptococci which presence has been more strongly associated with the incidence of gastrointestinal diseases. The emergency waterborne parasites such as *Cryptosporidium* have shown to cause outbreaks even when the conventional microbiological parameters are satisfactory, those making the concept for the classical indicators questionable. In response the UK, for instance, has introduced a requirement obligating the water providers to perform a risk assessment on the water treatment facilities and continuous monitoring for oocysts of *Cryptosporidium* (Barrell et al., 2000).

Indications exist that two weeks prior to the outbreak in Milwaukee consumer complains were registered on various taste, odor and color of the drinking water that have been probably disregarded at that time (Whelton et al., 2004). Therefore changes in the water quality aesthetic parameters have to be considered as appropriate non-specific signs for pollution with organic matters.

Based on the comprehensive evaluation of the contamination incidents and waterborne outbreaks five groups of incident triggers have been outlined:

- Inadequate performance of a sewage treatment plant discharging to source water, as well as inadequate performance of drinking water treatment plant are considered as process indicators;
- Any notification of events like spillage of a hazardous substance into raw water or power supply failure is informative for eventual adverse impact on the microbiological safety of drinking water;
- Extreme rainfalls, unusually high turbidity of the raw or treated water, taste, odor or appearance have to be considered as appropriate non-microbial indicators;
- Specific microbial indicators comprise unusually high faecal indicator or pathogen densities of the raw or treated water, and
- As suitable public health indicators are defined disease outbreak for which water is a suspect vector (Hunter et al., 2003).

Records on the incidents triggers could be helpful for developing appropriate action plans, planning response measures and health protection activities.

To the better management of the microbiological quality of drinking water may lead improvements in monitoring and risk characterization, health surveillance system and application of the multiple barriers concept (Krewski et al., 2004).

4. Water quality threats associated with the vulnerability of the supply system

Water protection activities and prescriptive management measures are necessary to ensure sustainable management and sound drinking water supply (Davies and Mazumder, 2003).

The possibilities for reduction of the water quality threats and likely subsequent adverse effects are closely related to the vulnerability of any particular point in the system (WHO, 2004). In Table 1 are presented the water supply links and the associated factors influencing the potential impact of contamination.

TABLE 1. Water supply chain and factors influencing the potential impact of water quality contamination (adapted according to WHO, 2004).

water supply link	vulnerability	note*	factors influencing the potential impact of contamination
Water source contamination	low	↓	dilution with large volumes of water
		↓	non-specific inactivation by hydrolysis, sunlight, degradation, soil attenuation etc.
		↓	likely subsequent treatment
	high	↑	vulnerable/ unprotected sources
		↑	absence/ non-effective treatment/disinfection
		↑	small sources
		↑	absence of regular raw water monitoring
Raw water mains contamination	relatively vulnerable	↓	likely inactivation by treatment
		↓	likely subsequent detection
		↑	inactivation not effective/ not applicable to all systems/ pollutants
Water-treatment facilities	high	↓	treatment/disinfection control - likely detection
		↑	disinfection reduction/interruption
		↑	poor treatment/disinfection control
		↑	no treatment in small/medium systems
Distribution system	vulnerable	↓	water delivered under pressure
		↑	possible contamination post treatment/disinfection
Water tanks/ towers	high	↑	gravity fed water/ low pressure
		↑	possible contamination post treatment/disinfection
Buildings distribution system	relatively vulnerable	↓	relatively small number of consumers
		↑	no dilution
		↑	no treatment/disinfection

* Note: (↓) factor decreasing the potential impact of contamination
(↑) factor increasing the potential impact of contamination

Possible actions for reducing the risk for negative impact on water quality:

- risk assessment in the catchment and water supply area;
- protective and security measures of the abstraction equipment and facilities;
- regular monitoring and data analysis of the water quality;
- optimization of the treatment and disinfection processes;
- enhanced control measures of the treatment and disinfection processes;
- regular inspection and control of the whole supply system;
- notification and registration system for waterborne diseases.

5. Conclusions

The ultimate consequence of the most cases of drinking water quality degradation is the risk for realization of adverse health effects. Diverse chemical agents (pesticides, organics, heavy metals) could be a reason for water quality deterioration on different scale in case of intentional/accidental pollution. Classical indicator parameters and consumer complains can provide the earliest warning for unsafe water. Therefore their causes have to be assessed and determined. Non specific indicators have to be under surveillance as regards possible biological contamination. The registration of accidents and introduction of recording system with information for incident triggers could contribute significantly to the overall water management.

6. References

Arnedo-Pena, A., Bellido-Blasco, J., Villamarin-Vazquez, J.L., Aranda-Mares, J.L,. J.L, Font-Cardona, J.L, Gobba, F., Kogevinas, M. 2003. Acute health effects after accidental exposure to styrene from drinking water in Spain, *Environmental Health: A Global Access Science Source*, 2.
(http://www.ehjournal.net/content/2/1/6)

Auld, H., MacIver, D., Klaassen, J. 2004. Heavy rainfall and waterborne disease outbreaks: the Walkerton example. *J Toxicol Environ Health A.* 67 (20-22),1879-1887.

Barrell, R.A., Hunter, P.R., Nichols, G., 2000. Microbiological standards for water and their relationship to health risk. *Commun Dis Public Health.* 3(1), 8-13.

Bratanova, Z. and Vassilev, K. 2001. Pesticide Residues in Ground and Surface Water in Bulgaria. *Fresen. Environ. Bull.*, 10 (4), 401-404.

Capel, P.D., Giger, W., Reichert, P., Wanner, O. 1988. Accidental Input of Pesticides into the Rhine River. *Environ. Sci. and Technol.* 22, 992-996.

Davies, J.M., Mazumder, A. 2003. Health and environmental policy issues in Canada: the role of watershed management in sustaining clean drinking water quality at surface sources. *J Environ Manage.* 68 (3), 273-86.

Exner, M., Gornik, V., Parasitic zoonoses transmitted by drinking water. Giardiasis and cryptosporidiosis. *Bundesgesundheitsblatt Gesundheitsforschung Gesundheitsschutz* 47(7), 698-704.

Gessner, B.D., Beller, M., Middaugh, J.P., Whitford, G.M..N. 1994. Acute fluoride poisoning from a public water system. *Engl J Med.* Jan 13; 330(2), 95-99.

Holt M.S., 2000. Sources of Chemical Contamination and Routes into the Freshwater Environment. *Food and Chemical Toxicology* 38 (Suppl.1), 21-27.

Hrudey, S.E., Payment, P., Huck, P.M., Gillham, R.W., Hrudey, E.J. 2003. A fatal waterborne disease epidemic in Walkerton, Ontario: comparison with other waterborne outbreaks in the developed world. *Water Sci Technol.* 47(3), 7-14.

Hunter, P.R., Y. Andersson, C.H. Von Bonsdorff, R.M. Chalmers, E. Cifuentes, D. Deere, T. Endo, M. Kadar, T. Krogh, L. Newport, A. Prescott and W. Robertson (2003) Surveillance and investigation of contamination incidents and waterborne outbreaks. In: Assessing Microbial Safety of Drinking Water- Approving Approaches and Methods. WHO, OECD, 205-236.

Kambourova,V., Manova, J., Bratanova, Z. 2005. Environmental Pollution with Organochlorine Pesticides by Small Scale Incidents. *Fresen. Environ. Bull.,* 14 (3), 181-184.

Kim DH, Lee SK, Chun BY, Lee DH, Hong SC, Jang BK. 1994. Illness associated with contamination of drinking water supplies with phenol. *J Korean Med Sci.,* 3, 218-223.

Krewski, D., Balbus, J., Butler-Jones, D., Haas, C., Isaac-Renton, J., Roberts, K., Sinclair, M., Managing the microbiological risks of drinking water. 2004. *J Toxicol Environ Health.* 67 (20-22), 1591-1617.

Lack, T., 1999. Water and health in Europe: an overview. *BMJ.* 318, 1678-1682.

Owen, P.J., Miles, D.P.B., Draper, G. J., Vincent, T. J. 2002. Retrospective study of mortality after a water pollution incident at Lowermoor in north Cornwall. *BMJ*, 324, 1189.

Penman, A.D., Brackin, B.T., Embrey, R. 1997. Outbreak of acute fluoride poisoning caused by a fluoride overfeed, Mississippi, 1993. *Public Health Rep.* 112(5), 403-409.

Petersen, L.R., Denis, D., Brown, D., Hadler, J.L, Helgerson, S.D. 1988. Community health effects of a municipal water supply hyperfluoridation accident. *Am J Public Health.* Jun; 78(6), 711-713.

Schoenen, D. and Kanaris, P., 2001. Beobachtungen uber parasitenbedingte Ausbruche durch Trinkwasser und Massnahmen zur deren Vermeidung. Teil II: Literaturuberblick uber trinkwasserbedingte Ausbruche durch Giardia lamblia, Cryptosporidium parvum und Toxoplasma gondii, Bundesgesundhbl 44, 371-376.

Schoenen, D., 2002. Role of disinfection in suppressing the spread of pathogens with drinking water: possibilities and limitations. *Water Res.* 36(15), 3874-3888.

Watson, S., 2004, Aquatic taste and odor: a primary signal of drinking-water integrity. *J. Toxicol Environ health A.* 67 (20-22) 1779-1795.

Whelton A. J., A. M. Dietrich, G. A. Burlingame, M.F. Cooney, Detecting Contaminated Drinking Water: Harnessing Consumer Complaints. AWWA WQTC Proceedings, San Antonio, TX,Whelton et al. (2004),Tuesday, Nov 10, 2004.

WHO. 1998. Guidelines for Drinking Water Quality. Vol. 2. Health Criteria and other supporting information. Addendum.

WHO. Precautions against the sabotage of drinking-water, food, and other products. Annex 5 in Public health response to biological and chemical weapons: WHO guidance. Ed 2. 2004.

QUANTITATIVE HEALTH RISK ASSESSMENT RESULTING FROM GROUNDWATER CONTAMINATION OF AN ABANDONED OPEN FIELD CHEMICAL WASTE BURNING SITE

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Abstract

Quantitative human health risk assessment was performed for the evaluation of health threat resulting from the chemical contamination of the soil and groundwater in the area of the former open field pharmaceutical waste burning site. The main aim of the study was the determination of the remediation target-value, in compliance with the No. 219/2004. (VII. 21.) Hungarian Government Decree on "The protection of groundwaters".

Keywords: risk assessment, exposure modelling, remediation target concentration

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1. Introduction

The term contaminated sites refers to industrial place and landfills where pollutants have leached into the ground and groundwater in the past as a result of poor handling, leakage, accidents or inadequate technical safety measures, consequently resulting in risk for the environment and human health. Risk assessment of contaminated land starts with detection of the presence of soil or groundwater pollution. It was revealed in abandoned tufa mine, which was used by the pharmaceutical factory, between 1964 and 1980 that the groundwater of the site had been heavily contaminated. The burning residue was removed from the mine pit in 1997 and transferred to a hazardous waste treatment facility. Groundwater contamination endangered not far off drinking water resource of the regional waterworks. Therefore setting up remediation concentration of soil and groundwater contamination was conducted to substantiate remediation process.

The study comprises:

- The brief description of concepts and methods of the environmental health risk assessment resulting from soil and groundwater contamination,
- The data used for the model-experiments simulating potential human exposures,
- Determination of the exposure routes from the source of contamination to the receptor, and the acceptable level of risk,
- The evaluation of human health risk resulting from the present state of contamination in the environment of the abandoned open field chemical waste burning site,
- Reverse risk assessment was carried out to calculate target concentration of contaminants for remediation.

2. Method and data used for risk assessment

The main parts of the study:

a). Assessment of the risks resulting from the following contaminants of soil and groundwater:

alkylbenzenes: benzene, toluene, xylenes, trimethylbenzene, m-diethylbenzene

volatile halogenated alifatic hydrocarbones: chloroform, chlormethane, 1,2-dichlorethanee, dichlormethane, 1,1,2-trichlorethanee, trichlorethylene, carbontetrachloride, vinylchloride *volatile halogenated aromatic hydrocarbones*: chlorobenzenes dioxines

other volatile hydrocarbones: diethoxymethane, 1-methoxy-2-propyl-acetate, glycolether, methylisobuthylketone

PAHs: fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benz[b]fluoranthene, benz[k]fluoranthene, benz[a]pyrene, indene[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benz[g,h,i]perylene, naphtalenes.

b). Summing up the chemical risks of the individual soil and groundwater contaminants.

c). Determination of the remediation target value for the contaminated soil and groundwater.

The remediation target concentration based on the relevant risk can be determined, when the site specific health risk exceeds the acceptable level. In those cases reverse risk assessment is carried out: according to this back up calculation, instead of determining the risk posed by the contamination, the residual level of the contaminants, the so-called „remediation target level" is calculated from the acceptable risk, below which no health impact occurs.

The risk assessment was accomplished on the basis of the national technical guidance (2004). We have also taken into consideration the recommendations of the US EPA technical guidance (Risk Assessment Guidance for Superfund, 1989) as well as UK Ready Reference (2002).

When determining the risk we had to aggregate the concentration data of the contaminants. The upper 95% confidece limits (UCL) of the average concentrations were calculated from the measured values of the contaminants, as shown below:

$UCL = x + t (s\sqrt{n})$

where

UCL	is the upper 95% confidence limit of the average
x	is the average
s	is the standard deviation
t	is the t upper 95% confidence limit value of the Student test
n	is the number of samples

In the risk assessment we applied the upper 95% confidence limit (95%UCL) values of the averages as representative for the entire contaminated area. The risk assessment calculations were based on soil and groundwater contamination concentrations presented in Table 1.

TABLE 1. Contamination data used for the exposure modeling.

Contaminant	Groundwater (mg/L)	Soil (mg/kg)
BTEX		
Benzene	91	980
Toluene	50	1700
Ethylbenzene	0,95	110
Xylenes	4,4	410
Chlorbenzene	49	8800
Dioxin (2,3,7,8-TCDD)	3,6E-08	155 ng/kg
volatile halogenated alifatic hydrocarbones		
Chloroform	29,7	
Chlormethane	0,009	
1,2 chlormethane	60	300
Dichlormethane	9,13	
1,1,2-trichlorethane	0,606	
Trichlorethylene	1,39	
Vinylchloride	0,0196	
Carbontetrachloride	0,496	
other volatile halogenated hydrocarbones		
Methoxypropylacetate	175	
Diethoxymethane	1806	
Ethylenglycol	49,5	
Methyl-ethyl-keton	8,3	
PAH-s		
Benzo(a)pyrene	0,000032	0,007
Benzo(g,h,i)perylene	0,000013	0,002
Benzo(k)fluoranhene	0,000074*	0,007*
Benzo(b)fluoranthene	-	-
Benzo(a)antracene	0,00015	0,001
Indeno(1,2,3,c,d)pyrene	0,000016	0,002
Chrysene	0,00021	0,053
Pyrene	0,00034	0,023
Phenanthrene	0,0019	0,24
Fluoranthene	0,00044	0,029
Anthracene	0,000032	0,014
Naphtalyne	0,13	18
Fluorene	0,001	0,031

* sum of Benzo(k)fluoranthene and Benzo(b)fluoranthene

The risk evaluation concept was based on the good knowledge of the local conditions after having the site examined. In our risk assessment we accomplished the complete evaluation of the possible exposure pathways from the source of contamination to the receptors.

We took the following receptors into consideration:

1.) The people working on the contaminated site,
2.) The residents of the adjoining area (in 150 meters).
3.) The regional drinking water resource at a distance of 800 meters in the direction of the groundwater flow,

Models for exposure assessment and contaminant transport were used to predict concentration at receptors and the actual uptake of chemicals. Health risk was expressed as ration of magnitude of exposure to acceptable level of contaminants intake taking into consideration local hydro-geologic, meteorologic conditions, daily activities of the people/workers on the site and the human physiological parameters.

3. Planning model calculations

Exposure models are used to predict human uptake of pollutants via contaminated environmental media directly (ingestion) or indirectly (inhalation of volatile vapours) depending on the land use and human activities.

Exposure situations were selected to characterize the real conditions of the affected people working on the contaminated site and living in the adjoining area, and the regional drinking water resource in the direction of the groundwater flow.

Two types of receptors were distinguished in the contaminated area: on site workers, who had been exposed to contaminants for a long time (25 years) and workers staying there only a short time (one year) dealing with for example maintenance, service or remediation, and technical intervention work.

Obviously, c*ontaminated soil* could have been handled only by the workers on site.

Drinking water consumption (via contaminated groundwater) of 1 litre per day on-site was assumed according to the exposure guides.

Exposure to o*utdoor air* is a reasonable situation, thus inhalation of volatile contaminants evaporating from soil and groundwater can be regarded as potential exposure routes. Container houses are built on the contaminated site, but exposure to *indoor air* pollutants was not considered a potential exposure route, because these constructions do not have traditional, firm foundation in the surface layer, to which exposure models refer.

The exposure resulting from living 150 meters away from the contaminated site and land use was based on assumption regarding consumption of 2 litres of groundwater per day.

We also accomplished the health risk assessment regarding to the drinking water resource of regional water-plant at a distance of 800 meters.

The Domenico model (Domenico, 1987)was used to predict concentrations at receptors of various distance from the source and examine the groundwater transport of alkylbenzenes, volatile halogenated aliphatic and aromatic hydrocarbons, dioxins, and PAHs.

The model predicts the movement of the plume of dissolved contaminants, but also has its limits, namely that simple groundwater flow is assumed. Because general knowledge is addressed, steady (isotropic and homogeneous) environmental and hydrogeologic conditions are used in the model. This simplifies the real local conditions.

The Domenico equations assume that the layer of contamination is vertical to the groundwater flow. Hereby simulates the movement of the contaminant plume with the groundwater, calculates the one-dimensional advective transport, the three dimensional dispersion and the linear adsorption. Since our model is conservative, the decay of contaminants was not taken into consideration.

Our aim was to calculate the risk from the predicted concentrations of the contaminants at the potential receptors, at distances of 150 and 800 meters, and provide additional data for the determination of the remediation target-value.

With the knowledge of site investigation, specific data, exposure routes, receptors and their distance from the source of contamination, using the RBCA software, human exposure modelling was accomplished to quantify the human health risk from exposure to contaminants in the abandoned open field waste burning site.

The hazard quotient and cancer risk were quantified using toxicometric values (RfD, RfC, SF, UR).

4. Results

Determination of the health risk values

We summarized the calculated values of the total heath risk (see table) resulting from the exposure of the investigated contaminants in case of each environmental media (air, soil, groundwater) and receptors (local workers, remediation workers, residents) with regard to the distance between the source of contamination and the receptors (150 m and 800 m).

The likelihood of the carcinogenic effects and the hazard quotient indicating systemic toxicity are shown in each case.

TABLE 2. Risk values related to 95% UCL of average contamination of the groundwater and soil.

	Likelihood of CARCINOGENIC RISK (excess risk)				Value of the HAZARD QUOTIENT (in excess of the toxicological threshold [RfD] value indicating health damage)			
	On-site		Off-site		On-site		Off-site	
	0 m	0 m	150 m	800 m	0 m	0 m	150 m	800 m
Environ mental media	Local workers	Remedia tion workers	Residents	Residents	Local workers	Remedia tion workers	Residents	Residents
Outdoor air	4,19E-5	NA	2,28E-5	9,77E-7	7,57	NA	5,16	0,22
Indoor air	NA	NA	NA	NA	NA	NA	NA	NA
Soil	3,00E-4	8,80E-6	NA	NA	49,7	36,1	NA	NA
Ground water	1,34E-2	NA	1,11E-2	6,37E-4	344	NA	225	13
Total	**1,37E-2**	**8,80E-6**	**1,12E-2**	**6,38E-4**	**401**	**36,1**	**230**	**13,2**

Table 2 shows the health risk posed by contaminants on site and 150 and 800 meters away from the site is very high.

Predicted concentrations calculated by the transport model

The Domenico model was used to predict groundwater flow, the plume of contamination and the expected concentrations of the contaminants at the assumed receptors at distances of 150 and 800 meters. Leaching from soil to groundwater and dilution, attenuation of the contaminants in groundwater were calculated separately. Model-examinations were completed for all contaminants. Considering the concentrations of the contaminants, the distance of the receptors and the natural dilution (attenuation) factor, we calculated, from the concentration-time relationship, the time period needed for the contaminants to reach the receptors. Steady state conditions were assumed, decay was not taken into consideration.

TABLE 3. Time periods needed for the contaminants to reach the receptors at distances of 150 and 800 meters, and their concentration in comparison with the limit values.

Contaminant	Period of transport at a distance of 150 meters (year)	Concentration at 150 m distance/ Limit value	Period of transport at a distance of 800 meters (year)	Concentration at 800 m distance/ Limit value
Dichlor-methane	2,4	115		
Chloroform	2,8			
Vinylchloride	3,1	10	29	0,5
Dioxin	3,5			
1,1,2-trichlorethane	3,9			
Trichlorethyl-ene	4,5	34	51	2
Carbontetra-chloride	7,1	60	63	3,5
Benzene	2	18000	14	1000
Toluene	16	450	-	26
Chloroben-zene	2	26000	-	800

Transport model indicates the high mobility of volatile organic contaminants. Due to high mobility and concentration as well as brief access time of benzene and chlorbenzene they threat quality of water at receptor in 800 meter distance.

Determination of the remediation value

The remediation target-value of the contaminants was calculated by reverse risk assessment with the aim of keeping the chemical burden of the assumed receptors resulting from soil and groundwater contamination below the acceptable level after having finished the remediation work. According to the above, the following remediation target-values were recommended for the soil and groundwater of the contaminated site:

TABLE 4. Proposed remediation target-values with regard to the actual contamination.

Contaminant	Groundwater ug/l	Soil mg/kg
Benzene	9,0	2
Toluene	1000* 20**	100* 5**
Xylenes	440* 20**	100* 5**
All alkylbenzenes	***50***	***13***
Chlorbenzene	500* 10**	100* 1**
Dichlormethane	50	10
1,2-dichlorethane	3,1	1,0
Chloroform	20	2,0
Carbontetrachlorid	3,0	0,2
Trichlorethylene	30	1,0
1,1,2-Trichlorethanee	3,0	1,0
Vinylchloride	0,7	NA
All chlorinated alifatic hydrocarbones	***110***	***15***
Dioxin (2,3,7,8-tcdd)	2 pg/L	5 ng/kg

Where,

NA no data available

* acceptable concentration from toxicological considerations, no threat of health damage

** concentration, which does not cause discomfort, determined by the organoleptic threshold value

The adequacy of the remediation target-values of the contaminants was verified by their cumulative risks. Our checking calculations indicate that the cumulative risk of the residual contamination, in accordance with the suggested remediation target-values, does not exceed the acceptability range.

5. Conclusions

Soil and groundwater chemical contamination exceeded the legally specified limit value in the area of the former open field pharmaceutical waste burning site. We found the health risk, calculated from the 95% confidence level of average concentration of the contamination at the 24 groundwater sampling points, extreme high (hazard quotient = 400). The results of the detailed quantitative risk assessment show that the likelihood of carcinogenic risk is also extreme high (risk probability = 1,8 . 10^{-2}). Remediation target-value of 6 soil and 12 groundwater contaminants were established, relying on the recalculation from the acceptable risk.

The required degree of decontamination ranges from 1 to 4 order of magnitude; f.e 32000 fold decontamination is required for 1,2-dichloroethylene. There is a need to reduce toluene, ethylbenzene, xilenes and chlorobenzene concentrations below the organoleptic threshold value in order to cease organoleptic discomfort and reach the suggested remediation target-value of 20 ug/l.

The following should be considered when evaluating the obtained values from human health perspectives:

1. The health risk assessment report is based on the assumption, that concentrations of the contaminants used in the model represent the level of contamination that people are exposed to during the given time of exposure.

2. The conclusions of the risk assessment report are based on the available data of measurements and refer to the contaminants.

3. The selected exposure situation influences the level of exposure. The actual exposure of people -depending on the lifestyle and daily activities – changes together with their participation in the exposure situation (activities in the contaminated area, potential off-site exposure, consumption of groundwater).

Contamination of groundwater reflects a conservative approach (worst case scenario). The risk is exaggerated in the case of the healthy adult population, but the protection of sensitive populations (small children, pregnant women, people suffering from chronic diseases) verifies its necessary.

4. The dosimetric and human-biological parameters (f.e body weight, age, exposed area of skin, absorption) describing exposure situations also influence the calculated values. Average population data and forms of daily activities were considered in the calculations, potential differences occurring between susceptible individuals and several risk groups (elderly people) were ignored, because there are no relevant data available.

5. The uncertainties of risk assessment –due to simplifying assumptions- and the variability resulting from the measurement of contamination (sampling, analytical measuring errors) are counterbalanced by the conservative approach.

6. The above introduced simplifying assumptions were used in our modelling and significant role was attributed to the distribution and transport

of contaminants in the environmental media. Therefore, it is important to support the modelling results with monitoring measurements. The high health risk value determined by the exposure and risk assessment model-examinations suggests further regular, carefully planned monitoring.

7. Because the assessed health risk of the people in the contaminated area –using worst case scenario of groundwater consumption- was reasonably high, a potential hazard should be presumed. Therefore, occupational exposure to the chemicals should be avoided. The followings are suggested:

- If the risk resulting from the contamination cannot be stopped, then the use of safety equipment is required,
- Safe working conditions are to be provided,
- The number of workers exposed to hazardous substances must be minimized,
- An action plan must be available in case of accident or disturbance,
- The chemicals, in connection with on-site activities, must be registered, in order to provide knowledge on the number of people exposed,
- Work activities must be suspended if the health of the workers is at risk. Registration of exposure is particularly important in the case of carcinogenic substances.

Keeping compliance with the work place regulatory values (average concentration, peak concentration) is essential. The employees must be educated and provided with information on risks of the occupational chemicals, health and safety hazards, exposure limit values and legal regulations by the employer. The employer should also draw the employees' attention to the risks of smoking, consumption of alcohol and interaction between chemicals in the contaminated area. Basic first aid lectures should be organized.

6. References

ASTM PS-104 standard (ASTM American Society for Testing and Materials: Standard guide for risk-based corrective action. ASTM PS-104, Philadelphia, PA, USA 1998),

Domenico P.A.: An analytical model for multidimensional transport of a decaying contaminant species. J.Hydrol. 91.49-58. 1987

Nathanail J., Bardos P., Nathanail P.: Conaminated Land Management: Ready Reference. Land Quality Press and EPP Publications, 2002

National Technical Guidance. The detailed quantitative risk assessment of contaminated sites. Kármentesítési útmutató 7. Ministry of Environment, Hungary, 2004

Risk Assessment Guidance for Superfund. Vol.1. Human Health Evaluation Manual (Part A.) US EPA Washington, 1989

ACUTE AND CHRONIC TOXICITY OF CHEMICAL WARFARE AGENTS AND WARFARE TOXINS IN DRINKING WATER

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Abstract

This short review collects the essential data on the acute and chronic oral toxicity of 6 Chemical-Warfare Agents (CWA) and 5 Warfare Toxins (WT). It evaluates the risk potential of each compound for drinking water supplies and consumers. With regard to toxicity on the one side plus cheapness and easiness of availability on the other side, VX and sulfur mustard present the highest risk potential among the CWA, whereas Ricin, Abrin and the Botulinum Toxins seem to contain the highest risk potential within the group of Warfare Toxins. Reproductive toxins (living microbial agents; viruses) are not included in this overview.

Key words: Warfare Agents/ Warfare Toxins/ Drinking Water/ Toxicity

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 23–41.

1. General aspects of chemical warfare agents (CWA) and warfare toxins (WT)[1]

1.1. CHEMICAL-WARFARE AGENTS (CWA)

Chemical Warfare Agents (CWA) represent a group of extremely toxic synthetic chemicals. They are designed for being used in armed conflicts and wars. Since purposes of armed conflicts and wars are not defined by science but by politics there is also no science-based definition of classification and purposes of CWA. They can, however, be classified under medico-toxicological aspects with respect to their (un)desired effects (toxic endpoints) and their main port(s) of entry into the target organism, who is mostly a human being or groups of such.

The most important classes of CWA, within the different "toxic endpoint"- or "desired effect are:

- herbicides and tear gases (both permitted), *and*
- pulmonary irritants, vesicant agents, cyanide, nerve agents (all prohibited),

All these could principally be deployed in effective doses and technically achievable amounts in drinking water, at least by contaminating small drinking water supply systems, mobile drinking water supplies, or bottled water.

The most toxic and at the same time technically easiest achievable among them are organophosphate based *nerve agents* and some *vesicant agents*.

But even if aimed to be ingested orally with drinking water these CWA may reach their targets not only via oral ingestion. Due to their sometimes high volatility and their hydrophilic as well as lipophilic properties they may be taken up also by inhalation or dermal contact during bathing / showering in or with a contaminated drinking water.

[1] Abbreviations within this article: ACh(E) = Acetylcholin(esterase); CWA = Chemical-Warfare Agents; LOAEL = Lowest dose with observed adverse effect; NOAEL = Highest dose with no-adverse-observed-effect; OP = Organophosphate; TDI = Tolerable daily intake for humans during chronic (up to lifelong) exposure; WT = Warfare Toxins

1.2. WARFARE TOXINS (WT)

Highly toxic structures of *biological* origin are not considered as "CWA". Their chemical structures are more complicated, cannot (yet) be "chemically" (artificially) synthesized and are called in the following "Warfare Toxins" (WT). They can be produced in large amounts by artificial cultures of specific non-infectious plants, fungi or bacteria. Nevertheless, also WT exert their detrimental effects on the basis of specific features of their (bio)chemical structure. They are also called "mid spectrum agents" between the purely chemical agents (CWA) on the one side and infectious/replicating agents (bacteria and viruses) on the other side (Russmann, 2003).

Due to their sometimes-good chemical stability in water at normal temperature and efficient intestinal resorption some WT have a considerable potential as (bio)chemical drinking water warfare agents. The most potent of them are Botulinum toxins, Ricin and its related compound Abrin, Saxitoxin, Staphylococcal Enterotoxins, and Tetrodotoxin. Some of them are efficient even after dermal exposure (Burrows and Renner, 1999).

2. Toxicity of CWA

2.1. NERVE AGENTS

2.1.1. Acute toxicity

Many reviews on the health impacts of OP nerve agents and insecticides after acute oral exposure have been published. Only a few essential facts are summarized here.

2.1.1.1. Overview. The group "nerve agents" as part of the synthetic chemical warfare agents comprises the most toxic known organophosphates (OP). Many agricultural (beneficial) pesticides of similar structure were or are commonly used in past and present.

The predominant toxic effect of OP nerve agents is the inhibition of a specific enzymatic activity, called acetylcholinesterase (AChE), a protein-bound catalytic entity with central significance for the regulation of chemical information transfer within an organism. It comprises the closely related, but not identical activities as follows (Encyclopaedia of Toxicology, AP 1998)

- butyrylcholinesterease in the *plasma*

- acetylcholinesterase in the *red blood cell*, and the
- acetylcholinesterase at *cholinergic receptor sites* in tissues.

TABLE 1 shows the OP nerve agents of highest military importance. All these compounds contain

- a phosphonate group mimicking the negatively charged acetyl group of the acetylcholine (ACh) molecule;
- an ester or thioester linkage;
- in most cases a positively charged group simulating the positively charged choline moiety of ACh.

2.1.1.2. Mechanism of acute toxicity. All toxic organophosphates are structural analogues of ACh (see last line of TABLE 1), the physiologic substrate of many different types of AchE's in the kingdom of animals.

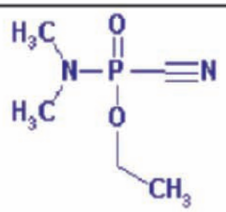
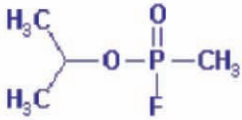
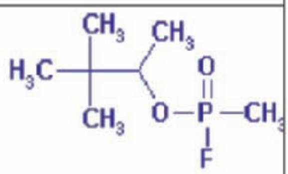
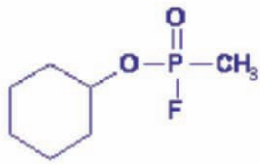
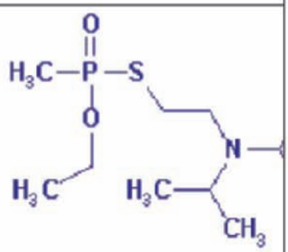
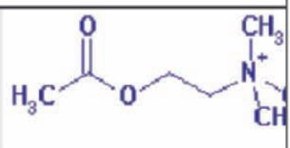
By mimicking the structure of ACh, they are able to specifically block the enzymatic activity by a slow reversible or completely irreversible covalent phosphorylation of the enzyme's serin residue within its active site. This reaction or blockage can be physiologically reversed by dephosphorylation, but the rate of this reaction is slower than the inactivation rate.

In addition, the nerve agent–enzyme complex can undergo an "aging" process, which consists biochemically in the separation of the alkoxy-group from the phosphate moiety. After the "leaving" of this group, the enzyme is irreversibly inhibited. Its activity cannot be reactivated any more by chemical antidotes (pyridinium oximes) but only be replaced by freshly synthesized AChE. The GA- and the GB-complexes with AChE age irreversibly within five hrs after complexation *in vivo*, whereas the VX-complex does not age significantly. Its rate of spontaneous reactivation is reported to be 1%/hr in humans (NRC 2000; Marquardt und Schäfer, 1994).

Once the enzyme is blocked, the natural substrate ACh has no access any more to the active catalytic site to be hydrolysed there into its acetate and choline moieties. The extent to which toxic organophosphates mimic the structure of ACh decides on their acute-toxic potential. Regarding the known warfare OP, the highest degree of structural analogy with ACh is realized in VX.

2.1.1.3. Acute Toxicodynamics. All OP nerve agents are very lipophilic, but also readily soluble in water / body fluids. After dermal contact, oral ingestion or inhalation, they are rapidly transferred into the bloodstream and from there to all organs including the CNS. The two blood AChEs (see above) reflect the tissue AChE-activity differently during acute exposure (indicator: butyryl-AChE in the plasma) and recovery (indicator: AChE of the red blood cells).

TABLE 1. Names of actual CWA (OP nerve agents of G and V type) of potentially high military significance *(lines 2-6)* and of the natural AChE substrate acetylcholine *(line 7).*

Line	CODE	Common Name	CAS-Nr.	Chemical Name	Structure
2	GA	Tabun	77-81-6	Ethyl-N,N-dimethyl-phos-phorami-docyanide	
3	GB	Sarin	107-44-8	Isopropyl-methyl-phosphon-ofluoridate	
4	GD	Soman	96-64-0	Pinacolyl-methyl-phosphon-ofluoridate	
5	GF	Cyclosarin	329-99-7	Cyclo-hexyl-methyl-phosphono fluoridate	
6	VX	TX-60	50782-69-9	O-Ethyl-S-[2-(diiso-pro-pylamino) ethyl]-methyl-phospho-nothioate	
7	--	*Acetylcholine; Cholin acetate*	*51-84-3*	*2-(Acety-loxy)-N,N,N-trimethylet hanamin-ium*	

Exposure of humans towards OP nerve agents results in the accumulation of the neurotransmitter ACh at neuromuscular junctions, in the parasympathetic nervous system and in a number of brain regions. This accumulation of AChE provokes the permanent excitation of the corresponding AChE-receptors (central, muscarinic or nicotinic).

After intoxication, the AChE activity of *red blood cell* regains its normal activity at the rate of red blood cell turnover, which is about 1% per day. Due to its slow restoration rate, the activity of this AChE is the most reliable tool to diagnose and quantify intoxication immediately after an assumed exposure. The *tissue and plasma activity* (which latter comes from the liver) are restored more rapidly by new synthesis of AChE.

2.1.1.4. Acute effects. The main clinical signs and symptoms in humans on the functional level are

- at the level of the *central nervous system*: giddiness, restlessness, headache, tremor, failure to concentrate, convulsions, respiratory depression;
- at the level of *muscarinic receptors*: Hyperactivity of glands (nasal and bronchial mucosa, sweat, lachrymal, salivary) and smooth muscle in iris, gut, bladder, heart;
- at the level of *nicotinic receptors*: Functional inhibition of skeletal muscles (Þfasciculations, weakness) and autonomic ganglia (Þhypertension, tachycardia, pallor, sympathetic effects)

The first effects are local effects in organs positioned closest to the path of entry. They vary accordingly. Other determinants of strength and site of toxic effects are the structure-specific absorption rate and the (bio)chemical stability of a given compound, its ability to cross the blood-brain barrier and its (bio)chemical behaviour within the active site of the AChE under concern.

The interval between exposure and first symptoms vary from minutes to hours, depending on exposure path, kind and seriousness of specific adverse effects. Pronounced miosis can be observed only after *local* eye exposure. After *inhalation*, eye and respiratory symptoms start within a few minutes, whereas *oral* exposure triggers gastrointestinal symptoms only within up to 2 hours. After *percutaneous* exposure, effects like local sweating and fasciculation occur within 15 minutes but also as late as after 4 hours. With heavy intoxications, all muscarinic symptoms start more or less at the same time, followed by nicotinic and central symptoms. In humans, the central respiration stimulus is rapidly suppressed or knocked out, whereas the circulation remains relatively stable until death, which normally occurs within 1h and latest 21 hours after exposure (Encyclopaedia of Toxicology, 1998; Bismuth et al., 2004).

2.1.1.5. Acute effect quantitation. The critical endpoint for defining a NO(A)EL in humans is the residual activity of red blood cell AChE. In humans, 15%-20% inhibition is considered generally as evidence just for exposure, hence as a minimal change, since this degree of biochemical effect at the toxic endpoint is not yet associated with adverse symptoms, even not very light ones (NRC, 2000). A small human subpopulation with a genetic defect in red blood cell AChE, exhibiting in homozygous individuals only 8-21% of the normal mean activity, could be unusually sensitive to the toxicity of OP nerve agents (and insecticides).

TABLE 2 contains different acutely toxic effect doses in humans and animals of the four most important OP nerve agents. More levels and details can be found in textbooks and reviews (Encyclopaedia of Toxicology, 1998; Marquardt und Schäfer, 1994). The most toxic compound, VX, would need to be present at 2,5 mg/L in drinking water when ought to reach a concentration equivalent to the LD_{50} for a normal population. Its adjustment in a 1.000 m³-reservoir would require the production, transport and rapid dissolution in water of ca. 12.5 kg VX.

TABLE 2. Acutely toxic doses in humans and in animals (if stated) of four OP nerve agents from table 1[1)] (*Data from* Encyclopaedia of Toxicology 1998; Marquardt und Schäfer, 1994).

	Tabun (GA)	Sarin (GB)	Soman (GD)	VX
LD_{50} i.v. [mg/kgbw]	0,0045 (rat)	0,039 (rat) 22,3 (monkey)	--	0,008
LD_{50} l.p.c. [mg/kgbw]	14-21	24	15	0,04
LD_{50} p.o. [mg/kgbw]	5	0,14 0,55 (rat)	0,14	0,07
LD_{50} (p.o.) in 0,4 L DW (= cups) for a 70 kg-man [mg/L]	875	24,5	24,5	12,5
ED_{t50} p.o. (gastrointestinal symptoms) [mg/kg]		0.022		0.002-0.005
ED_{t50} (p.o.) in 0,4 L DW (= 2 cups) for a 70 kg-man [mg/L]	[136]	3.8	[3.8]	0.35-0.875
EC_{t50} (miosis) [mg·min/m³]	0,9	2-4	0,5	0,5

[1)]Abbreviations in table 2
LD_{50} fatal dose for 50% of exposed individuals; i.v. = intravenous; l.p.c. = liquid percutaneous; p.o. = per os (orally); inh = per inhalation;
ECt_{50} Concentration·time-product for *minimal* effects in 50% of exposed individuals
EDt_{50} Dosis for minimal effects in 50% of exposed individuals. Numbers between [ ] were estimated by analogy from the respective oral LD50-values.

According to an evaluation by the National Research Council's National Advisory Committee for Exposure Guideline Levels for Hazardous Substances (NAC), VX after inhalation and at different grades of toxicity is 6- to 7-times more potent than Soman and about 10-times more potent than inhaled Sarin or Tabun (NRC, 2004).

2.1.2. Delayed and (sub)chronic/low dose toxicity

2.1.2.1. General . In the context of "chronic toxicity" of OP nerve agents one has to discriminate between "delayed" toxicity after acute/short time exposure and "chronic" effects possibly showing up only after prolonged or "chronic" exposure.

Delayed toxic effects come to surface days or weeks after an acute or short time exposure event. Effects of this kind have been observed in humans mainly after short-time exposure to structurally related OP insecticides (e.g. paraquat). They are classified into

- *Organophosphate-induced delayed neuropathy*, which manifests itself within 5 – 30 days after acute exposure as muscle weakness, twingling, twitching and – finally – paralysis. It is correlated with the inhibition of an enzyme termed provisionally "neuropathy target esterase".
- *Longer than "acute" electroencephalograph changes.* They are considered as clinically insignificant since not correlated with biochemical and histopathological changes.
- *Long-term psychological disturbances* have been reported after short time exposure of humans to certain OP insecticides.

Some indication exists on the possibility of an *intermediary* delayed syndrome after acute intoxication with OP insecticides 1 – 3 days after exposure (Marquardt und Schäfer, 1994).

2.1.2.2. Quantification of « (sub)chronic » and other low dose/exposure effects. Subchronic and chronic toxicity data are of special importance for assessing the risk potential of *environmental* contaminants. OP nerve agents potentially are such contaminants, since "many military bases are contaminated with CWA as a result of storage and past disposal practices" (NRC, 2000). If such places are to be transferred to civilian use, they must be cleaned to levels in soil and water which are safe for chronic (lifelong) exposure of humans and wildlife.

The availability of (sub)chronic human or animal toxicity data of OP nerve agents was described in detail by NRC (2000) and is summarized in TABLE 3.

TABLE 3. Availability (+) of insufficient (±) chronic or subchronic human and experimental/animal data on the toxicity of OP nerve agents (NRC 2000).

Agent	Human data available on				
	Chronic toxicity	Subchronic toxicity	toxicity to re-pro-duction	Carcino-genicity	Geno-toxicity
Tabun (GA)	--	--	--	--	--
Sarin (GB)	±	--	--	--	--
Soman (GD)	--	--	--	--	--
VX	--	--	--	--	--

— = no data

Agent	Experimental and animal data available on				
	chronic toxicity	Subchronic toxicity	toxicity to re-pro-duction	carcino-genicity	Genoto-xicity
Tabun (GA)	--	+	+	--	+
Sarin (GB)	+	+	+	±	+
Soman (GD)	--	+	--	--	+
VX	--	+	+	±	+

— = no data

Data on the chronic and subchronic toxicity of OP nerve agents in *humans* during or after long-term exposure are practically not existent in the literature, except for one retrospective workplace study of questionable importance and some chronic inhalator animal studies with Sarin. No exposure-related chronic effects could be identified in these animal studies.

GA, GB, VX and probably GD are practically not *teratogenic* and have also no toxic potential for *reproduction* at doses at up to 4 µg/kg·d (VX) and 100 µg/kg·d (GA, GB). The *carcinogenic* potential of OP nerve agents seems negative. Their g*enotoxic* potential is weakly (GA and VX) or clearly (GB and GD) negative.

To define lifelong health based exposures or *TDI-values* (TABLE 4) on the basis of the available subchronic animal studies, either their NOAEL-values as estimated by means of an extrapolation factor EF_a (GB, GD, VX) or a directly measured (GA) NOAEL was used as the starting point. The NOAEL is the dose at which any observable AChE activity (mostly red blood cells) in the exposed animals is decreased at most by 20%. According to the U.S.-EPA, this degree of AChE inhibition would not give rise to any adverse clinical effect in humans (NRC 2000).

TABLE 4. TDI-values for GA, GB, GD and VX and the corresponding extrapolation factors EF_i to extrapolate an animal NOAEL to humans[1)] (NRC 2000).

	Oral NOAEL [µg/kg·d]	EF_b	EF_c	EF_d	UF	MF	Human TDI [µg/kg·d]	TDI-equ. in 2 L of DW [µg/L]*)
Tabun (GA)	115	3	10	10	3	3	0.04	1.4
Sarin (GB)	18	3	10	10	3	1	0.02	0.7
Soman (GD)	4.15	3	10	10	3	1	0.004	0.14
VX	0.02	3	1	10	1	1	0.0006	0.02

1) Note: The extrapolation factors EF_i are used to consider extrapolation from subchronic to chronic exposure (EF_b), animal to human extrapolation (EF_c) and sensitive subpopulations (EF_d). The uncertainty factor (UF) has to compensate for data base (in)completeness whereas the modifying factor (MF) is used if a non-oral study was the starting point to derive an oral TDI.
*) human TDI-equivalent in drinking water, calculated for a 70 kg-person consuming 2 L of contaminated water per day for at least several (up to 70) years.

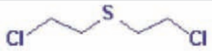
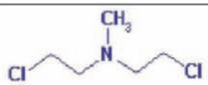
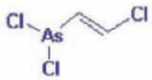
2.2. VESICANT AGENTS

2.2.1. Acute toxicity

2.2.1.1. General. Vesicant agents exert their toxic effect by alkylation of DNA, of enzymes (proteins) and of Glutathion. The most important consequence is disturbance of energy pathways, contributing to cellular damage and finally dermal blister formation. A second effect is Glutathion depletion, resulting in disrupture of cell membrane integrity and/or inhibition of the detoxification of free radicals.

The most potent vesicant agents (see TABLE 5) are sulphur mustard, nitrogen mustard and lewisite.

TABLE 5. Some vesicant agents of potentially high military significance.

Common Name (Code)	CAS-Nr	Chemical Name	Structure
Sulfur mustard (HD)	505-60-2	di-2'-chloroethylsulfide	
Nitrogen mustard (example) (HN-2)	51-75-2	bis(2-chloroethyl)-methylamine	
Lewisite (L)	541-25-3	dichloro(2-chlorovinyl)-arsine	

All these agents are easily and cheap to manufacture and to store. Exposure may be oral, percutaneous and by inhalation and will provoke local and systemic effects.

2.2.1.2. Mechanism of action (Bismuth et al., 2004). In presence of water, sulphur and nitrogen mustards form the highly reactive and strongly electrophilic episulfonium- or aziridium-cation, respectively. This cyclic cation has a very high affinity for nucleophilic centers in biological macromolecules. The alkylation of DNA is the key reaction, because it activates the chromosomal poly(ADP)-ribose)-polymerase which in turn depletes intracellular nicotinamide-dinucleotide (NAD) and by this way inhibits glycolysis. This stimulates the hexose monophosphate shunt and proteolysis, leading finally to cellular damage and blister formation.

Lewisite, in contrast to sulfur and nitrogen mustard, reacts preferentially with thiol-containing enzymes of energy pathways, and with glutathion. Since it does not require cyclization before the reaction, onset of symptoms is not only after several hours or days but much faster.

2.2.1.3.Toxicodynamics. Vesicant agents are very lipophilic compounds and penetrate easily the skin and all lipid barriers within an organism. At the same time they are highly reactive.

When applied on human skin, about 80% of sulphur mustard evaporates and 20% penetrate the skin. 10% of this smaller fraction bind to the skin and the other 10% exert systemic toxic effects after being absorbed.

It can be assumed that already 1 h after end of exposure the parent toxicant is not present any more in the body (or compartments of it) in toxicologically significant concentrations.

2.2.1.4. Acute effects. The two mustards and lewisite are incapacitating agents. Mortality during World War I by sulphur mustard intoxication was only 2%. The agents affect primarily

- the *eyes* by erythema, edema, lachrymation, severe pain, blindness;
- the *skin* by erythema, edema, necrosis, vesicles (no burns);
- the *respiratory tract* by tracheobronchitis, bronchospasm, bronchial obstruction, hemorrhagic edema.

Symptoms are often identical with those known from radiation therapy or chemotherapy (radiomimetic effects).

Some quantitative data on the acute toxicity of HD, HN-2 and L for humans have been collected in TABLE 6 (Marquardt und Schäfer 1994). The most relevant effect at low concentration in drinking water is conjunctivitis. To provoke minimal conjunctivitis in drinking water consumers, only 1 – 2 g of sulphur mustard would be necessary to contaminate a 1.000 m^3 drinking water reservoir. This concentration is lower by a factor of about 2 than the concentration corresponding to 100% of the TDI in 2 L drinking water per day (TABLE 7).

TABLE 6. Overview on acute human effect and no effect doses/concentrations for the vesicant agents in (TABLE 5)[1].

	Sulphur mustard (HD)	Nitrogen mustard (HN-2)	Lewisite (L)
Oral LD_{50} [mg/kg]	--	2 (estimated)	
Percutaneous LD_{50} [mg/kg]	40-60 (estimation)	12 (estimated)	38-54 (estimated)
LC_{50} after inhalation [mg·min/m³] No effect dose	1500 (estimation) 2	1500 (estimated)	1200-1500 (estimated)
Mimimal effective doses skin irritation blistering conjunctivitis	 0.01 mg/cm² 0.1-0.15 mg/cm² 0.0012 mg/L (30 min)	 0.001 mg/cm² (HN-3) 0.1 mg/cm² (HN-3) 0.0007 mg/L (15 min; HN-3)	 0.5-0.1 mg/cm² 0.2 mg/cm² 0.01 mg/L 15 min)

[1] abbreviations see TABLE 2.

2.2.2. Delayed and (sub)chronic/low dose toxicity

2.2.2.1. Overview (Marquardt and Schäfer). About 80% of persons exposed or treated for therapeutic reasons with alkylating mustards exhibit late (or delayed) eye effects from which 75% are minor and reversible. In serious cases chronic conjunctivitis may be a consequence of exposure. Superficial skin lesion may need several weeks or even months to heal.

70% of the patients exposed during the Gulf War I (1980-1988) suffered from complications within the respiratory tract, mostly chronic asthmoid bronchitis. 41% had chronic skin problems (abnormal pigmentation), 36% suffered from eye complications (mostly chronic conjunctivitis), and 45% had neuropsychological disturbances, depressions and identity problems.

2.2.2.2. Quantification of (sub)chronic and low dose/exposure effects. The 1st paragraph of section 2.1.2.2. applies equally to this section. The overall evaluation of the *teratogenic* potential of **mustard** compounds in humans and in animal studies (rats and rabbits) is inconclusive. Some positive human data exist from World War II CWA factory workers in Germany on enhanced mortality of male offspring and on disturbed spermiogenesis. A slightly enhanced incidence between 1983 and 1988 of Iranian children with palate cleft was associated with exposure of parents to sulfur mustard during the Gulf War I. On the other hand, the evaluation of mustards as positively *mutagenic, genotoxic and carcinogenic compounds* in humans is unequivocal (Marquardt und Schäfer, 1994).

Human data regarding reproductive/developmental effects due to **lewisite** exposure are inconclusive because of confounding factors such as concurrent exposure to other agents and incomplete exposure data. The carcinogenicity of lewisite per se is equivocal and cannot be assessed quantitatively. However, several of its degradation products (inorganic As, vinyl chloride) are proven human carcinogens (NRC 2000).

An *oral TDI for chronic exposure* towards **sulphur mustard** was based on a 42 week 3-generation animal study from 1989. Its LOAEL was 0.022 mg/kg. The human TDI is 0.007 µg/kg; its derivation from the LOAEL is explained with TABLE 7.

For **lewisite**, a *chronic oral TDI* can be based on a 90-day subchronic study from 1989. After comparing this study with the results from two other ones, a scientifically plausible NOAEL for the chronic toxicity of lewisite for rats was numbered at 0.44 mg/kg. The chronic human TDI as derived (see TABLE 7) from this NOAEL is 0.15 µg/kg.

TDI-values for sulphur mustard and lewisite and the corresponding extrapolation factors EF_i as applied on the respective LOAEL or NOAEL

TABLE 7. TDI-values for sulfur mustard and lewisite and the corresponding extrapolation factors EF_i to extrapolate an animal NOAEL or LOAEL to humans[1)] (NRC 2000).

	Time weighted LOAEL or NOAEL in rats [mg/kg]	EF_a	EF_b	EF_c	EF_d	UF	MF	human TDI [µg/kg]	TDI-equ. in 2 L of DW*) [µg/L]
Sulfur mustard (HD)	0.022 (LOAEL)	3	10	10	10	1	1	0.07	2.5
Lewisite (L)	0.44 (NOAEL)	1	10	10	10	3		0.15	5

1)Note . The extrapolation factors EF_i are used to consider extrapolation from LOAEL to NOAEL (EF_a), from subchronic to chronic exposure (EF_b), animal to human extrapolation (EF_c) and sensitive subpopulations (EF_d). The uncertainty factor (UF) has to compensate for database (in) completeness whereas the modifying factor (MF) is used if a non-oral study was the starting point to derive an oral TDI.

*) Human TDI-equivalent in drinking water as calculated for a 70 kg-person, consuming 2 L of contaminated water per day during many (up to 70) years.

3. Acute/short time toxicity of warfare toxins (WT)

Details: Russian (2003), Burrows and Renner (1999), Marquardt und Schäfer (1994)
Note. Data on the low dose or (sub)chronic toxicity of WTs are not existent in the literature.

3.1. BOTULINUM TOXINS (BT)

These seven closely related neurotoxic peptides are produced by *Clostridium Botulinum sp.* They form the most toxic known substance group of biological origin and are ubiquitously present in many normal environments (e.g. food, soil). The subtypes A to G all inhibit the release of the neurotransmitter AChE at the nerve endings. A special feature of the BTs is their higher toxicity after ingestion when compared to inhalation. Exposed persons are progressively paralysed but remain mentally alert. Death results from inability to breathe. Theoretically, 1 mg of BT would be enough to kill about 1.000 - 2.000 persons by oral exposure (LD_{50} = 0.4 µg/person). Infant botulism from contaminated food is the most common form of intoxication with BT (Encyclopedia of Toxicology, 1998)

3.2. RICIN AND ABRIN

The plant toxin Ricin is most often cited when speculating on possible attacks by terrorist groups by contamination of food or (small) drinking water supplies. Ricin inactivates the ribosomes within the cells and thereby inhibits the cellular protein synthesis. After ingestion it produces gastrointestinal haemorrhage with organ necrosis. Inhalation leads to severe lung toxicity becoming manifest within 8-24 h. Exposure to aerosols is more toxic than oral exposure. Ricin is produced by the plant *Ricinus communis*. The cultivation of this plant for the production of castor oil represents an important economic factor in many tropic and subtropical countries. The waste mash from oil production contains 3-5% of Ricin. From there it can be prepared liquid or crystalline without great technological expense (Bismuth et al. 2004). This explains its high availability and easiness to obtain. A structurally related and yet more toxic compound, Abrin, is produced by the bean *Abrus precatorius*. The LD_{50} of Abrin is about100 times lower than the one of Ricin (see TABLE 8).

3.3. SAXITOXIN

This low molecular weight heat-resistant neurotoxin is produced by marine dinoflagellata, esp. *protogonyaulax spp.* It is part of the group of paralytic shellfish poisons, because it accumulates in mussels, snails and fish. Its biochemical effect consists in blocking the postsynaptic sodium channels without influencing the potassium channels. First signs of oral Saxitoxin intoxication are numbness in the mouth (tongue and gums), in the fingertips and toes, followed by paralysis of other body regions and eventually death by failure of respiration. The substance is possibly most toxic after inhalation. Saxitoxin was weaponized for covert purposes. Together with Ricin, Saxitoxin is included in the international treaty on prohibition and non-proliferation of B- and C-weapons from January 13, 1993.

3.4. TETRODOTOXIN

This low molecular weight bacterial toxin exerts is biochemical effect by the same mechanism as Saxitoxin although its structure is completely different. It can be found in different marine organisms where it seems to be produced directly; possibly it accumulates also within the marine food chain. Highest concentrations are found in Japanese pufferfish, causing the death of about 125 people worldwide per year due to improper preparation of the fish before being consumed. Tetrodotoxin could present a drinking water threat because of its sufficiently good solubility in water.

3.5. ENTEROTOXIN B

This toxin from the ubiquitous bacterium *Staphylococcus aureus* is written also SEB and is found preferably in contaminated food. The biochemical effect mechanism of Enterotoxin B is very complex, comprising among others overstimulation of T-cells and overproduction of cytokines. Enterotoxins are parts of degraded/denatured bacterial cell walls and also called superantigens. The effect of SEB may incapacitate exposed persons for up to 2 weeks by vomiting, gastrointestinal pain, diarrhoea (after ingestion), fever, chills, non-productive cough (if inhaled), and some effects more. Lethal doses are at least 100-times higher than necessary for incapacitation (20–25 μg per person after oral ingestion). Inhalation of contaminated aerosols is ca. 1000-times more efficient in producing systemic toxicity than oral uptake of SEB.

TABLE 8. Data on the acute toxicity of 5 WTs (Russmann 2003; Burrows and Renner 1999).

	Oral LD_{50} [µg/kg]	LD_{50}-equ. in 1 L of DW*) [µg/L]	Oral TDI [µg/kg]	TDI-equ. in 1,5 L of DW**) [µg/L]
BT	0.001-0.006	0.07-0.4	$0.001 \cdot 10^{-2}$	$6 \cdot 10^{-5}$
Abrin	0.04	2.8	?	?
Ricin	3.0	210	0.43	2.0
Tetrodotoxin	8.0-30	560-2100	0.02	0.1
Saxitoxin	10.0	700	0.02	0.1
SEB	$\leq$27	$\leq$1890	0.002	0.01

*) LD_{50}-equivalent in drinking water as calculated for a 70 kg-person after ingestion of a single 1 L-portion of contaminated water within not longer than 1 h

**) human TDI-equivalent in drinking water as calculated for a 70 kg-person, consuming 1,5 L of contaminated water per day during at least several months

4. Properties of CWA and WT in aqueous media with respect to their drinking water risk potential

Details: see Burrows and Renner (1999).

The **OP nerve agent** with highest *stability in water* is VX. 50% of the substance need several 100 h to be hydrolysed in water at 20°C and a pH of around 7. The next water stable structure is GD, followed by GB and GA, the latter having a half time in water at 25°C and pH 8-9 of only 2-3 h.

The best *solubility in water* among the OP nerve agents exhibits GB. This compound is completely miscible with water, whereas GA, VX and GD are soluble in water at 20°C to 72 g/L, 30 g/L and 15 g/L, respectively. These concentrations, however, are much higher than all concentrations known to be linked with toxic effects.

The *volatility* of GB and GD from water is comparable (both ca. 10 mg/L at 20°C), whereas GA is only weakly (0.6 mg/L) and VX practically not volatile (0.01 mg/L at 25°C) from aqueous solutions.

The vesicant agents sulphur mustard (HD), the nitrogen mustards HN-1, HN-3 and lewisite have a comparably poor solubility in water (less than 1 g/L). However, this relatively low concentration is much higher than any of the known toxic effect concentrations. The hydrolysis of HD, HN-1 and HN-3 in water is very slow, only HN-2 and lewisite hydrolyse rapidly. Chemically pure mustards and lewisite have no odour. Their synthesis is simple and cheap. The effects of the mustards after dermal and oral exposure have a lag time of at least several hours if not some days. An effective antidote (British Anti-Lewisit, BAL) exists only against lewisite. For all these reasons, mustards and especially the most toxic one, HD, have a high potential to be (ab)used to contaminate small drinking water supplies (see TABLE 6).

None of the **Warfare Toxins** is volatile. Some of them, but not Staphylococcal Enterotoxins, Tetrodotoxin and Saxitoxin, are easily inactivated by boiling in water. Almost each WT can be eliminated from drinking water by filtration over charcoal. The only exception is Saxitoxin due to its strong polarity (positive charge) at normal pH of drinking water (Burrows and Renner, 1999). The presence of free chlorine at >50 mg/L would inactivate Saxitoxin and Tetrodotoxin (the latter only at a pH below 3 and higher than 9), but not Ricin. The ”disinfection efficacy” of Staphylococcal Enterotoxins is unknown. Botulinum toxins in drinking water would be inactivated by moderate (several mg/L) to low free available chlorine (as common in municipal disinfection procedures). BTs are also destroyed by sunlight (within 1-3 h) and contact with air (within 12h).

5. Conclusion

Taking together stability in water, acute toxic potential and technical possibilities to protect or clean a drinking water supply from a warfare agent, the dissipation of the chemical warfare agents VX and sulphur mustard seems to be the most dangerous for drinking water supplies. From the Warfare Toxins, Ricin and Abrin but also the BTs seem to represent a risk potential for drinking water consumers, Ricin and Abrin for their high availability and/or toxicity and stability, and the BTs for their extreme toxicity (albeit its low stability in water and under air).

6. References

Note: A large body exists of original and secondary literature (including textbooks and reviews) dealing with CWA and WT. The informations and evaluations given in this article were compiled under the aspect "drinking water" from the following textbooks and review articles. It was not possible to associate each information or evaluation with a specific source or citation (exceptions see text).

Bismuth C., Borron S.W., Baud F.J., and Barriot P., 2004. Chemical weapons: documented use and compounds on the horizon. Toxicol. Lett 149, 11-18

Burrows W.D., and Renner S.E., 1999. Biological Warfare Agents as Threats to Potable Drinking Water. Environ. Health Persp. 107 (12) 975-984

Encyclopedia of Toxicology,1998. 3 volumes (Wexler P, Editor-in-Chief), Academic Press

Marquardt H. und Schäfer S.G., 1994. Lehrbuch der Toxikologie *(Textbook of Toxicology)*. BI Wissenschftsverlag, Mannheim, Leipzig, Wien, Zürich, ISBN 3-411-16321-6

National Research Council (NRC) Committee on Toxicology (COT)/National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances (NAC), 2004. http://www.epa.gov/oppt/aegl/results66.htm (last updated on Wednesday, April 14th, 2004)

National Research Council (NRC) Committee on Toxicology (COT)/ Subcommittee on Chronic Reference Doses (RfD) for Selected Chemical-Warfare Agents, 2000. Report on the Evaluation of the army's interim RfD for the nerve agents GA, GB, GD,VX, the vesicant agents sulfur mustard and lewisite. J. Toxicol. Environ. Health Part A, 59: 281-360 (evaluations), 361-526 (Appendices A-G).

Russmann H., 2003. Biogene Gifte und potentielle Kampfstoffe *(Biogenic toxins and potential warfare agents; in German)*. Bundesgesundheitsbl-Gesundheitsforsch-Gesundheitsschutz 46:989-996

LESSONS LEARNED FROM THE CYANIDE AND HEAVY METAL ACCIDENTAL WATER POLLUTION IN THE TISA RIVER BASIN IN THE YEAR 2000

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Abstract

On 30 January 2000, a tailings pond burst at a facility near the city of Baia Mare, Romania which was reprocessing old mining tailings and re-depositing the waste sludge into a new tailings pond. This led to approximately 100,000 m^3 of waste water containing up to 120 tons of cyanide and heavy metals being released into the Lapus River, then traveling downstream into the Somes and Tisa rivers into Hungary before entering the Danube.

The cyanide caused acute toxicity for different aquatic organisms (fish, phytoplankton, zooplankton, macrozoobenthos).

On 10 March 2000, another tailings dam burst in Baia Borsa in the same region close to the Ukrainian border. While some of this material was retained within the dam complex, 20 thousand ton of sediments containing high concentration of lead, copper and zinc were then released into the Novat River, a tributary of the Viseu and Tisa rivers.

The heavy metals were transported mainly in the suspended sediments along the Tisa River. In different sedimentation zones the settled polluted sediment increased the lead, copper and zinc concentration of the bottom sediment up to 1000 mg/kg order of magnitude.

The above noted accidents revealed the lack of information on the potential pollution sources in the Tisa river basin. A relevant inventory of the potential

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 43–50.

pollution sources was compiled for the Tisa river basin after the above noted accidents.

Keywords: Cyanide/heavy metals/Tisa river/tailings pond

1. Introduction

The Tisa River is the longest (977 km) tributary of the River Danube, having the largest drainage basin as well. It drains water from the eastern Carpathian Basin and discharges into the Danube. The drainage basin area is 157 200 km^2 amounting to 20% of the total catchments area of the Danube. The Tisa basin is shared by Ukraine, Romania, Slovakia, Hungary and Serbia-Montenegro.

Two serious accidental spills (a cyanide spill and a heavy metal spill) occurred in the upstream region of the Tisa river basin in January and March of the year 2000. Both accidents had the similarities that enclosure dams of industrial impoundments collapsed in extreme weather conditions (László et al. 2000).

2. Evaluation of the cyanide pollution

The first accident occurred near the city of Baia Mare at a tailings pond operated by AURUL, a joint-venture company. AURUL had been established to re-process the tailings of an old abandoned tailings pond, extracting gold and silver and other metals and, at the same time, removing the tailings from their existing site close to a residential area to a more remote site 8 km from the city of Baia Mare (Baia Mare Task Force, 2000).

The facility had been designed as a ‘zero discharge’ process, with no emissions of process water to local rivers. In line with the design of the process, the tailings pond received process water containing high levels of cyanide, which is used in the gold extraction process. The process water was then recycled to the plant, thus reducing the amount of new cyanide that had to be added into the process and reducing the operating costs of the facility. After seven months of operation in 1999-2000, a dramatic failure of the retaining embankment wall led to the release of tailings water into local rivers.

The sequence of events leading to the accident was as follows:

- Throughout 1999, the tailings dam was developing as intended, with the hydrocyclones building the embankment walls higher as re-mined tailings and waste process water was pumped into the tailings pond.
- Over the course of the winter of 1999, a significant amount of rain and snow fell on the tailings pond, and the pond became covered in a thick layer of snow and ice.
- Heavy (but not exceptional) rain and snowfall in December 1999 and January 2000, combined with rapid snowmelt from 27 January 2000 as the temperature rose suddenly from below freezing to 9.5 °C, and nearly 40 mm of rainfall on 30 January 2000 caused water levels to reach critical levels. The embankment walls became saturated and unstable as the snow melted directly on their surfaces.
- On 30 January, the dam overflowed and washed away a stretch of embankment wall 25 m long and 2.5 m deep. Approximately, 100,000 m^3 of tailings water containing cyanide began to flow into the nearby Lapus River. AURUL stopped processing operations and began activities to close the breach.

Repair of the dam of the process water pond was completed on the 31 of January, thus eliminating the continuation of the spill.

The pollutant discharge consisted mostly of cyanide complexes bound to readily water-soluble metals. In addition to analyzing for the cyanide content of the water, dissolved heavy metals (of complex forms) were also analyzed. Measurement results indicated that copper was the dominant heavy metal in the river water, although zinc concentrations also exceeded the natural background levels and lead and silver were also detected. Regarding concentrations the maximum cyanide concentration was in the range of 20-30 mg/l in the Hungarian part of the River Szamos and of 10-15 mg/l in the Tisa River, downstream of the confluence with the River Szamos. Further downstream in the Tisa River the concentration became gradually lower upon the diluting effect of the tributary rivers and also due to the release of clean water from the reservoir Kisköre (Lake Tisa), which had been filled with clean water before the pollution wave arrived. The maximum cyanide concentration of the Tisa water, when leaving the country, was 1.49 mg/l.

The cyanide and the copper remained dissolved in the pollution plume, therefore the transport of the pollutants in the river was basically determined by the longitudinal dispersion and by the dilution of water discharge from the tributaries of the Tisa River.

The cyanide caused acute toxicity for different aquatic organisms (fish, phytoplankton, zooplankton, macrozoobenthos).

Plankton in the Somes and upper Tisa river in Hungary (closest to the accident) was completely killed, and in the middle and lower reaches of the Tisa between 30-60% of plankton were killed by the passage of the pollution plume. Within days of the spill materials passing, phytoplankton and zooplankton had begun to recover throughout the entire river system.

The number and species composition for phytoplankton has substantially returned to normal over all the stretches of the river. A major factor which appears to have assisted the process of recovery, is the flooding which occurred in March, and presented ideal conditions for plankton growth.

In general it appears that the populations of macro-invertebrates were damaged from spill but not completely eliminated as originally feared. Recovery of the diversity of species and numbers has progressed rapidly during the first growing season following the spill.

The visible death of fish was a clear indication of the immediate impact of the accident at Baia Mare. Hungarian authorities report a total of 1240 tons of fish that were killed as a result of the spill. Of this amount 33.8% were predatory fish, 13.5% Carp, 8.1% Sturgeon, and 44.6% herbivorous fish. The fish collected included nearly all the fish known to be present in the river. It is clear, however, that not all fish were affected equally. The herbivorous fish, the Silver carp (*Hypophthalichthys molitrix*), in particular seemed to be very vulnerable to the cyanide and made up a large percentage of the fish that died.

3. Evaluation of the heavy metal pollution incident

The second accident occurred at the Novat tailings management facility (TMF) at Baia Borsa. In addition to the primary dam, a second and third dam had been constructed downstream from the primary dam. The second dam was designed to support the primary dam structure as it reaches its final height. The third dam was built of concrete and was designed to collect water that leaked from the first two dams for re-pumping to the main pond.

The dam overflowed and burst on 10 March 2000. 100,000 m^3 of water and 20,000 tons of tailings sludge containing heavy metals flowed out of the dam. While some material was retained between the two lower dams, the rest flowed downstream of the dam and into the Novat and Vasar rivers, from where it entered the Viseu and finally the Tisa River.

Due to the downstream area from the dam being a specially protected nature area, no emergency discharge of water is permitted from the dam. As a result, the dam system is a closed-cycle design with no discharge downstream of the third dam.

The process was designed as a partially closed-circuit system, with process waters discharged into the pond being recycled through the metal extraction facility. In addition, the pond also receives direct rainfall and indirect surface run-off from the surrounding hill-slopes. Evaporation and the recirculating of water back to the main mine complex was supposed to ensure that water levels in the pond were controlled, with the main stream in the valley bypassing the pond. The pond complex, however, contained no provisions for emergency discharges downstream of the pond. As a result, if water levels reached critical levels, there was no way that water levels could be reduced.

Over the winter of 1999-2000, heavy rainfall and rapid snowmelt caused the water level in the pond to reach critical levels and for the dam walls to become unstable. As the pumps designed to pump water out of the pond, back to the processing plant and into other ponds were not working, it was impossible to avoid the overflow and breaching of the dam wall.

The sequence of events leading to the accident was as follows:

- In early December, heavy rain fell into the reservoir and surrounding catchments;
- From mid-December 1999 to late January 2000, more than 120 mm of precipitation as snow fell on the reservoir and surrounding catchments;
- Temperatures fell below 0 °C from 21 December 1999 and were below –10 °C from 22 January 2000;
- On 27 January 2000, the temperature began to increase rapidly, rising above 0 °C on 30 January;
- On 8-10 March 2000, torrential rainfall and rapid snowmelt led to increasing water levels in the reservoir, and the pumping systems for the pond failed;
- On 10 March at 11-00 a.m. a breach 25 m wide and 10 m high occurred in the dam, leading to the spillage of 20,000 tons of tailings into the Novat river;
- The tailings overflowed the second and third dams to enter into the river system, flowing along the Ukrainian border, before flowing into Hungary.

The pollution plume carrying lead, copper and zinc arrived at the Hungarian Tisa section one day after the accident. The maximum concentration of total lead and zinc was 2.9 mg/l, while that of copper was 0.86 mg/l. Before the arrival of the pollution wave the characteristic concentrations of the above named heavy metals were below 0.1 mg/l.

As the pollution wave traveled downstream, the heavy metal concentration were gradually decreasing, due to the effect of settling, longitudinal dispersion and to the dilution water provided by the tributary streams.

The impact of the pollution wave on the composition of the sediment was detectable at some location in the upper Hungarian reach of the Tisa, in the zones of sedimentation.

Results of the analysis of sediment samples, made until the end of March 2000, showed that heavy metals deposited from the pollution wave increased the lead concentration of the sediment to about 900 mg/kg, the copper and zinc concentrations to about 500 mg/kg and 1500 mg/kg respectively. These data represented about ten-fold concentration increase in comparison to background data (characteristic concentration ranges of non-polluted bottom sediment of the Upper Tisa are 20-70 mg/kg for lead and copper and 100-400 mg/kg for zinc.

The above results were in harmony with the composition of the suspended sediment of the pollution wave: the lead concentration of the suspended sediment was 1500-1800 mg/kg, while the respective values of copper and zinc were 900-1100 mg/kg and 2700-3300 mg/kg.

Comparing the suspended sediment and bottom sediment contamination data to the respective soil and sediment quality limit values (Table 1) one can derive the following statements:

- the background concentrations of lead, copper and zinc of the sediment of the Tisa river are generally lower than the limit values for sediment and soil,
- lead, copper and zinc concentrations of the suspended sediment, as arrived with the pollution wave, were exceeding the limit values of the qualification system of soil and sediment,
- contamination levels of bottom sediment in the upper section of the Tisa River were higher at some locations than the limit values of the soil and sediment qualification systems.

TABLE 1. Limit values of lead, copper and zinc in soil and sediment.

Heavy metal	Maximum allowed concentration in soil (mg/kg dry soil)	Probable effect level of heavy metals in sediment for aquatic organisms (mg/kg dry sediment)
Lead	100	91
Copper	75	197
Zinc	Í200	315

Sediment pollution surveys were continued in the years 2000 and 2001. Extreme high floods resuspended the bottom sediment and redistributed the sediment along the Tisa River. As a consequence of the high floods the heavy metal concentrations in the bottom sediment became more uniform.

4. Inventory of the potential pollution sources

The above noted accidents revealed the lack of information on the potential pollution sources in the Tisa basin. The International Commission for the Protection of the Danube River (ICPDR) initiated and organized the compilation of an inventory of the potential pollution sources. The information for the inventory was provided by the countries in the Tisa river basin (ICPDR 2000).

5. Conclusions

- The accidents were caused by the use of inappropriately designed tailings management facilities, inadequate monitoring of the construction and operation of the dams. The above flows were triggered by severe but not exceptional weather.
- The immediate environmental impacts (plankton, fish, macro-invertebrate mortality) were serious, but the recovery rate of the Tisa River has been impressive.
- Urgent action was needed to identify the potential pollution sources in the Tisa River basin.

6. References

Baia Mare Task Force, 2000. Report of the International Task Force for Assessing the Baia Mare Accident. Baia Mare Task Force document.

ICPDR, 2000: Regional Inventory of Potential Accidental Risk Spots in the Tisa catchments area of Romania, Hungary, Ukraine and Slovakia. ICPDR August 2000.

László, F., B. Csányi and P. Literáthy, 2000. Cyanide and heavy metal accidental pollution in the Tisa river basin. Consequences on water quality monitoring and assessment. In: Proceedings of International Workshop on Information for Sustainable Water Management. Ed.: J.G. Timmerman et al., 65-70.

ENVIRONMENTAL CONTAMINATION ON FORMER MILITARY SITES AND HAZARDS TO THE DRINKING WATER IN GERMANY

Inventory and health risk assessement of environmental contaminants

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Abstract

An assessment concept was developed accordingly to the claims of "*Vorsorge*" (precaution) of the drinking water hygiene, which authorise a prospective evaluation of potential environmental contamination. The problematic is represented by the example of military contaminated sites in Germany and generalised by an adequate and extensive system of assessment for soils and waters. Over the description of substance properties of the environmental contaminants, values of substance characteristics (SC-Values) will be calculated. The combination of different values of substance characteristics shows a potential exposition and health risk over the drinking water path. The identification of hazards is presented, in a second step, with explicit health related guidance values (GV) and in form of measure values (short term health related guidance values GV_{SE})[1] in the context of human toxicological assessments. Another approach is the calculation of permissible bearable maximum concentrations (BMC) through an aqua toxicological evaluation. With these two concentrations - the human-tox and the aqua-tox derivated - values, one can decide on the fact whether the chemical quality

[1] SE: Short Term Exposure

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 51–64.

of contaminated drinking water is (still) healthy safe or whether the aquatic biocoenosis could be adverse influenced.

Keywords: Military contaminated sites/ drinking water/ environmental contamination/ human toxicity/ aqua toxicity/ ecological toxicity/ health assessment/ biochemical degradability/ mobility.

1. Basics

The exposition of humans opposite chemical substances released through anthropogenic influence based on the steady growing chemical production and the decades long use of these substances, despite of the strengthened contrary efforts[2], must be classified with increase (INC 2000). These environmental chemicals are to be differentiate into such, regarding their origin area, which was brought deliberately and use-oriented into the environment, e.g. plants treatment means (particularly herbicides, insecticides and fungicides) as well as antibiotics (e.g. penicillin, chloroamphenicol) and into such, which arrived or still arrive unintentional, careless or from unsatisfactory *Vorsorge* (precaution = "pre-care") (e.g. polycyclic aromatic hydrocarbons and dioxins) into the environment. Thereby, in the past, chemical contaminated site had represented a considerable part in these environmental contaminations. The *Vorsorgeprinzip* (precautions or *pre-care* principle) is applied during the assessment of the dangerousness of substances of the first mentioned origin area. Environment relevant former contaminated sites can only be solved through the *Nachsorge* (aftercare). Thereby, a particularly possible attention should be paid to potential and real contaminations regarding to the food chain and the drinking water resources.

The transition of the contaminated site substances of the environment media water, soil and air into the human food chain signified then, in particular, a health risk, if the substances are toxic and biochemical stable in the environment or if their metabolites are evaluated more critically as the original substances. Therefore, toxicity and degradability form the key criteria of this risk assessment.

The different objectives of *pre-care* and aftercare become particularly clear in the military activities: In peace times, the precaution principle is also

[1] e.g. the ban covered substances of the POP convention (as "…according to international binding law instrument for the implementation of international measures regarding to certain persistent organic parameter." - POP- Convention v. 10.12.2000 in Johannesburg; cp. Umwelt Nr. 2 /2001, BMU, Berlin)

apply in many regards at the military (compare e.g. “minimisation commandment” in the German drinking water regulation), unless perhaps without restrictions. Military conflicts are always based on their destructives aims and associated with the release of dangerous and toxic substances that concern all environmental compartments including ground and raw waters. Apart from a possible direct immediate side-effect of sabotage toxins, weapons and explosives at human’s military activities lead among other also to a direct and indirect endangering of the drinking water resources. Dangers for humans and nature after military practices or warlike conflicts could only be minimised in the way of an intensive aftercare remains through rehabilitation or restoration measures.

The statement of possible health dangers through adverse effects of the substances takes place via scientific methods and assessment criteria. These should consider knowledge gabs and show the correlation between exposition and effect of pollutants in the environmental media and drinking water. In this article, the danger criteria for humans, especially for the drinking water path, are systematised and the congruence is proved between legal normative standards - and deduced measures for the environmental media (soils, ground water and drinking water) - and management of risk on scientific basis. The execution deficit of measures up to now will get clear from the hygienic quality requirements in drinking water and the divergence between “pre-care claim” and “aftercare success” in danger defence.

2. Conclusion to the hazard statement of military contaminated sites in the drinking water supply in the new Federal *Länder* of Germany

The massive potential groundwater pollution from military operations became apparent and subject of scientific research in the early 1990s, in the wake of the *détente* process between East and West. This scarcely confirmed the often-expressed hope that many of the military chemicals, which are classified as dangerous, would quickly be degraded in soil to non-hazardous concentrations (Mulisch et al., 1999 a. b).

In the intention to obtain a representative statement on consequences of the military contaminated sites on the drinking water supply in Germany, were stood researches in the surrounding field of former WGT-areas (WGT = west’s group of the troops of the former Soviet army) in the central point of the assessment of health risk through the drinking water contamination. Supplementary former NVA-areas (= *Nationale Volksarmee*, German troops of the national people army) in the free state of Saxony were included into these investigations (Mulisch and Schorling, 1997; Mulisch, 1998).

2.1. Inventory

The WGT-areas were isolated for decades from the public. Activities, material and many accompanying factors like e.g. potential pollutant and permanence effect were unknown. The assessment of the respective hazard potential for drinking water was significantly complicated through it, which was usually missing accurate substance statements.

Basics of the inventory are examinations of the Federal Ministry for Environment, Nature Protection and Reactor Security respectively, executed by the Federal Agency for Environment, which covering altogether 1,026 areas (BMU, 1995). Beyond this supplementary statements from the countries, the Federal Financial Administration and the Federal Armed Forces (Bundeswehr) and Researches of the Health Authorities were taken up to the data acquisition, particularly of special parameters, like chlorinated hydrocarbons substance and explosives (FKST, 1994). Through the definition of different types of utility areas, it is possible to conclude on suspicion and priority contaminants that were proved in suspect cases by health authorities over a corresponding analytics by soil and water samples (Thieme et al.,1994).

In the result of these studies altogether 33,750 suspicion contaminated site areas (SCSA = Altlastverdachtsflächen) were determined. 32 % of those (= 11,079 SCSA) were classified as an endangered ground water. From these, 53.8 % (= 5,960 SCSA) is located inside drinking water protected areas.

The results represented here, refer to a subset of 929 of these WGT-areas, which were carried out in the frame of BMU's environmental research plan until the year 1999. In doing so, suspicion contaminated site areas (SCSA) were detected and documented in 140 military training sites, 406 garrisons, 80 airports, 147 camps and bunkers as well as 42 large fuel depots. These environmental relevant SCSA form a contaminated total area of appreciatively 5,700 ha.

Focuses of environmental pollutions are the utility areas

- fuel depots, petrol stations, airports, wash and maintenance ramps,
- munitions and arsenals, shooting facilities, explosive places and fire places,
- burials and shifted areas,
- defective canalisations as well as sewage plants,
- unordered waste deposits and scrap places.

Without meaning in the sense of the aim position 29,382 SCSA are registered with waste mineral origin. Only in some cases, 4,715 SCSA with vegetable wastes as well as the 6,165 with settlement wastes are of relevance of ground and drinking water. The studies, highlighted on the basis of few established analyses, had shown that also "radioactive wastes" are not significant for the drinking water supply.

On the other hand, the "wild waste deposits" are evaluated as critical. Altogether about 465,000 tons of material of all kind of wastes, inclusive munitions rests, were illegally disposed on "shifted and burials areas". Large insecurities exist particularly in connection with shifted and burial areas inside drinking water protected areas, because specific evidences referring to their composition were missing and it is no longer possible to get this information after the departure of the WGT.

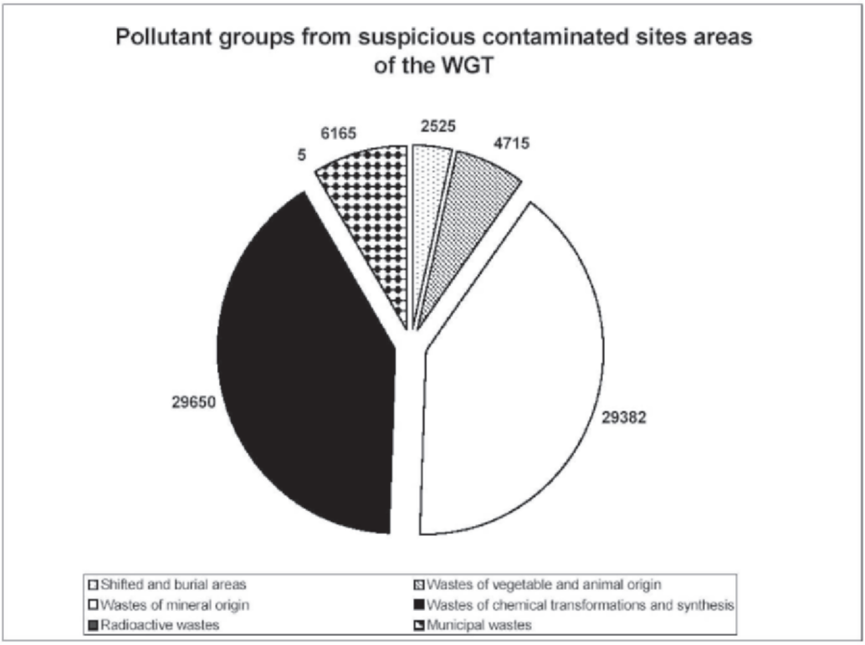

Figure 1. Pollutant Groups from Suspicion Contaminated Sites Areas WGT-areas.

The overview in Figure 1 shows the determined materials on the SCSA according to the generic terms defined in the WGT program: shifted areas, burials, wastes of mineral origin, radioactive wastes, wastes of vegetable and animal origin, wastes of chemical transformation and synthesis products as well as municipal wastes.

The pollutants, which are combined under the generic term “wastes chemical transformation and synthesis chemical products“, represent, beside the munitions residues, the main group of the drinking water supply endangering material. The materials or groups of materials designated here are classified in the Table 1 as well as in Figure 2 over the environmental relevant quantities in tons (t).

TABLE 1. Pollutant Groups on SCSA and their relative Parts on WGT-properties.

Code Nr.	Description	Part SCSA [%]	Estimated Relative Mass [%]
5.1	Oxides, hydroxides, salts	2%	5%
5.2	Acids alkaline solutions, concentrates	2%	<1%
5.3	Pesticides and pharmaceutical articles	1%	1%
5.4	Mineral oil product	51%	71%
5.5	Organic solvents, paints, lacquers, adhesives, mastics, resins	11%	1%
5.7	Plastic and rubber wastes	19%	11%
5.8	Textile wastes	4%	<1%
5.9	Other wastes of chemical production	10%	10%

The group of pollutants of 5.7 and 5.8 are dangerous materials for the drinking water supply of small importance. Relevantly are in particular the group 5.4 “petroleum products”, further the group of 5.9 “other wastes of chemical production” as well as the group of 5.5 “organic solvents, paints, lacquers, adhesives, mastics, resins”, in which for 148 SCSA is specified contamination with halogenated solvents. Despite the altogether very small estimated pollutant quantities of < 1% of the total loads, a high contamination potential for raw water is to be set for chlorinated hydrocarbons (CHC)[3]. This applies also to burials of all kinds, there here the circumstances permitting

Environmental Relevant Masses (t) with Wastes from Chemical Transformations and Synthesis Products

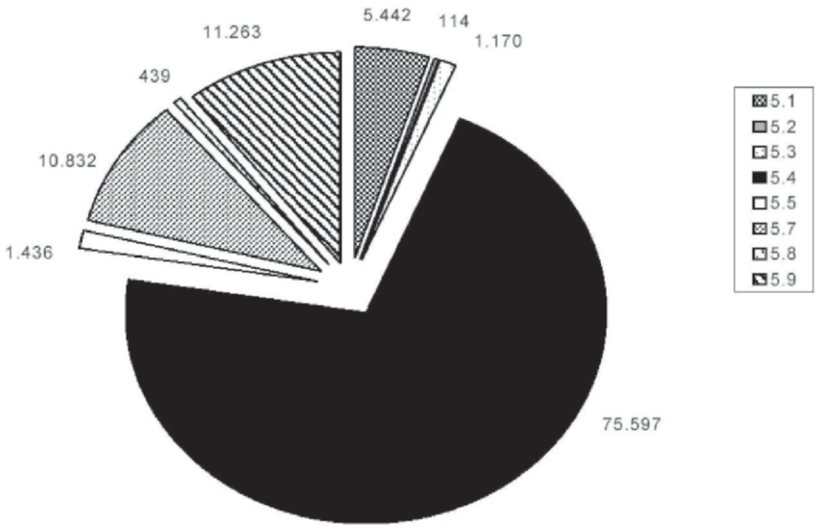

Figure 2. Estimated Environmental Relevant Masses in Tons (t) of Contaminated Site Materials from Wastes of Chemical Transformations and Synthesis Products (code No. 5) on SCSA of the WGT.

possibly materials from special waste and munitions into the underground to be set free under the term “other wastes of chemical production”.

Under the term “other wastes of chemical production” are combined, special chemicals and all military weapons. This concerns both explosives and chemical agents. Chemical agents come into question, however only in few exception cases as suspicious contaminants.

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[1] The group of the halogenated solvents became - with appropriate specifications on the individual substances - in the WGT project reports only with 21 SCSA specified (1,2-dichlorobenzene - 7 ALVF, chlorobenzene - 1 SCSA, dichloromethane - 2 SCSA, tetrachloroethene - 1 SCSA, tetrachloromethane - 2 SCSA, trichloroethene 8 ALVF). This, for the drinking water supply sometimes very problematic compounds, seems to be under represented in the WGT-project reports.

The very strong group 5.4 of the mineral oil hydrocarbons (MHC) covers quantitatively those dominating contaminated site materials, which causes substantial drinking water hygienic problems. To this belong the petroleum products diesels, gasoline, kerosene and other fuels, waste oils and PCB products as well as emulsions and mud from petroleum products.

In summary, following materials and group of materials can be determined as suspicious contaminants for drinking water relevant from military contaminated sites, due to the investigation of:

- fuels for tanks, commercial and passenger car,
- airport and missile propellants,
- hydraulics -, transmissions -, lubricating materials and antidegradants as well as waste oils of all kinds,
- chlorinated hydrocarbons e.g. trichloroethene and tetrachloromethane as solvents for tanks, engine and uniform laundry,
- weapon e.g. explosives such as 2,4,6-trinitrotoluole among other things,
- mineral acids as cleaner,
- lacquers and paints and solvents for lacquers and paints,
- glycol as anti-freeze,
- polycyclic aromatic hydrocarbons and dioxins from burn processes (also in the course of the evacuation of the properties)

A contamination potential by chemical warfare agents, that we found on armaments contaminated sites, could not be proved in the context of investigations on military sites.

2.2. ASSESSMENT

The specific difficulty in assessing the potential for chemical impairments to ground or row water from military sites is that used substances are often subject to secrecy, while their identification in a historical review of site-specific activities would greatly support situation assessment. Only if the substances to be expected are known, their hazard potential can be determined for a given site on the basis of substance-specific data. Investigations of the complex biophysical, chemical and biochemical transfer processes as well as of microbial metabolism of organics further supplement are the basis for a prognosis of the likely groundwater impacts in the recharge area, including contaminant fate, distribution, bioavailability, and degradation in the subsurface (Mulisch et al, 1996; Mulisch et al., 2000)

For the evaluation and classification of the hazard potential of military chemicals or compounds of contaminated sites we use the so-called substance-characteristic-system (SCS) as a modular constructed system for the complete assessment of environmental contaminants in drinking water in form of standardized coefficients (SC-values). On this basis, obtained chemical expositions and hazard potentials for humans and aquatic organisms can be recognized in time, quantified in soil and waters and repelled if necessary (Mulisch et al., 2003).

In the first precaution level of the risk assessment, the complex biophysical, chemical and biochemical transmission paths as well as the microbial metabolisms are systematised. It essentially covers the parameter SC_{BIO} for the biochemical degradation in the environment as well as parameters SC_{TOX} and SC_{AQU} for the harmfulness of the environmental contaminants in relation with the human organism and the aquatic environment. The mathematical operation of the individual SC-values results to the SC_{TOR} with the statement of the environmental toxicological relevance of the environmental contaminants. Supplementary substance specific mobility in the environment is measured as SC_{MOB} (see Table 2). In those cases, when SC-values

- predict a certain exposure and hazard potential or
- show an existing not early enough predicted exposure or hazard potential, that has to be repulsed

short to medium-term restoration decision are necessary (e.g. to the assurance of the hygienic harmlessness of drinking water for food purposes). The result of the first taking “precaution level” of the SCS-procedure must then, in the second “aftercare level” be supplemented through

- aqua toxicological substance assessments in form of aqua toxicological bearable maximum concentrations (BMC) or
- human toxicological substance assessments in form of health bearable guidance values for drinking water (GV).

TABLE 2. Representations of the Substance Characterisation Systems (SCS).

First Level: Substance Characterisation with SC-values		**Second Level: Hazard Characterisation**
Substance characteristics	Range of SC-values	Health guidance values for drinking water - GV
SC_{TOX}	1,0 - 4,0	GV_{70}, GV_{10}, $GV_{1,5}$, GV_{SK}
SC_{BIO}	1,0 - 2,0	HSL
$SC_{TOX} + SC_{BIO} = SC_{TOR}$	2,0 - 6,0	
SC_{MOB}	1,0 - 4,0	
SC_{AQU}	1,0 - 2,0	Bearable Maximum Concentration in Waters (BMC)

Legend:
Substance Characteristics SC
TOX = Human Toxicity
TOR = Toxicological Relevance
ADS = Adsorptivity
BIO = Biochemical Degradation
SOL = Water Solubility
LOEC = Aqua Toxicological Threshold Values

GV = Hazard Characterisation over Health Risk Assessment
GV = Health Guidance Values
GV_{SE} = Guidance Values for Short Term Exposure
GV_{BI} = Guidance values for Babies and Infants for Short Term Exposure
HSL = Hygienic Sensory Limit
BMC = Bearable Maximum Concentration (Aqua Toxicity)

Formally the complete assessment of dangers from military areas and activities for drinking water respectively, is divided into an assessment complex with five parts of criteria, which cover the on side parameter on the basis of not sample criteria and local site investigation as well as the criteria of the substance characterization. “Characteristic numbers “ necessary for the correct description of all results of the assessment criteria are measured on the basis defined work procedures and in the form of an evaluation raster by hazard levels (HL) for drinking water. From this, the necessary action need, can be derived through the safety precaution of the drinking water supply (see Table 3).

TABLE 3. Basis of the HL-Assessment Raster.

Group	Statement/Consequence	Hazard Level
1	Statement: No hazard and no direct need for action regarding the drinking water supply Consequence: none	HL I - HL III
2	Statement: Potential or assume contamination of raw water in the catchments area of water supply plants Consequence: Immediate reconnaissance and investigation measures	HL IV
3	Statement: Missing data records; in individual cases contradictory statements in situation and investigation reports Consequence: Execution of appropriate searches	HL V
4	Statement: Proved hazard for the drinking water (acute exposition) and acute hazard suspicion through a high probability of expected contamination in the drinking water (latent exposition) respectively. Consequence: Direct need for action	HL VI

After the hazard statement, the clear health-referred exposure limits in form of measure values (short term health guidance values GV_{SE}) were designed in the context of human toxicological assessments as well as permissible bearable maximum concentrations (BMC) through aqua toxicological assessments and determined regarding the restoration needs.

The priority setting of a restoration needs is oriented thereby at the lowest of the both calculated values of aqua and human toxicity. If we have to take the human toxicological derived value for a substance, an additional calculation of the temporal priority setting of restoration measures is possible with the accumulation trend of this substance present in the human organism. This calculation of the temporal structuring of these measure values takes place in accordance with art. 9 of the European Union directive 98/83/EC.

3. Results

The international comparison shows strong differences between inventory, investigation, assessment and restoration of military suspicion contaminated site areas (SCSA) in environmental contaminations. A “phase wise” procedure is formalised in no other country except in Germany. The hazard based

TABLE 4. Results of the Assessment of WGT-properties in Hazard Level (HL_{A-B} I – VI) for the Drinking Water Supply in the *Länder* Berlin (BE), Brandenburg (BB), Mecklenburg-Western Pomeranian (MV), Saxony (SN), Saxony-Anhalt (SN) and Thuringia (TH), (Mulisch et al., 1999 b).

HL	BE		BB		Group-Total	MV		Group-Total	SN		Group-Total	ST		Group-Total	TH		Group-Total	Total		Group-Total
	N	%		%	BB	N	%	MV	n	%	SN	n	%	ST	n	%	TH	N	%	All *Länder*
Ia	2	13	86	18		21	30		17	15		23	13		21	24		170	18	
Ib	1	6	48	10		13	18		19	16		52	30		11	13		144	16	
Ic	7	44	37	8		3	4		10	9		4	2		7	8		68	7	
II	0	0	0	0		0	0		0	0		0	0		0	0		0	0	
IIIa	0	0	97	21	311	16	23	60	33	28	94	35	20	123	6	7	50	187	20	648
IIIb	0	0	43	9	67%	7	10	85%	15	13	80%	9	5	72%	5	6	58%	79	9	70%
IVa	3	19	38	8		0	0		2	2		6	3		7	8		56	6	
IVb	0	0	15	3		5	7		1	1		2	1		0	0		23	2	
IVc	3	19	67	14		4	6		16	14		36	21		5	6		131	14	
Va	0	0	11	2		1	1		0	0		0	1		16	19		28	3	
Vb	0	0	8	2		0	0		3	3		1	0		1	1		13	1	
Vc	0	0	3	1	156	0	0	11	0	0	23	0	0	49	4	5	36	7	1	281
VI	0	0	14	3	33%	1	1	15%	1	1	20%	4	2	28%	3	3	42%	23	3	30%
Total	16	100	467	100		71	100		117	100		172	100		86	100		929	100	
% of all properties in HL IV-VI (*Länder* comparison)					56%			4%			8%			17%			13%			
% of all properties in HL I-III (*Länder* comparison)					48%			9%			15%			19%			8%			

(retrospective) approach, identifies a toxic substance and introduces from a certain parameter value a corresponding measure, in order to eliminate the danger. In the frame of this work, additionally a prospective precaution assessment in the form of substance characteristics (SCS) is introduced and systematised.

The fact that an assessment result cannot obligatory certify the actual conditions is connected in particularly with the case of an uncertain or incomplete data situation. This case could be minimized with the fact that data gaps were also included into the assessment. But the individual substance assessments need a minimal inventory of data to be documented and it is necessary to take in consideration their quality and up-to-dateness. Eventual experimental data gaps are to be compensated over additional (facultative) statements and safety factors (SF), the results of the individual assessment and the complete statement must come very close to the actual condition. This methodology for the description and consideration of the data gaps into the assessment procedure is applicable in order to meet and to temporally clear insecurities during the assessment due to an inhomogeneous data situation until better data for the regulation are available.

The results of the accomplished investigations and assessments show, that from each third former WGT and/or part property respectively, there is a hazard potential for the drinking water supply (see HL IV to VI in Table 4). Immediate measures were introduced in 23 cases, in order to exclude a direct hazard for the human health. Over 80% of the examined former NVA-properties in Saxony were stated at the assessment, that a long-term effect of environmental contaminations cannot be expected to surrounding drinking water resources. On almost any fifth of these NVA-properties, suspicion contaminated site areas (SCSA) or still contaminated sites with water endangering toxic substances was determined, which represent a potential hazard of drinking water resources. Immediate measures could be introduced in 2 cases.

As a further conclusion it is recommended to include assessment criteria of the drinking water hygiene strengthened into the practical work of the inventory, assessment and restoration of military contaminated sites.

4. References

BMU, IABG (1995). Ermittlung von Altlast-Verdachtsflächen auf den Liegenschaften der West-gruppe der Truppen (WGT) - Abschlussdokumentation - Band 1: Zusammenfassung. Otto-brunn, Industrieanlagen-Betriebsgesellschaft mbH im Auftrag des BMU / Umwelt-bundesamt: 73.

INC 5 (10.12.2000). Völkerrechtlich bindendes Instrument zur Implementierung internatio-naler Maßnahmen hinsichtlich bestimmter persistenter organischer Stoffe - geächtete und mit einem Anwendungsverbot belegte Substanzen. POP-Konvention, Johannesburg.

FKST (1994). Trinkwasser - Mögliche Auswirkungen militärischer Altlasten auf die Trinkwasserversorgung in den neuen Bundesländern - Erfassung militärischer Standorte. Zwischenbericht der Arbeitsgemeinschaft Militärische Altlasten / Trinkwasserversorgung der Fachkommission Soforthilfe Trinkwasser (FKST). Berlin, Bundesministerium für Gesundheit und Landesfachgruppen Trinkwasser.

Mulisch, H.-M. (1998). Trinkwasserschutz im Umfeld von Liegenschaften der ehemaligen Nationalen Volksarmee im Freistaat Sachsen. Berlin, Umweltbundesamt Berlin: 130.

Mulisch, H.-M., H. Schörling, Ed. (1997). Trinkwasserressourcen im Umfeld militärischer Liegenschaften. WaBoLu-Hefte. Berlin, Institut für Wasser-, Boden- und Lufthygiene.

Mulisch, H.-M., W. Winter und A. Grohmann (1996). "Assessment of the hazards to drinking water from former military sites." J. Water SRT - Aqua 45(2): 72-75.

Mulisch, H.-M., H.H. Dieter und G. Möschwitzer (1999 a). Militärchemische Altlasten. Umweltmedizin. Volker Mersch-Sundermann. Stuttgart, New-York, Georg Thieme Verlag: 740.

Mulisch, H.-M., W. Winter, S. de Lima (1999 b) Trinkwasserschutz im Umfeld von Liegen-schaften aus der militärische Nutzung durch die Westgruppe der Truppen der Sowjet-armee (WGT). Texte. Berlin, Umweltbundesamt Berlin. 77/99: 303.

Mulisch, H.-M., W. Winter, H.H. Dieter, H. Kerndorff (2000). Kriterienkatalog zur Beurteilung von Gefahren in Einzugsgebieten von Trinkwassergewinnungsanlagen am Beispiel militärischen Altlasten. Berlin, WaBoLu-Hefte 6/99, Umweltbundesamt.

Mulisch, H.-M., W. Winter, H.H. Dieter (2003). "Modulares System zur Gesamtbewertung von Umweltkontaminanten in Boden, Gewässer und Trinkwasser." Bundesgesundheitsblatt - Gesundheitsforsch - Gesundheitsschutz 8: 668-676.

Thieme, J., Appler, B., Bassek, H., Haas, R., Kopecz, P., Niclauß, M. (1994): Branchen-typische Inventarisierung von Bodenkontaminationen auf Rüstungsaltlast-standorten. Umweltbundesamt Texte 43/94, Berlin

CONTAMINATION OF WATER BASINS OF ARMENIA BY PERSISTENT ORGANIC POLLUTANTS

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Abstract

In 2002-2003, studies were performed in concern of persistent organic pollutants: DDT, HCH, Hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) in open water basins of Armenia.Main goal of the study was to trace their fate in such specific media as surface waters. Samples of water were taken from the Lake Sevan and rivers Argichi, Arpa, Debet, Gavaraget, Hrazdan, Karchaghbyur, Pambak, Vardenik, Voghchi, and Vorotan. Analyses were performed by means of gas chromatography. Research findings indicate that in samples taken from rivers, at which hydro power plants are functioning, the content of PCBs is extremely high, as compared to the levels of HCH and DDT. This signifies that PCBs are a real problem for Armenia and the energy sector is the main source of PCB-related pollution in rivers of Armenia.

Key words: Contamination/ environment/ environmental pollution/ organochlorine pesticides/ persistent organic pollutants (POPs)/ polychlorinated biphenyls/ surface waters.

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1. Introduction

Monitoring studies were performed in 2002 -2003 in concern of persistent organic pollutants (POP's): DDT, exachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and HCH in surface waters in order to reveal the current situation of the environment of Armenia.

Within the frames of these studies the following water reservoirs were selected for investigation:

- water reservoirs associated with agricultural production (Rivers Arpa and Pambak);
- water reservoirs associated with energy/electricity production (Rivers Vorotan, Hrazdan);
- water reservoirs, at the water collection area of which there are industrial enterprises (Rivers Debet, Voghchi);
- relatively clean reservoirs (Sevan Lake);

2. Results

There are more than 200 streams and rivers in Armenia, none navigable, however, because of their steep descents and rapid currents. The Armenian countryside also boasts some 100 small, but picturesque lakes. One of the largest mountain lakes in the world is Lake Sevan. It should be specially mentioned that Sevan is considered a reservoir of drinking water, as the country is locked in the Lesser Caucasus Mountains.

As it is presented in Table 1, the values of persistent organic pollutants content in water samples taken from the rivers of the Republic of Armenia never exceed Maximum Allowable Concentration (MAC) of Organochlorine pesticides (OCPs) and PCBs and correspond to the Former USSR established standards, which are still used at present by the corresponding services in the Republic of Armenia. Evaluation of data presented signifies that amongst rivers studied River Pambak, at which HCH was not revealed, could be considered clean. If we take into account the results of the investigation for PCBs content in water samples from the studied rivers, contamination of waters of River Pambak is at the same level as the River Debet: PCB levels make 0.83 and 0.68 mcg/L, appropriately. The characteristics given as "relatively clean water reservoir" is, most probably, conditioned by the fact that there are no hydroelectric power plants at these 2 rivers and in concern of OCPs the region is not characterized as an area with intense agricultural production.

TABLE 1. Samples of water were taken for analyses by means of gas-liquid chromatography.

Rivers	HCH				DDT and metabolites				HCB	PCBs
	α	β	γ	Σ HCH	DDT	DDE	DDD	Σ DDT		
Vorotan	0.18	NR	0.2	0.38	0.13	0.16	1.68	1.97	0.036	1.49
Voghchi	0.04	0.02	0.04	0.10	0.02	0.01	0.007	0.037	NS	1.33
Pambak	NR	NR	NR	-	0.02	NR	0.01	0.03	0.006	0.83
Debet	0.13 (α+β)	NR	0.01	0.14	0.004	0.004	NR	0.008	NR	0.68
Hrazdan	0.035	0.015	0.06	0.11	0.09	0.007	0.06	0.157	NS	1.82

Contamination of waters of the rivers Vorotan, Voghchi and Hrazdan was similar to that of rivers Pambak and Debet, in waters of which PCBs content was insignificantly higher than in the above mentioned.

PCBs make the exception. PCBs are detected in waters of these rivers almost 2-fold higher than in waters of Pambak and Debet. This difference is obviously conditioned by the fact that at Vorotan River there are 3, while at Hrazdan River there are more than 5 functioning hydroelectric power plants, which present the main cause of PCBs concentration increase in these rivers.

PCBs content is relatively higher in water samples of Voghchi river and makes 1.33 mcg/L; this latter can be explained only by the presence of Kadjaran copper-molybdenum Combinat (Industrial Complex) at the water collection area of Voghchi River. There is a similar industrial complex (copper-smelting one) in the water-collection area of Debet River, however, in water samples of this river PCBs residues are revealed to be 2-fold less (Table 1).

To our view, DDT amounts revealed in the above-mentioned water reservoirs are resulting from recent application of this compound, as DDT was banned already in 1970. The detected level of DDT can be considered as the consequence of limited use at some private farms and not because of large-scale application. Otherwise, DDT levels could be much higher. To the "fresh" application of DDT, signifies also the fact that no metabolites were revealed. Moreover, DDT itself was registered in water samples.

In case with HCH we are also inclined to think that there takes place the fresh application of HCH (á+â) and Lindane (ã-HCH), because during the last years before the prohibition to use HCH in the Republic of Armenia, Lindane was applied as a more efficient compound compared to HCH. On assessment of the revealed residual amounts at this point we had no task to determine HCH (á+â), as it is less resistant than Lindane. But the obtained results suggest to the freshly applied HCH and Lindane. In addition, the half-life of these formulations is less than 10 years and there was no import of these formulations during the period of more than 15-20 years.

The phenomenon thus stated signifies that the a.m. compounds are non-officially imported to the Republic of Armenia or the compounds are taken out of pesticide burial or somewhere else. Some quantity of these compounds was hidden and stored at the period of USSR collapse and now is used for illegal business.

HCB residues in water samples from rivers Vorotan and Pambak can be explained either by direct use of this compound as a pesticide or by its presence due to some other ways of formation or application. There are scientific publications on both the penetration of Hexachlorobenzene into the environment jointly with other pesticides and on its formation during various industrial production processes and its subsequent penetration into the environment. It is considered that HCB can be formed in the process of obtaining aluminum production (1 kg of Hexachlorethane yields 4.3 g Hexachlorobenzene), due to the use of chlorinated solutions, on burning of town and other wastes, on burning coal, tilt/sludge, biomasses, in cement production, etc. HCB is also known as an accompanying compound in a number of pesticides such as Atrazine, Daktal, Lindane, Pentachlorphenyl, Pentachlornitrobenzene, Likioram, Simazine, and HCH.

The factor of all the above mentioned processes is undoubtedly present in Armenia and one can state that HCB determined in our study to some degree has a significant part in environmental pollution.

In order to make data obtained as a result of monitoring study more representative and to present processes of DDT and HCH degradation during 2-3 decades after prohibition and cessation to apply them, the summary table given below reflects the content of these pesticides determined in water basins of Armenia in the period of 1969-1970s (Table 2).

TABLE 2. DDT and HCH Content in some Open Water Basins (rivers, water reservoirs, lakes, etc.) of the Republic of Armenia, 1969-1970 (mg/l).

Water Sources	Pesticides	Average pestcide content in samples	Average pesticide content (as related to all samples	Exceeding MAC, %
rivers, lakes, water reservoir s, channels	DDT+ DDE	0.021 0.055	0.013 0.028	26.6
	HCH	0.01 0.025	-	Not revealed

Data presented indicate that during the years after ceasing to apply DDT and HCH a shift occurred in concern of degradation of the above-mentioned pesticides in rivers of Armenia.

Another investigation was performed to analyze samples of water from rivers of the Sevan Lake basin (i.e. rivers feeding the lake): Arpa, Argichi, Gavaraget, Karchakhpyur and Vardenik.

The results of the study on contamination of the Lake Sevan and rivers feeding it are presented in Table 3.

Comparing these results with data on water contamination in rivers as presented in Table 1, we can note that the waters of Lake Sevan and rivers feeding this Lake can be considered mostly clean as only ã-HCH, DDE and PCBs were revealed. Low level of persistent organic pollutants determination (in %) was observed; likewise the content of the above-mentioned persistent organic pollutants was lower than in other rivers. In rivers feeding the Lake Sevan PCBs content was 50% less than in other water basins. Such difference is explained by the fact that in the water collection area of these water basins there are neither big industrial enterprises, nor power stations and the agriculture is characterized by the absence of such branches as wine-growing, horticulture, melon-growing; therefore pesticide application levels are lower.

The evaluation of water contamination by persistent organic pollutants in Lake Sevan and rivers feeding it indicate that the level of all determined persistent organic pollutants is almost the same. There was no difference in respect of the assortment of the organic pollutants revealed, i.e. water pollution level in Lake Sevan corresponds to the level of pollution in rivers feeding it, as levels of persistent organic pollutants determined in the Lake Sevan are conditioned by that occurring in the rivers.

Absence of DDT in water samples signifies that in water collection area this compound is not applied; the results of investigations of waters from rivers feeding Sevan signify also to the same. DDT and its metabolites determined in water samples from Arpa River were mainly revealed in samples taken below the level of Kechut Water Reservoir; this latter explains that the pesticides do not penetrate into Lake Sevan.

The phenomenon of DDE determined in waters of Sevan can be related to degradation of DDT previously applied in the Sevan basin: it persists in soil and sometimes penetrates into the Lake Sevan because of rains and waters from melted snow from Sevan water collection area.

The results of water samples analyses for HCH indicate that in waters from Sevan Lake and rivers flowing into it only ã-HCH (Lindane): this signifies, on the one hand, to the fact that farmers of this region have and use only Lindane and, to the other hand, to the absence of HCH as such, containing isomers.

The absence of HCH and Hexachlorobenzene signify that no other pesticides are used in the area of Sevan, with which these compounds, as accompanying components, could penetrate into the Lake or rivers feeding it.

TABLE 3. Persistent Organic Pollutants in Lake Sevan and Rivers Feeding the Lake mcg/L, (2002-2003).

Water Basin	HCH				DDT and metabolites				PCBs
	α	β	γ	Σ HCH	DDT	DDE	DDD	Σ DDT	
Sevan Lake	NR	NR	0.067	0.067	NR	0.016	NR	0.016	0.50
Arpa River	NR	NR	0.060	0.060	0.53	0.250	0.83	1.610	1.57*
Gavaraget River **	NR	NR	0.100	0.100	NR	0.009	NR	0.009	0.75
Argichi River **	NR	NR	0.023	0.023	NR	NR	NR	-	0.42
Karchakhbyur River **	NR	NR	0.023	0.023	NR	NR	NR	-	0.44
Masrik River **	NR	NR	0.039	0.039	NR	NR	NR	-	0.42
Dzknaget River **	NR	NR	0.100	0.100	NR	0.019	NR	0.019	0.45

* PCBs content was determined in 1 sample of water
** Data presented is based on the results of one water sample.

TABLE 4. Average Pesticide Content in water of Sevan Lake and the rivers flowing into Sevan, 1980 (in mg/l).

Water reservoir	% of determination	DDT	% of determination	DDE	% of determination	HCH
Small Sevan	92.3	0.0004 0.00007	30.8	0.00000021	100	0.0028 0.0017
Bigger Sevan	92.7	0.0028 0.0024	50	0.0001 0.00007	100	0.0034 0.0016
Masrik river	100	0.005 0.004	40	0.0002 0.00017	100	0.0034 0.002
Gavaraget river	80	0.0005 0.0001	20	0.00004 -	100	0.0024 0.0004
Argichi river	75	0.0013 0.0028	-	NR	100	0.001 0.0004
Vardenik river	80	0.0028 0.002	-	NR	100	0.005 0.004
Karch Akhpyur river	80	0.008 0.0006	20	0.001 -	100	0.0016 0.001
Arpa river (Arpa-Sevan channel)	50	0.0005 0.00004	50	0.0001 0.00005	100	0.0006 0.0002

For the assessment of HCH (á, â, ã) and DDT with the metabolites DDE, DDD in waters of the Lake, Table 4 is presented below reflecting the average content of such pesticides as DDT and HCH in water of Sevan and rivers feeding it as of 1980. Concentration of the pesticides mentioned is given in mg/L.

However, if the current situation will persist in water collection area of Sevan Lake in concern of application of persistent organic pollutants (DDT, HCH), in the nearest few years DDT and HCH will completely degrade. In the waters of the lake and rivers flowing into it (feeding it) only PCBs will be found, as half-life of some of these compounds/congeners is longer than half-life of DDT, while some of them, according to scientific publications, do not degrade.

Our findings indicate that the organochlorine pesticides and PCBs in Sevan hydroecoecosystem are resulting from migration and trophic chain transfer of POPs.

Research outcomes of monitoring studies revealed that the environment (surface waters) of Armenia is entirely contaminated, especially by PCBs. This signifies that PCBs are a real problem for Armenia and the energy sector is the main source of PCB-related pollution in rivers of Armenia.

PESTICIDE RISK ASSESSMENT TO PROTECT AQUATIC SYSTEMS

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Abstract

Directive 91/414/CEE (1991), concerning the placing on the market of plant protection products, states evaluation criteria to assure that no harmful effect on human or animal health and no unacceptable influence on the environment occur after pesticide use.

Pesticide movement to surface waters is an area of concern in many European countries where regular use of pesticides is an integral part of crop management. Such pesticide losses can be rapid and can result in contamination of water bodies and may cause environmental damage.

An appropriate ecotoxicological risk assessment, including aquatic risk, is one of the main objectives of authorisation directive.

In this paper the pesticide risk assessment scheme to protect aquatic systems in the framework of Directive 91/414/CEE is presented.

Keywords: Directive 91/414/CEE, aquatic risk assessment.

1. The "Authorisation" Directive

Council Directive 91/414/EEC of 15th July 1991 concerning the placing of plant protection products on the market describes the requirements, which

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have to be fulfilled in order to obtain an authorisation for a plant protection product.

The main elements of the Directive are as follows:

- To harmonise the overall arrangements for authorisation of plant protection products within the European Union. This is achieved by harmonising the process for considering the safety of active substances at a European Community.
- To establish a positive list of active substances (Annex I), that have been shown to be without unacceptable risk to people or the environment.

The data to be submitted by the companies when applying for the authorization of a plant protection product are contained in the Annexes II (for the active substance) and Annex III (for the plant protection product). The data required are:

- identify an active substance and plant protection product;
- describe their physical and chemical properties;
- their effects on target pests, and;
- allow for a risk assessment to be made of any possible effects on workers, consumers, the environment and non-target plants and animals.

The "Uniform Principles" (Annex VI of Directive) establishes the decision making criteria for evaluating products at a national level.

Application of the Uniform Principles ensures that authorizations issued in all Member States are assessed to the same standards.

2. Ecotoxicological risk assessment

Risk assessment is a process which includes: exposure assessment, effects assessment, risk characterisation.

2.1. EXPOSURE ASSESSMENT

The level (concentration and duration) of exposure to which non-target organisms may be exposed during and after application of the product to the target is an essential element in risk assessement process. For a pesticide risk assessment, the exposure characterization describes the potential or actual contact of a pesticide with a plant, animal, or media. The objective is to describe exposure in terms of intensity, space, and time and to describe the exposure pathway(s).

Aquatic systems may be exposed via spray drift, run-off and drainage.

The exposure assessment for aquatic organisms is carried out calculating Predicted Environmental Concentration (PEC) for each pathway of exposure. Appropriate models (FOCUS SW 2001; FOCUDS GW 2000) are used following a tiered approach (from a *worst case* scenario to a *realistic worst case* scenario).

2.2. EFFECT ASSESSMENT

Effect assessment means to measure the extent and type of negative effects associated with a particular level of exposure in order to know exactly what dose (amount) of a particular pesticide causes what effects (dose-response assessment). Dose-response assessment includes acute and chronic tests.

The testing scheme is a tiered one and is based on the use and toxicity of the pesticide active ingredient. Depending on the results of studies conducted at a lower level and on the risk assessment, testing can progress from basic laboratory tests to applied field tests in the highest level.

Concerning aquatic system, Annex II of Directive 91/414/EEC requires acute and chronic effects testing in fish, invertebrates and algae.

These studies aim at:

- providing toxicological thresholds for organisms being representative of the most sensitive ones among three aquatic trophic levels, predators (fish), secondary consumers (invertebrate species) and primary consumers (algae); thresholds for these species are also used in the classification process;
- identifying the most sensitive group of organisms, which the risk for aquatic systems should be based on;
- if necessary, i.e. in cases where sensitivity thresholds are very low and could be encountered through the intended uses of a compound, providing sufficient understanding of the nature of the possible risks (high tier studies) in order to define an exposure level or concentration being ecologically acceptable (Ecologically Acceptable Concentration - EAC).

2.3. RISK CHARACTERISATION

Risk characterisation uses the results from the preceding stages to identify and estimate (usually quantitatively) the likely incidence and consequence of adverse effects in the environment resulting from actual or predicted exposure to a pesticide.

The estimated initial exposure levels are compared to the effects data (LC_{50}, EC_{50}, NOEC, etc.) of a product, to calculate for each group of organisms ratios called “Toxicity Exposure Ratios (TER)”. For aquatic organisms TER values are calculate in acute (TERst) and long term (TERlt) pattern. TERs are compared with the trigger values of 91/414 Annex VI and, if sufficiently high, the environmental risk is negligible for a given compartment and its organisms.

When TERs are rather low and ecological risks cannot be excluded on the basis of the estimated initial exposure levels and the available ecotoxicity data, several risk refinements could be applying.

Ecological risk assessment in the EU is evolving rapidly into a well-structured, tiered approach to assess potential risks, with substantial developments having taken place in both the exposure and effects sides of the risk equation. Much of the development of tiered exposure assessment over recent years has come about through the efforts of the FOCUS groups.

The framework for assessing the effects aspects of aquatic ecological risk assessment has also become increasingly harmonized over recent years, and higher-tier effects approaches are now well-established (e.g. via HARAP (Campell et al 1998) and CLASSIC (Giddings et al 2001) and the EU Aquatic Guidance Document).

Effects of pesticides on communities of organisms under simulated field conditions can be carried out, performing a microcosm or a mesocosm study.

Microcosm study can provide effects data under more realistic exposure conditions. For example, the degradation is allowed to proceed in the test system under environmentally relevant conditions, meaning that the degree to which this degradation mitigates the risk can be assessed. Similarly, the extent to which partitioning to sediment and microbial activity affects the risk can also be taken into account with the presence of sediment in the test system. Mesocosm studies usually include a wider range of species and generally offer a greater potential to assess the response at the population and, especially, the community level. Microcosm and mesocosm studies can also allow the quantification of rate and extent of recovery.

Methods to refine the exposure assessment potential approaches to mitigate risk are currently developing at EU level. A FOCUS working group was established on 2002 on Landscape And Mitigation Factors In Aquatic Risk Assessment. The aim of this group is to give raccomandations on including landscape and mitigation factors in higher-tier exposure assessments.

Padovani et al. (2004) reported a case study in a mediterranean Area in wich a landscape-level approach to assess aquatic exposure via spray drift for pesticides was applied.

Verro et al. (2002) developed a GIS-based system for surface water risk assessment of pesticide at regional level.

Risk mitigation measures currently used in EU Member States to protect aquatic life within the authorisation procedure of plant protection products are no-spray buffer zones (most widely used) and drift-reducing techniques are also considered in several Member States.

3. Case study

Aquatic risk assessment for a substance called X for reservation purpose, is presented as case study. Both a first tier and refined risk assessment is reported.

In Table 1 are reported the results of acute and chronic toxicity tests. The most sensitive and relevant end-points identified within the toxicity studies were selected for the risk assessment (values in bold).

Predicted Environmental Concentrations (PECs) to surface water were calculated considering spray drift as the main route of contamination. Due to the rapid dissipation of the X substance run-off is not likely to occur. Estimated initial aquatic concentrations (PECi) for a depth of 30 cm are presented in the Table 2.

The estimations of the PECsw were calculated assuming that X substance is applied at: 2.4 kg active ingredient/hectare on orchards; 1.6 kg a.i./ha on field crops. Drift values have been derived from the new table of BBA.

As first tier risk assessement (*worst case* scenario), short term and long term toxicity/exposure ratios for X substance were calculated and reported in Tables 3 and Table 4, respectively.

TABLE 1. Summary effects of X substance to water organisms.

Test species	Test type	Duration of exposure	Results
	FISH		
Bluegill	Acute	96 h	LC50: 0.083 mg a.i./l NOEL: 0.056 mg a.i./l (actual)
Rainbow Trout	Acute	96 h	LC50: 0.074 mg a.i./l NOEC 0.041 mg a.i./l(actual)
Fathead minnow	Early life stage	33 d	NOEC 5.2 µg a.i./l (actual)
Fathead minnow	Early life stage	34 d	NOEC 2.19 µg a.i./l LOEC 4.56 µg a.i./l (actual)
	INVERTEBRATES		
Daphnia magna	Acute	48 h	LC50: 1 mg a.i./l NOEC: 0.46 mg A.I. /l (nominal)
Daphnia magna	Acute	48 h	EC50: 0.073 mg a.i./l NOEC: 0.031 mg a.i./l (actual)
Daphnia magna	Chronic	21 d	EC50: > 53 µg a.i. /l NOEC: 7.3 µg a.i. /l (actual)
	ALGAE		
Scenedesmus subspicatus	Growth Inhibition	96 h	ErC50: 2.21 mg a.i. /l (nominal)
Selenastrum capricornutum	Growth Inhibition	72 h	ErC50: 1.249 mg a.i. /l NOEC: 0.25 mg a.i. /l (nominal)

Values in bold have been selected for the risk assessment

TABLE 2. Surface water PECs.

Crop	Distance (m)	% Drift	Application rate (kg/ha)	PEC_{sw} (mg/l)
Field	1	2.77	1.6	0.015
Orchard	3	29.2	2.4	0.022

TABLE 3. Short term toxicity/exposure ratios for X substance for the most sensitive aquatic organisms.

Target crop	Distance (m)	Test species	Effect concentration (mg a.i./l)	Estimated initial concentration (mg a.i./l)	TERst	Trigger
Field	1	fish	0.074	0.015	5.01	100
Orchard	3	fish	0.074	0.22	0.32	100
Field	1	Invertebrate	0.073	0.015	4.94	100
Orchard	3	Invertebrate	0.073	0.22	0.31	100
Field	1	algae	1.29	0.015	87.32	10
Orchard	3	algae	1.29	0.22	5.52	10

TABLE 4. Long term toxicity/exposure ratios for X substance for the most sensitive aquatic organisms.

Target crop	Distance (m)	Test species	Effect concentration (mg a.i./l)	Estimated initial concentration (mg a.i./l)	TERlt	Trigger
Field	1	fish	0.00219	0.015	0.148	10
Orchard	3	fish	0.00219	0.22	0.009	10
Field	1	Invertebrate	0.0073	0.015	0.49	10
Orchard	3	Invertebrate	0.0073	0.22	0.03	10

TERs calculated for X substance, in a *worst case* scenario, are below the corresponding triggers of 91/414 Annex VI (TERst is < 100 or TERlt is < 10) and show a high risk for aquatic organisms. Therefore a refinement of risk is necessary. Considering the rapid degradation of X substance (DT_{50} 2-3 hours), for chronic risk the exposure was refined calculating PEC which take into account the degradation (Time Weight Average PECs). Thus PECs after 21 days (for daphnia) and 28 days (for fish) were considered. Mitigation measures such as safety distances were adopted (a buffer zone of 20 m for orchard). New TERs values are reported in Table 5.

TABLE 5. Long term toxicity/exposure ratios for X substance for the most sensitive aquatic organisms with TWA PEC.

Target crop	Distance (m)	Test species	Effect concentration (mg a.i./l)	PECtwa (mg a.i./l)	TERlt	Trigger
Field	1	fish	0.00219	0.000073	30	10
Orchard	20	fish	0.00219	0.000109	20	10
Field	1	Invertebrate	0.0073	0.000097	75	10
Orchard	20	Invertebrate	0.0073	0.000146	50	10

To refine the short term risk and further refine the chronic risk a mesocosm was performed by notifier, focussed on the phyto & zooplankton communities, and on benthic organisms. Fish were not included in the study.

Based on the results of the mesocosm study an Ecologically Acceptable Concentration (EAC) in a pond community after the eightfold application of X substance can be set at 32 µg X substance/L. Mesocosm studies allow reduction of uncertainty in the effect assessment, therefore it is not necessary to apply trigger values. New TER values are reported in Table 6.

TABLE 6. Toxicity/exposure ratios for X substance for mesocosm aquatic organisms.

Target crop	Distance (m)	Test species	Effect concentration (mg a.i./l)	Estimated Initial Concentration (mg a.i./l)	TER	Trigger
Field	1	Mesocosm	0.032	0.015	2.17	1
Orchard	20	Mesocosm	0.032	0.22	1.44	1

Long term TERs calculated with twa PECs show an acceptable risk for aquatic organisms.

Mesocosm studies provide arguments in favour of considering the compound safe for aquatic invertebrates and algae at the application rates intended. In fact the TERs calculated using the Ecologically Acceptable Concentration (EAC) of 32 μg/l are above the trigger.Therefore it can be concluded that, introducing a buffer zone of 20 m, adequate margins of safety exist to non target aquatic organisms during normal agricultural practice, although X substance is toxic in laboratory tests.

4. Conclusions

Pesticide risk assessment scheme to protect aquatic systems in the framework of Directive 91/414/CEE was described.

According to this scheme, authorizations of products which present unacceptable ecological risk under standard use conditions can be made subject to the application of a suitable restrictions ensuring mitigation of the risk.

5. References

Campbell, P.J., Arnold, D.J.S., Brock, T.C.M., Grandy, N.J., Heger, W., Heimbach, F., Maund, S.J. and Streloke, M. 1998 Guidance document in Higher tier risk assessment for pesticides .(HARAP). Proceedings from the HARAP workshop. SETAC pub. ISBN 90-5607-011-8.

Council Directive 91/414/EEC of 15 July 1991 concerning the placing of plant protection products on the market. *Official Journal* L 230 , 19/08/1991 p. 0001-0032.

Giddings, J.M., Brock, T.C.M., Heger, W., Heimbach, F., Maund, S.J., Norman, S.M., Ratte, H.T., Schafers, C. and Steloke, M., 2001 Community – Level aquatic system studies – interpretation criteria. Proceedings from the CLASSIC workshop. SETAC pub. ISBN 1-880611-49-x.

FOCUS GW 2000, FOCUS groundwater scenarios in the EU plant protection product review process. Report of the FOCUS Groundwater Scenarios Workgroup, *EC Document Reference Sanco/321/2000.*

FOCUS SW, 2001, FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC. Report of the FOCUS Working Group on Surface Water Scenarios, *EC Document Reference SANCO/4802/2001-rev.1*.

Padovani, L., Capri, E. And Trevisan, M., 2004. Landscape-Level Approach To Assess Aquatic Exposure via Spray Drift for Pesticides: A Case Study in a Mediterranean Area. *Environ. Sci. Technol*. 38, 3239-3246.

Verro, R., Calliera, M., Maffioli, G., Auteri, D., Sala, S., Finizio, A. And Vighi, M., 2002. GIS-Based System for Surface Water Risk Assessment of Agricultural Chemicals. 1. Methodological Approach. *Environ. Sci. Technol.* 36, 1532-1538.

IDENTIFICATION AND CHARACTERIZATION OF BIOLOGICAL RISKS FOR WATER

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Abstract

Life on this planet is dependent on water but our health is greatly impacted by the quality of that water. The global water crisis is clear, one only needs to quote the statistics on the billions of people without access to safe water, sanitation and the global estimates of the burden of waterborne disease. The greatest sources of biological contaminants associated with this disease burden in water remains human and animal feces. There is a critical need to develop a science-based program to address both water quantity and quality of water, water uses and discharges. Recommendations to achieve better access to scientific information for decision making include: 1) develop watershed approaches for determining the source and the behaviour of water-borne biological contaminants which can be used within Water Safety Plans, 2) utilize new tools and technologies for measuring the hazards and the exposure within a risk assessment framework and 3) develop a global data base and goals for biological contaminant loading for achieving safe water.

Keywords: Waterborne disease/parasites/viruses/monitoring/microbial risk assessment.

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1. Introduction

The terrifying tsunami and the subsequent events which unfolded in Asia at the end of 2004 exemplify many of the challenges facing the management of water resources for achieving water safety and public health protection. Displacement of people, disruption of services with the destruction or lack of infrastructure, inadequate water treatment, flooding (storms) and thus widespread fecal contamination, all resulting in the fear of massive waterborne disease particularly impacting those individuals who are most susceptible, the children and those with weakened systems due to stress, poor nutrition, (other diseases such as AIDS) and lack of medical care. The assurance of safe water and adequate control of fecal contamination of water continues to be a common struggle for millions and these same issues which have been extolled for the tsunami victims are those that the global health and water science and technology community must address to meet the Millennium Development Goals for water and sanitation (UN, 2000; 2002). Yet unfortunately, water quality problems and massive fecal contamination remain invisible, with little water quality data available for those who need to know and make decisions and thus it takes a massive and dramatic crisis, before even minimal attention is given to those dealing with these challenges on a daily basis. The World Health Organization has estimated that 40% of the world's people lack sanitation (2.4 billion people) and 1.1 billion people lack access to safe water (WHO, 2000). Up to 2.2 million children will die from diarrhea annually. Significant issues will need to be addressed regarding the biological agents found in water and the infectious diseases associated with these agents in order to make progress without slipping further and further behind in achieving the MDG. Fecal contamination and the loading of pathogens to water need to be determined and then strategies and goals for reducing this burden can be implemented. New tools can be used to build a global water quality data base on fecal contamination of waters, identifying biological agents in a risk-based scientific framework and thus will enhance the implementation of Water Safety Plans providing a true basis for measuring and achieving safe water (WHO, 2004).

2. Emerging and persistent biological contaminants

Studies of emerging infectious diseases (Taylor et al. 2001; Cleaveland et al. 2001; Ewald 1996) in human and animal populations have revealed the following:

- Viruses, prions, bacteria, and protozoa are more likely than fungi or helminths to be associated with emerging infections.
- Zoonotic pathogens comprise 75% of emerging infectious diseases.
- Pathogens which are subject to relatively frequent mutation or genomic reassortment events (e.g. RNA viruses and viruses with segmented genomes) are more likely to emerge.
- Pathogens which infect multiple hosts or pathogens that infect species that can harbour multiply closely related agents providing an opportunity for reassortment or recombination (e.g. SARS in cats) are likely to emerge.
- Agents transmissible by more than one route or by indirect contact, e.g. water, food, environmental contamination, vectors, etc, are likely to emerge.

Hundreds of pathogens are found in the feces of humans and animals all ending up excreted into the environment. Population growth, urbanization, increased animal concentration exacerbated by lack of infrastructure and waste treatment, climate variations (floods and droughts) all influence the occurrence and spread of biological agents of concern in water.

Viruses, due to their small size and structure, their environmental stability and low infectivity, remain biological contaminants which elicit a high probability of infection via ingestion of contaminated water (Haas et al., 1999). Viruses cause a wide-range of significant diseases many which may have chronic outcomes including polyomelitis, meningitis, myocarditis, and hepatitis. Viral agents have been implicated in endemic diarrheal disease due to contaminated groundwater in rural areas in Wisconsin likely associated with septic tanks. Children were shown to be at particularly high risk of illness (Borchardt et al. 2003). The coliform indicator bacteria did not prove to be a sufficient measure of risk. Therefore viral contamination of groundwater needs to be particularly assessed as children are very susceptible to severe disease; bacterial indicators are not indicative of viruses and groundwater is often used without disinfection.

TABLE 1. Some Viruses of Emerging Concern.

Virus	Type	Diseases	Occurrence in Water	Other Key Points
Adeno Viruses	DNA	Respiratory & gastroenteritis	Detected in ground, surface and drinking water	High concentrations in sewage, long-term survival in water.
Coxsackie	RNA	Respiratory, gastrointeritis, meningitis, myocarditis	CB 5 found to be one of the most prevalent viruses in sewage and polluted waters.	Cause of chronic diseases.
HEV	RNA	Hepatitis		Genetically related to that found in Pigs. High mortality in Pregnant women.
Noroviruses	RNA	Gastroenteritis	Sewage, surface and groundwaters	Common cause of recreational and drinking water disease.
Polyoma Viruses	DNA	Brain, colorectal cancers and urinary tract disease	Feces, urine and sewage.	Survives in water but oral transmission uncertain.

Hepatitis E virus (HEV) is an enteric RNA virus isolated from humans and causes jaundice and clinical signs similar to hepatitis A virus. HEV is transmitted by the fecal-oral route and has caused devastating waterborne disease outbreaks particularly in tropical and subtropical countries with inadequate sanitation (Aggarwal and Naik 1997; Balayan 1997). In Kanpur, India in 1991, there were 79,000 cases of HEV due to sewage contamination of the drinking water. The earliest confirmed outbreaks occurred in the 1950s in India (Bradley 1992). Children are often asymptomatic and the mortality rate is between 0.1 and 4% (Grabow et al. 1994). In pregnant women in their third trimester, the mortality rate can exceed 20% (Hurst et al. 1996). There has been speculation that HEV is endemic in various parts of the world and subclinical cases may be contributing to the spread of the disease. HEV is also found in wild and domestic animals. Studies using genetic sequencing have found that human and pig HEV are genetically similar and belong to the same genotype and swine HEV is widespread in U.S. swine herds (Huang et al. 2002; Smith 2001). Thus zoonotic transmission seems quite likely and at least one strain can infect across species barriers (Smith 2001). Recent studies in the U.S. have shown that swine veterinarians are at in increased potential risk of zoonotic HEV infections (Meng et al. 2002). The fecal contamination of water from pigs continues to challenge the human population with potential risks associated with the transmission of these agents. The survival and resistance of HEV to water treatment has not been well studied but is presumed to be very similar to Hepatitis A Virus. As enteric viruses, they are stable in the water environment particularly at lower temperatures. In addition, during water disinfection, the viruses are more resistant to chlorination than bacteria although good inactivation can be achieved with free chlorine. Chlorine disinfection does not inactivate viruses in wastewater as effectively as it does in drinking water because of interference by dissolved organics and suspended particulates; the resulting disinfectant is combined chlorine, which inactivates viruses less effectively than free chlorine does (Mahin and Pancorbo, 1999).

Adenoviruses are double-stranded DNA viruses and they are extremely stable in the environment. (Table 1). Several studies have suggested that adenoviruses outnumbered other enteric viruses in sewage-contaminated waters and may survive longer than other viruses in water (Enriquez et al. 1995; Pina et al. 1998). Adenovirus 40 and 41 are enteric based and are the second most important etiologic agents of childhood gastroenteritis after rotavirus. The number of waterborne outbreaks caused by adenoviruses might have been underestimated because they are not being routinely screened for in outbreak samples. These viruses are commonly detected in coastal systems likely influencing recreational risks and indicative of the sewage discharges to the coast (Griffin et al., 2003) and both respiratory and enteric adenoviruses have been detected in treated drinking water when disinfectant contact times and concentrations were too low for virus inactivation (Lee and Kim, 2002).

Formerly classified as Norwalk-like viruses, the Noroviruses are highly infectious and can cause prolonged asymptomatic shedding in infected individuals for up to two weeks. Noroviruses are extremely stable in the environment, they are stable in less than 10 parts per million (ppm) chlorine and can withstand freezing and heating to 60 °C (Nwachcuku and Gerba 2004). Substantial strain diversity leads to short-lived host immunity to infection permit re-infection and make the development of a vaccine that offers lifelong protection impossible (Glass et al. 2001). The estimated total number of cases of norovirus infection per year is 23,000,000 in the United States alone (Mead 1999). There has been a world-wide occurrence of norovirus outbreaks in the last few years, causing problems with cruise ships, hotels, drinking water, recreational water and in nursing homes where mortality has been reported. Just in the US. the number of drinking water-related norovirus outbreaks has increased from three during 1999-2000 to five during 2001-2002 (Prevention 2004). Norovirus outbreaks constituted for 9% of waterborne-disease outbreaks of gastroenteritis associated with recreational water during 1993-2002 and 16.7% waterborne-disease outbreaks of gastroenteritis associated with recreational water during 2001-2002.

There are disturbing new reports regarding the potential for waterborne transmission of the cancer-causing viruses, the polyomaviruses (Bofill-Mas et al., 2001). The polyomaviruses include the JC and BK viruses, which cause brain, colorectal cancers and urinary tract disease. Polyoma viruses are non-enveloped double-stranded DNA viruses with diameter between 38 to 43 nm. JC virus, a polyoma virus, is etiologically linked to progressive mulfocal leukoencephalopathy, a fatal demyelinating disease (Nwachcuku and Gerba 2004). Polyoma viruses can be excreted in urine of infected persons and have been detected in sewage worldwide (Bofill-Mas and Girones 2003). They have been detected at concentrations of 10^1 to 10^3 viral particles per ml in sewage in studies in the US, Europe and Africa. The viruses have been shown to be stable with T-90 (time for 90% decrease in numbers) from 26 days for JCV to 53 days for BKV at 20°C. However, very little is known in regard to transport and exposure of these viruses as emerging waterborne agents.

The parasites *Cryptosporidium* and *Giardia* remain a concern in water world-wide and are probably the most common waterborne infection globally (Leclerc et al., 2004). Characteristics that make these parasites a top priority include:

- concentrations in sewage and feces
- zoonotic nature
- extreme resistant to chlorination
- environmental stability
- low infectivity

Cryptosporidium remains a specific problem for those with AIDS, while *Giardia* remains the most wide-spread parasitic infection in the world, leading to chronic infections. Children are most susceptible to infection and severe outcomes. Recurrent diarrheal disease and chronic parasitic infections in children have been associated with impaired cognitive ability later in childhood (Berkman et al., 2002).

Levels of cysts and oocysts in surface waters can be very high depending on the amount of fecal contamination. These parasites have been detected throughout the world and are now currently monitored for more than any other pathogen in water. Filtration or some type of physical removal is needed, as the organisms are resistant to chlorination, or if economically feasible uv disinfection is possible (Rose et al., 2002; Betancourt and Rose, 2004). Interestingly, the parasites are more susceptible to heat inactivation, therefore solar water pasteurization systems may provide some protection against parasites, however this has yet to be proven.

It is quite clear that the coliform indicator bacteria do not always provide the necessary measure of microbiological safety of water, especially with respect to viral and parasitic pathogens. The spread of waterborne parasitic and viral diseases will not be addressed or contained via a total coliform test and new tools, alternative indicators, pathogen monitoring and molecular characterization of the organisms in the water will be needed in the future. The most widespread alternative indicators in addition to *E.coli* that have had usefulness include coliphage (bacterial viruses that are easily and cheaply monitored for) and Enterococci (enteric bacteria which have been related to groundwater contamination, recreational risk and improved assessment of wastewater disinfection).

3. General Approach to Microbial Risk Assessment

Significant technical advances have now been made in microbiology and molecular biology that have influenced all associated fields including medicine, food safety, microbial ecology, environmental forensics, and water microbiology. Thus while traditional culture-based methods for bacteria have been and will continue to be used in water, antibody-based and genetic-based methods can be used for almost any biological hazard. Polymerase chain reaction (PCR) the method by which specific identifying genes can be amplified and detected allows for specific, sensitive and fairly rapid analysis of any pathogen of interest, whether culture methods exist or not.

These advances have lead to the ability to build data bases that can be used to identify and characterize the biological hazards in water.

3.1. SOURCE TRACKING

Microbial source tracking is an emerging field of investigation, which has attempted to determine the source of the fecal pollution in waterways, whether it be human or animal (Sinton et al., 1998; Scott et al., 2002; Simpson et al., 2002). While it is acknowledged that exposure to animal fecal wastes represent a human health risk often it is human feces, septic effluent and septage, cess pool discharges, and sewage that would signal a greater risk for the presence of human pathogens, particularly human viruses. Different types of methods have been examined and they can be classified into two separate groups,

- library-based methods rely on the building of a watershed specific database most often for *E.coli* or Enterococci from fecal sources (eg. Birds, cows, humans etc) and comparing that to water isolates and includes ribotyping, pulsed-field gel electrophoresis, repetitive element PCR and multiple antibiotic resistance (Simpson et al. 2002). Round robin studies have shown that library based methods have limited accuracy and lead to high false-positive rates (Griffith et al., 2003).
- library-independent methods rely on the identification of host-specific markers in *Bifidobacterium* spp., *Bacteroides fragilis* bacteriophages, F^+-specific RNA coliphage and Enterococci (Griffith et al., 2003, Scott et al., 2002; 2004).

Enterococcus faecalis and *Enterococcus faecium* are predominant in human feces and as such have the potential to be excellent indicators of human fecal pollution and a method has been recently developed that can be used with current water sampling approaches to evaluate the presence of human fecal contamination (Scott et al., 2004). The enterococcal surface protein (esp) found in *E. faecium* was the target of the host-associated molecular marker used to develop the human fecal maker. Currently the method is the most robust and sensitive (60 CFU) of all the host-specific approaches and after examination of 65 wastewater and septic samples and 102 animal samples, no false positives were examined and the presence of human fecal material was detected accurately in 97% of the samples, exclusively indicates the presence of human wastes without the need to build a library.

3.2. PATHOGEN MONITORING

An understanding of the ecology of the infectious agents will be crucial in understanding the distribution and dissemination of the environmental forms, these data will be necessary to address risk and prevention strategies. Thus pathogen monitoring will be a part of the future for characterizing biological hazards in water. Any pathogen of concern can now be monitored for in water. Filtration techniques, followed by clarification methods (e.g. immunomagnetic separation), cultivation, antibody-based detection or molecular detection have been used for detection of bacteria, viruses and parasites. PCR methods can be developed for any microorganism of interest. Most recently the National Academy of Sciences, Organization for Economic & Community Development, and the American Academy of Microbiology have all summarized the methods available for monitoring any pathogen of interest in water (Rose and Grimes, 2001; NRC, 2004; OECD, 1998). Rapid tests are being examined which include antibody-based methods addressing both the traditional and alternative indicators as well as pathogens such as *Cryptosporidium*. A recent example of the benefits of such approaches has been the use of molecular methods which have been used for monitoring sewage to evaluate the transition of wild type poliovirus infections to the vaccine strain in order to assess the vaccination programs in communities.

No global assessment of any one method has been undertaken for more than 20 years. And while there are continued reports of pathogen levels and indicator levels in waters through out the world, there is no central clearing house for reporting or compiling these data.

Pathogen monitoring is needed if the risk is to be appropriately addressed. The classical risk assessment/risk management paradigm, is widely accepted as the primary basis for regulatory decision making on environmental issues. In this conceptual model, the environmental risk assessment process is initiated by what has been termed "hazard assessment" which can be thought of as identification of an agent capable of causing an adverse health effect. The actual risk that a biological agent poses results from a combination of exposure and infectivity and pathogenicity. The integrity of the risk assessment process thus depends primarily on the base of scientific information related to exposure and disease potential. Both can be exceedingly complex, and rarely is a complete understanding available on how an agent is released, how an agent is transported and transformed in the environment (and also in engineered systems), how exposure occurs, and how exposure relates to disease based at both the individual and population levels.

One can conceptualize a "source-to-disease" structure around water-related disease-causing agents, and if the critical scientific gaps in understanding how these agents behave from the point of release to the resultant health effect are to be addressed then pathogen monitoring is needed.

3.3. QUANTITATIVE MICROBIAL RISK ASSESSMENT QMRA

The definition of 'microbiologically safe water' is evolving from the utopian concept of pathogen-free water to a more realistic goal of providing drinking water for human consumption (European Union Council Directive 98/83/EC and WHO guidelines as quoted by Szewzyk et al. 2000) to be, "…free from microorganisms and parasites ….. which, in numbers or concentrations, constitute a potential danger to human health." These statements must be interpreted along with a definition of acceptable risk. The U.S. Environmental Protection Agency defines acceptable risk of potable water to be 1:10000, i.e., 1 case of the disease in 10,000 exposed persons (Szewzyk et al. 2000). These types of guidelines can be used to conduct mathematical modelling of the risk to public health due to the concentrations of various agents in water. However to conduct this risk assessment, key pieces of information are required to be known, or at least predictable, based on databases and applied models. Quantitative microbial risk assessment (QMRA) procedures which address hazard identification, dose-response, exposure assessment and characterization have been defined (Haas et al. 1999), yet this system needs to incorporate both indicator data and treatment strategies.

During water quality monitoring the initial testing is via bacterial indicators which have limitations regarding risk assessment interpretation. Yet by addressing both sources, and pathogen monitoring, transport and fate into the risk assessment framework, exposure and the characterization of the biological contaminants in water and finally, the risk can begin to be elucidated (Figure1). Thus appropriate management strategies can be implemented.

The infectious dose-response of the pathogen of interest; the concentration at which the agent can be found in water, and finally the strategies for prevention of pollution and various water treatment strategies for the reduction the biological contaminants make up the final framework for risk assessment.

Data from both indicators and pathogen occurrence can be used to evaluate the fate and behaviour of a substance in the environment (Exposure Assessment). Other medical data can be used to assess the potential Hazard posed by biological contaminants. The results of the exposure assessment and the hazard assessment are combined to produce an overall risk assessment. Such data are generated from an increasingly comprehensive series of studies termed *higher tier studies*. At each tier a relevant comparison has to take place between the estimated exposure and the estimated hazard and there are thus separate tiers for both exposure and hazard estimation.

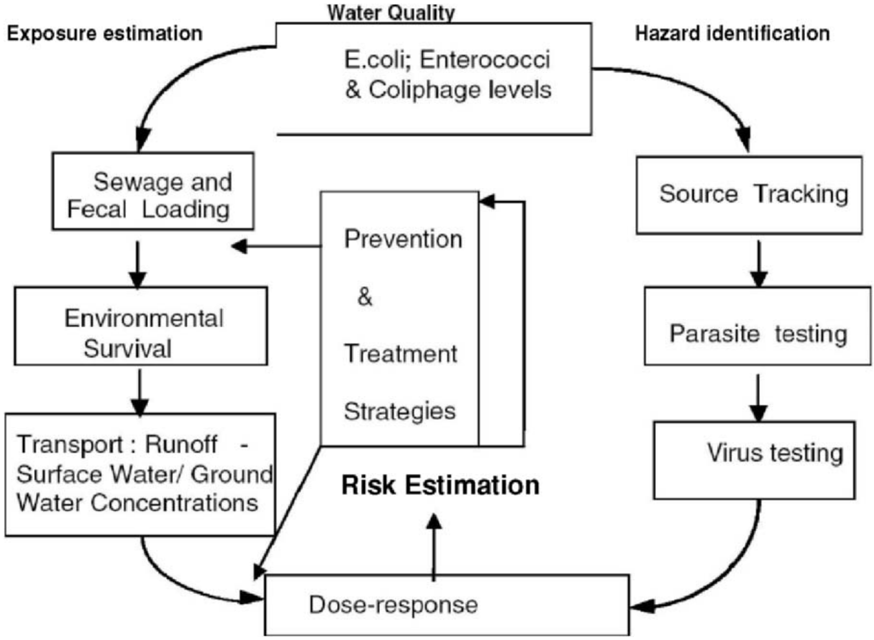

Figure 1. Water Quality Monitoring as Part of the Risk Assessment Framework.

4. Need for a Global Water Monitoring Network for Fecal Contamination and Biological Contaminants

Many countries have a health goal of no pathogens in drinking water and require no detectable live (cultivatable) total coliform bacteria per a 100mL sample volume. The WHO drinking water criteria focuses on the absence of cultivatible *E.coli* per 100mL. There are no identifiable goals for ambient water quality for waters used as a potable water supply.

Despite the development of a variety of methods and a global indicator system based on coliform bacteria and *E.coli* very little comprehensive information is available on the quality of the global water supply. The lack of data has been suggested as the main deterrent to developing a vested interest in water systems and the implementation of policies and programs to improve water quality at the local and national levels (Barker, 2004). The United Nations World Water Assessment Programme was set up to address comprehensive water quality monitoring data bases yet, the UN Global Environment Monitoring System for Water (GEMS/Water) created in 1978, has only 104 governments participating and while there are physical and chemical water quality data there are minimal microbial data focused on fecal coliform bacterial levels with poor resolution and no ability to readily compare the data (eg. via mapping). [www.gemswater.org; www.unesco.org/water/wwap]

In many countries the clinical and medical system is not separate from the public health system. The WHO global Laboratory Network is centred around infectious diseases important to the country. In the US, CDC has established the Global Health Initiatives, more recently to focus on the AIDS issue. While laboratory infrastructure is being assessed, methods and supplies to address the diagnostics are moving forward, there is no reason why the testing of water can not be incorporated into these plans. The building and rebuilding of laboratory capacity is ongoing. As coordination, protocol development, training, technology transfer, assessment and updates move forward, the concept of inclusion of water quality as a key indicator of community health could begin to be developed.

Prioritization of key laboratories to assist in this effort and training of personnel will be needed. This will also require the coordination and communication between Ministries of Health and Ministries of the Environment.

As with other global goals the measuring and improvement of water quality should begin with an action plan. This would address:

- Prioritization of water basins
- Technology to be used and tested
- Development of a tiered testing protocol for addressing risk (Figure 1)
- Development of a common methodology for reporting spatial and temporal data sets.

5. Conclusions

The identification, measurement and control of infectious disease remain a focus of the global health community. It is clear that in most countries some type of system is available for addressing the spread of disease and mobilization of the global and local community medical and public health systems was clearly evident during the recent SARS epidemic; and yet the morbidity and mortality associated with SARS pales in comparison to the numbers of individuals who become ill, are hospitalized and who die as a result of contaminated water.

To really meet the millennium goals, both access to "safe" drinking water and sanitation will be critical. Comprehensive watershed assessment, planning and integrated programs to address both water quality and quantity are likely to be effective at the community level and may be much more cost-effective with long-term sustainability in comparison to plans which address temporary access only at the household level through house-hold treatment (Souter et al. 2003). This approach underscores the need to enhance and refine the detection of contaminants in water, monitoring of changes in observable water quality, assessment of exposure and the potential public health impacts and improvements made with the investment in public works.

Development of appropriate databases is necessary. Recommendations to achieve better access to scientific information for decision making include: 1) develop watershed approaches for determining the source and the behaviour of water-borne biological contaminants which can be used within Water Safety Plans, 2) utilize new tools and technologies for measuring the hazards and the exposure within a risk assessment framework and 3) develop a global data base and goals for biological contaminant loading for achieving safe water.

6. References

Aggarwal, R. and Naik S.R., 1997 Epidemiology of hepatitis E: past, present and future. *Trop. Gastroenterol.* 18, 49-56.

Balalyan, M.S., 1997 Epidemiology of hepatitis E virus infection. *J. Viral Hepatitis* 4, 155-165.

Barker, S. 2004. Staying on Target. Environmental Protection, Feb. 23-27.

Berkman, D.S., A.G. Lescano, R.H. Gilman, SL. Lopez, M.M. Black, 2002. Effects of stunting, diarrhoeal disease, and parasitic infection during infancy on cognition in late childhood: a follow up study. *Lancet* 359:564-571.

Betancourt, W.Q. and Rose, J. B. 2004. Drinking water treatment processes for removal of *Cryptosporidium* and *Giardia* Vet. Parasit. 126:219-234.

Bofill-Mas S., Formiga-Cruz M., Clemente-Casares P., Calafell F., Girones R., 2001. Potential transmission of human polyomaviruses through the gastrointestinal tract after exposure to virions or viral DNA. *J Virol.* 75(21):10290.

Bofill-Mas S., Girones R., 2003. Role of the environment in the transmission of JC virus. J. Neurovirol. ;9 Suppl 1:54-8.

Borchardt, M.A., P. Chyou, E.O. DeVries, and E.A. Belongia, 2003 Septic system density and infectious diarrhea in a defined population of children. *Environ. Health Perspectives* 111: 742-748.

Bradley, D.W. 1992. Hepatitis E: epidemiology, aetiology and molecular biology. *Rev. Med. Virol.* **2**, 19-28.

Cleaveland, S. Laurenson, M.K. and Taylor, L.H., 2001 Diseases of humans and their domestic mammals: pathogen characteristics, host range, and risk of emergence. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 356(1411), 991-999.

Enriquez, C. E., C. J. Hurst and C. P. Gerba, 1995. "Survival of the enteric adenoviruses 40 and 41 in tap, sea, and waste water." Wat. Res. 29(11): 2548-2553.

Ewald, P.W. 1998. The evolution of virulence and emerging diseases. *J. Urban Health* 75(3), 480-491.

Glass, R. I., J. Bresee, B. Jiang, J. Gentsch, T. Ando, R. Fankhauser, J. Noel, U. Parashar, B. Rosen and S. S. Monroe (2001). Gastroenteritis viruses: an overview. Symposium on Gastroenteritis viruses, Novartis Foundation Symposia. 238: 5-19/ 19-25.

Grabow, W.O.K., Favorov, M.O., Khudyakova, N.S., Taylor M.B. and Fields H.A., 1994. Hepatitis E seroprevalence in selected individuals in South Africa. *J. Med Virol.* 44, 384-388.

Griffin, D.W., Donaldson, K.A., Paul, J.P. and Rose, J.B., 2003. Pathogenic Human viruses in Coastal Waters. *Clin. Microbiol. Rev*. 16(1):129-143.

Griffith, J. F., Weisberg, S. B., and McGee, C. D., 2003. Evaluation of microbial source tracking methods using mixed fecal sources in aqueous test samples. J. Water and Health. 01:141-152.

Haas, C.H., Rose, J.B., and Gerba, C.P. (eds), 1999. *Quantitiative Microbial Risk Assessment.* John Wiley and Sons, NY, NY.

Huang, F.F., Haqshenas, G., Guenette, D.K., Halbur, P.G. , Schommer, S.K., Pierson, F.W., Toth, T.E. and Meng, X.J., 2002. Detection by reverse transcription-PCR and genetic characterization of field isolates of swine hepatitis E Virus from pigs in different geographic regions of the United States. *J. Clin. Microbiol.* 40(4), 1326-1332.

Hurst, C. J., Clark, R. M. and Regli, S. E. , 1996 Estimating the risk of acquiring infectious disease from ingestion of water. In *Modeling Disease Transmission and Its Prevention by Disinfection*, (ed. C. J. Hurst) , pp. 99-139, Cambridge University Press, Great Britain.

Leclerc, H., Schwartzbrod, L., and Dei-Cas, E. 2004. Microbial agents associated with waterborne diseases. IN: *Microbial Waterborne Pathogens*. Cloete, T.E., Rose, J., Nel, L.H. and Ford, T. (eds) IWA publishing, London.

Lee, S. H., and S. J. Kim. 2002. Detection of infectious enteroviruses and adenoviruses in tap water in urban areas in Korea. Water Res. 36:248-256

Mahin, T. and Pancorbo, O., 1999. Waterborne pathogens. *Water Environ. Tech.* 11(4), 51-55.

Mead, P. S., L. Slutsker, V. Dietz, L. F. McCaig, J. S. Bresee, C. Shapiro, P. M. Griffin, and R. V. Tauxe. (1999). “Food-related illness and death in the United States.” Emerg. Infect. Dis. 5(5): 607-625.

Meng, X.J., Wiseman, B., Elvinger, F., Guenette, D.K., Toth, T.E., Engle, R.E., Emerson, S.U. and Purcell, R.H. , 2002. Prevalence of antibodies to Hepatitis E Virus in veterinarians working with swine and in normal blood donors in the United States and other countries. *J. Clin. Microbiol.* 40(1), 117-122.

NRC, 2004 (National Research Council), Committee on Indicators for Pathogens in Water. National Academy Press, Washington, D.C.

Nwachcuku, N. and C. P. Gerba 2004. “Emerging waterborne pathogens: can we kill them all?” Current Opinion in Biotechnology 15(3): 175-180.

OECD 1998. Proc. OECD Workshop Interlaken ’98, pp. 1-16. OCED and Switzerland.

Pina, S., M. Puig, F. Lucena, J. Jofre and R. Girones , 1998. “Viral pollution in the environment and in shellfish: human adenovirus detection by PCR as an index of human viruses.” Appl. Environ. Microbiol. 64(9): 3376-3382.

Prevention, C. f. D. C. a., 2004. Surveillance for waterborne-disease outbreaks associated with recreational water-United States, 2001-2002 and Suiveillance for waterborne-disease outbreaks associated with drinking water-United States, 2001-2002. Morbidity and Mortality Weekly Report. Atlanta, CDC: Vol. 53, No. SS-8.

Rose, J.B. Huffman, D.E and A. Gennaccaro, 2002. Risk And Control Of Waterborne Cryptosporidiosis. *FEMS Microbiology Reviews* 26:113-123.

Rose, J.B. Grimes, D.J. 2001. Reevaluation of Microbial Water Quality. Powerful New Tools for Detection and Risk Assessment. Report of American Academy of Microbiology. Washington, D.C.

Scott, T. M., Rose, J. B., Jenkins, T. M., Farrah, S. R., and Lukasik, J. 2002. Microbial source tracking: Current methodology and future directions. Mini-review. Appl. Environ. Microbiol. 68:5796-5803.

Scott, T. M., Jenkins, T. M., and Lukasik, J. and Rose, J.B . 2004 Potential Use of a host associated molecular marker in *Enterococcus faecium* as an index of human fecal pollution. Environ. Sci. Technol. In Press.

Simpson, J. M., Santo Domingo, J. W., and Reasoner, D. J. 2002. Microbial source tracking: State of the science. Environ. Sci. Technol. 36:5279-5288.

Sinton, L. W., Finlay, R. K., and Hannah, D. J. 1998. Distinguishing human from animal faecal contamination in water: a review. N. Z. J. Mar. Freshwater Res. 32:323-348.

Smith, J.E. 2001 A review of Hepatitis E virus. *J. Food Protect*. 64(4), 572-586.

Souter, P.F.; Cruickshank, G.D.; Tankerville, M.Z., Keswick, B.H., Ellis, B.D.; Langworth, D.E., Metz., K.A., Appleby, M.R., Hamilton, N., Jones, A.L. and Perry, J.D. 2003. Evaluation of a new Water treatment for Point-of-use household applications to remove microorganisms and arsenic from drinking water. J. Wat. and Hlth. Vol 1 (2) 73-84.

Szewzyk, U., Szewzyk, R., Manz, W. and Schleifer, K.H. 2000 Microbiological safety of drinking water. *Annu. Rev. Microbiol.* 54, 81-127.

Taylor, L.H., Latham, S.M. and Woolhouse, E.J. , 2001. Risk factors of human disease emergence. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 356(1411), 983-989.

UN, 2000 (United Nations.). The Millennium Goals. United Nations Millennium Declaration A/RES/55/2 8 Sept. 2000. United Nations, New York.

UN, 2002 (United Nations). Report of the World Summit on Sustainable Development Johannesburg, South Africa, 26 August- 4 September 2002. UN Document. A/CONF.199/20. New York. Available as of January 2004 at http://ods-dds-ny.un.org/doc/UNDOC/GEN/N02/636/93/PDF/N0263693.pdf?OpenElement

WHO, 2000 (World Health Organization). Global Water Supply and Sanitation Assessment 2000 Report. Available as of January 2004 at http://www.who.int/water_sanitation_health/Globassessment/GlobalTOC.htm

WHO, 2004 (World Health Organization).3rd Edition of the Drinking Water Guidelines http://www.who.int/mediacentre/news/releases/2004/pr67/en/water.

BIOLOGICAL AGENTS LIKE THREAT CAUSING ONES OR TOOLS FOR DETECTING HAZARDS

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Abstract

Greater and greater demand is needed to detect and identify the new emerging biological agents in drinking water supply. The so called indicator organisms like bacteria (E. coli, coliform bacteria etc.) often do not indicate the real danger for human health because of their higher sensitivity to chlorination for e.g. The other pathogen organisms like *Cryptosporidia, Giardia, Cyanobacteria* and their toxins, viruses, *Legionella,* fungi have higher resistance in other words lower sensitivity to chlorine. So some water borne disease can emerge beside the indicator parameters are satisfying. A case study in Hungary could prove this. Calicivirus caused outbreak in two villages spreading by the network of potable water. There are some indicators in legislation used in Hungary with similar sensitivity like pathogens to point out the possibility of occurrence of pathogens. These organisms are not pathogens but their appearance indicate the neglected condition of the network and the procedure of treatment plant. On the other hand the organisms can be used for detecting hazards like chemicals, genotoxic agents etc. Two technical workshops were organised on Toxicity for Biodefense in Oregon State University, USA and University of Pecs, Hungary. Both of the workshops were organised on the idea that each participant/group brought everything that were needed to carry out toxicity bioassay(s). All participants were given identical samples, and results were compared. Both toxicity and

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 103–111.

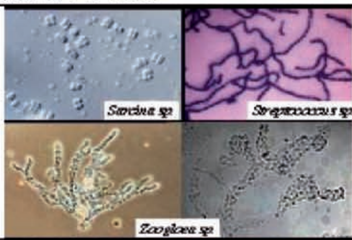
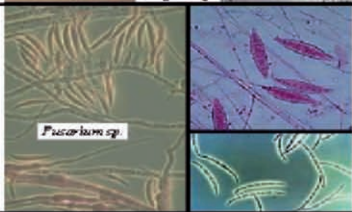
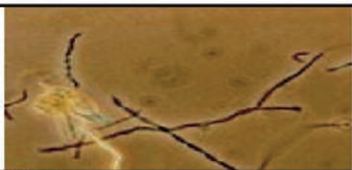
genotoxicity assays were included; both commercial kits and those under development were considered.

Keywords: Indicator organisms, Giardia, Cryptosporidium, Cyanobacteria, Legionella, biodefense

1. Possible new indicators

Infectious diseases caused by pathogenic bacteria, viruses and parasites (e.g. protozoa and helminths) are most common and widespread health risk associated with drinking water (WHO 2004). The conventional indicators like *E. coli* and coliform bacteria etc. are sensitive to chlorination however pathogen viruses or protozoa show high resistance to chlorine. That is why it is needed to develop new indicators with similar chlorine resistance like the non bacterial pathogens. The concept of using indicator organisms as signals of faecal pollution is a well established practice in the assessment of drinking water quality. In Hungarian legislation on drinking water quality beside the bacterial and chemical parameters to be determined there are the so called biological parameters that can be detected by microscope. The Governmental Decree on Requirements on Drinking Water Quality and the Order on Monitoring (2001) came into force in 2001. Determining the biological parameters is a useful and quick method for informing on problems and conditions in distribution networks and in the treatment plants. The required frequency of microscopic examinations is based on the amount of water supplied by the treatment plant, but every network must be examined at least once a year. The appearance of the biological parameters indicates the contamination of polluted soil or waste water (e.g. during the changes of pipes in the network) with drinking water or the naturally occurring high dissolved organic carbon or the neglected procedure of ferric and/or manganese removing by aeration. In TABLE 1 the biological parameters are shown with microscopic appearance.

TABLE 1. Biological parameters for drinking water.

Parameters	Limit	Unit	Comment	View
Sediment	0,1	mL/L	Amount of sediment after 0.45 m membrane filtration of 1 L water	
Bacteria indicating contamination with waste water	0	Number /L	distinguishable, clearly recognizable bacteria	
Fungi	0	Numer /L	Sediment must not contain fungi at all	
Protozoa	0	Number /L	Indicating pollution or pathogens	
Helminths	0	Number /L	Species of Nematodes, Oligochaetes, Ascarides, Gastrotriches and their eggs	
Iron and manganese bacteria	$2*10^4$	Number /L		
Sulphur bacteria and cyanobacteria	10^2	Number /L		
Algae	10^4	Number /L	Just for surface water treatment plants	

The organisms listed above have higher resistance to chlorine than bacteria. The protozoa and helminths (non pathogens) can live and proliferate on dissolved organic carbon or the organisms in the biofilm in the pipelines. In the same time these invertebrates serve as a potential carbon source, which could promote the growth of bacteria. Some papers referred on invertebrates present in distribution systems of drinking water (Török 1937, 1954, 1956, Smerda et al., 1971, Levy et al., 1986, Funch 1996, Wolmarans et al., 2004). Invertebrates can contribute to the organic load and could decrease the effectiveness of disinfection processes by increasing the chlorine demand and by protecting ingested bacteria from chlorine disinfection (Levy 1990). Wolmarans (2004) emphasizes the public health concern of existing invertebrates in the distribution systems because 10 to 4000 bacteria per organism could be estimated by culturing bacteria from intestines of invertebrates. Both Gram negative and Gram positive isolates could be identified as a number of bacterial genera and species that are pathogenic or opportunistic pathogens of humans. So these invertebrates should be considered as 'sacks' of bacteria and other micro particles.

2. Case study in Hungary

In Trans-Danubian region an outbreak was registered with symptoms of diarrhoea and vomiting in 16.5% of inhabitants of the village in the period of 13.11.2004 till 24.11.2004 (Figure 1).

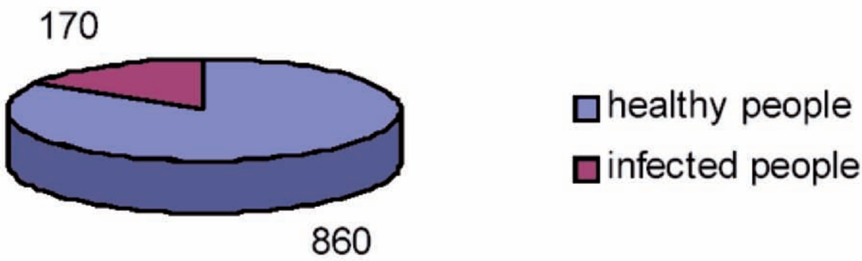


Figure 1. Total number of infected people during the outbreak.

A typical graph (WHO 2004) of waterborne diseases was received after analysing the numbers of cases (Figure 2).

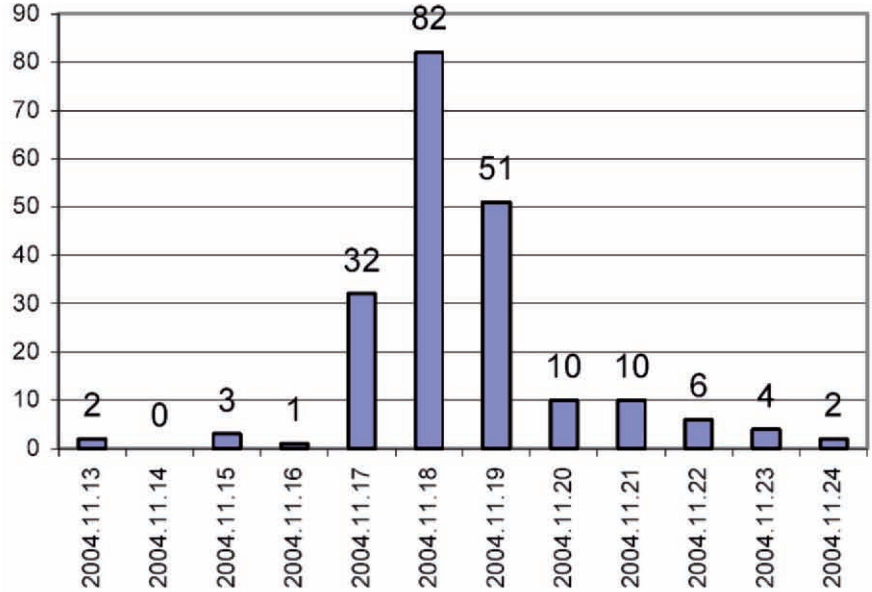


Figure 2. Number of infected people during the outbreak.

Calicivirus could be detected in the faeces of the patients. However the calicivirus could not be detected in the water because of the unsatisfied method. By the way the routine bacteriological and chemical parameters did not refer on the neglected quality of the drinking water only the biological parameters detected by microscope pointed out the unsatisfied quality of the water. Namely Rotifers (Figure 3.) and testaceous Rhizopoda (Figure 4.) could be identified in large number (300 ind/l) in the water.

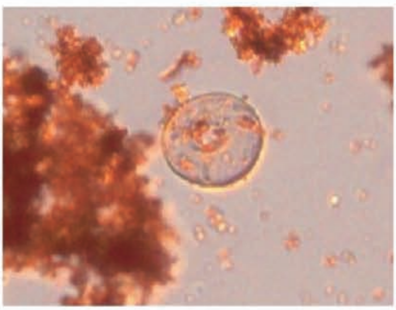


Figure 3. *Rhizopoda* sp.

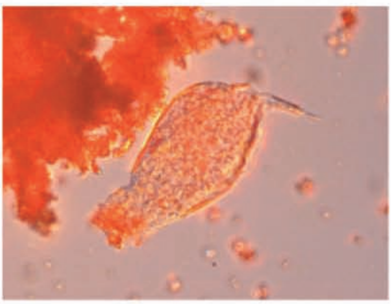


Figure 4. *Rotatoria* sp.

The detected number of Rotatoria of the drinking water was similar to the number of organisms of wetlands and polluted rivers. The limit for these invertebrates in drinking water is 0 individuum/liter in the Hungarian legislation. The rapid measurements on the basis of biological parameters for stopping the drinking water supply could prevent the development of larger outbreak. The total volume of water used for washing through the pipelines was 1000 m^3. These indicator organisms disappeared after the wash of pipelines.

This case also proved that new indicators should be introduced for safe drinking water supply.

3. Microorganisms like tools for detecting hazards

3.1. Workshops on toxicity for biodefence

On the other hands microorganisms can be used for detecting chemical, genotoxic etc. hazards in water as well. Two technical workshops were organised on Toxicity for Biodefense in Oregon State University, USA in 2002 and University of Pecs, Hungary in 2004. Both Workshops were based on the concept that the participants had to bring their own equipment and materials to analyse the same blind water samples. At the end of the Workshop the results from the different test methods were compared and the chemical composition of the samples was disclosed.

In the workshop at Oregon State University 10 bioassay technologies with different endpoints and development status were applied to 17 spiked samples (Pancrazio et al. 2004). The endpoints ranged between mortality of larvae and stress gene promoter modulation linked to luminescence or aggregation/dispersion of cellular pigment. In general, the biological component could be separated into three groups consisting of bacteria, cells or organisms. The bacterial group included both native and genetically modified strains where either sensitivity to specific threats or functional damage to pathways could be discerned optically. Although only one of these assays is presently commercially available, the bacterial approach is attractive in that is amenable to high-throughput evaluations and the bacteria can be preserved easily for prolonged shelf-life. In addition, bacteria can be relatively easily genetically engineered to respond to predetermined classes of toxicants. The cellular group contained both fish chromatophores and mammalian cell lines in formats that ranged from single to 96-well plates. The organism group which included crustaceans and fish utilizing lethality and behaviour endpoints, respectively, is well suited for aqueous-phase sample evaluations with little or no preparation (Törökné 2004). The biological component of the commercially available systems could be preserved easily for long shelf-life and ease of delivery. This evident with respect of the aquatic microorganisms and one of the bacterial assays. The biological components underlie these bioassays have reached a level of maturity and robustness such that technical demonstrations and can be used in military settings. Some observations emerged from the workshop findings: no false positives were reported across any of the technologies. Toxic metals and organophosphates often associated as threat agents or environmental contaminants, such as mercury, arsenite, cyanide, metham sodium, chlordimeform and phosdrin, were identified as toxic by 70-80% of the technologies.

Following the Oregon workshop eventually 15 different assays, encompassing toxicity, mutagenicity, genotoxicity tests and detection endocrine disruptors were applied in the Workshop at Pecs, with both commercial kits and methods still under development.

Thirty blind samples had to be analysed which when their nature was disclosed appeared to be composed of natural waters (surface waters, ground waters, tap water and sediment waters, industrial waste water) which had been either or not spiked with one or several chemicals in different concentrations. These chemicals belonged to endocrine disruptors, DNA adducts and heavy metals. All the thirty samples were tested only by three test methods because of time constraint. The endocrine disruptors, arsenic and DNA adducts could not be detected by the tests working with whole organisms. By the way the special methods worked out for detecting of DNA adducts and endocrine disruptors could not detect e.g. heavy metals and KCN at all. By conclusion it is needed a battery of tests to be sure of safe drinking water.

3.2. Derection of cyanobacterial toxins in source water

The eutrophication of surface waters often causes severe problems in drinking water supply and usage, as well as for recreation. The eutrophication of water can result commonly in the excessive growth of cyanobacteria (blue-green algae). The fact that cyanobacteria can be toxic has been known since at least the 19th century. Many species are known to produce toxins, i.e., “cyanotoxins”, a number of which are of concern for health. To date the main efforts are concentrated on monitoring the appearance of toxins by biological assays and chemical analyses. The ip. mouse assay (Carmichael, 1981) is used most commonly to detect cyanobacterial toxins causing different symptoms in mice. However there is an urgent need for simple, low cost alternative bioassays for routine testing because the mouse assay is expensive, demands well-skilled expertise and cannot be used routinely. Cyanotoxins vary in structure and may be found within cells or released into water. There is wide variation in the toxicity of recognized cyanotoxins (including different structural variants within a group: e.g. more than 70 variants in microcystins), and there are further toxins remain unrecognised. Chemical analysis of cyanotoxins is not the preferred focus of routine monitoring because of it requires time, equipment and expertise and expensive. So the chemical analysis cannot solve alone the detection of the cyanotoxins because there are unidentified toxins and the lack of analytical standards hampered the analysis. That is why it is necessary to detect cyanobacterial toxins with rapid biological tests independently from the quality and the mechanism of the effect of toxins in source water. It turned out that the Thamnotoxkit assay working with crustacean larvae can detect all kind of unknown and known hepatotoxins, neurotoxins and cytotoxins produced by cyanobacteria respectively (Törökné 1999, 2000, Törökné et al., 2000).

4. References

Carmichael, W.W. 1981. Freshwater blue-green algae (Cyanobacteria) toxins- A review, P. 1-14. *In* The Water Environment, Plenum Press, New York and London

Funch, P., Segers, H., Dumont, H.J., 1996. Rotifera in tap water in Gent, Belgium. Biol. Jaarb. Dodonaea 63. 53-57

Guidelines for drinking-water quality, 2004. vol.1. WHO Geneva

Levy, R.V., Hart, F.L., Cheetham,R.D., 1986. Occurence and public health significance of invertabrates in drinking water systems. J. AWWA 78; 105-110

Levy, R.V., 1990. Invertebrates and associated bacteria in drinking water distribution systems. In: Drinking water microbiology. G.A. McFeters (ed.) Springer Verlag, Berlin

Smerda, S.M., Jensen, H.J., Andreson, A. W., 1971. Escape of Salmonella from chlorination during ingestion by *Pristionchus cheritieri* (Nematoda: Diplogasterinae)

J. Nematology 3. 201

Török, P., 1935. A budapesti víz szüredékének faunája. Matematikai és Természettudományi értesítõ, 53. 637-659

Török, P., 1954. Biological investigation on waterworks supplied by spring water. Acta Biologica V-VI. 9-54

Török, P., 1956. Zwei interessante Rotatorien des Budapester Leitungswassers. Acta Zoologica II. 301-305

Törökné K. A., 1999. A new culture-free microbiotest for routine detection of cyanobacterial toxins Environ.Toxicol.14(5). 466-472

Törökné K. A. The potential of the Thamnotoxkit microbiotest for routine detection of cyanobacterial toxins. In: New Microbiotests for Routine Toxicity Screening and Biomonitoring, eds.G. Persoone, C. Janssen W. De Coen, Published Kluwer Academic/Plenum Publishers 533-539. (2000)

Törökné, A.K., László, E., Chorus, I., Sivonen, K., Barbosa, FAR., 2000. Cyanobacterial toxins detected by Thamnotoxkit. Environ. Toxicol. 15/5. 549-553

Wolmarans, E., du Preez, H.H., de Wet C.M.E., Venter, S.N., 2004. Significance of bacteria associated with invertebrates in drinking water distribution networks. CD on IWA World Water Congress and Exhibition, Marrakesh, Morocco

MICROBIAL RESISTANCE TO CHEMICAL CONTAMINANTS - AN ESSENTIAL PRECONDITION OF NATURAL ATTENUATION IN GROUNDWATER AQUIFER

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Abstract

Since groundwater represents a capital resource of drinking water in many countries, there is a growing public concern with contamination of groundwater aquifers by different health relevant chemicals. Based on an expected ability of autochthonous microbial populations and other natural factors over time to bring about reduction or even elimination of health hazard for humans and animals, natural attenuation might stand for remedy of aquifers and other contaminated sites. To be effective in transformation or degradation of chemicals, microorganisms indigenous to groundwater should be capable of resisting to chemical pollutants, above all. In our laboratory experiments, microorganisms indigenous to an unpolluted deep groundwater aquifer were enriched, and in portions, the microbial biomass obtained was exposed to different organic chemicals in samples of groundwater. The effect of the chemicals on the size of biomass (ATP contents), and metabolic activities (dehydrogenase, and respiratory activity) was measured. The results indicate toxic effects to be predominantly caused by very high concentrations of the chemicals, sometimes even near to the full water saturation capacity. On the other hand, a few chlorophenols, anilines and nitrated aromatic

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 113–127.

hydrocarbons demonstrated a high degree of toxicity at rather low concentrations.

Keywords: Groundwater / chemical contaminants / microbial resistance / natural attenuation

1. Introduction

Groundwater may represent less than 1% of all waters on the Earth but simultaneously it stands for some 90% of fresh water reserves (Stetzenbach et al., 1986; Coates and Aschenbach, 2002). In industrial countries such as USA, Germany, and others about 50%, and over 70% of drinking water, respectively, originate from groundwater resources (Schleyer and Kerndorff, 1992). Usually, deep groundwater aquifers guarantee higher water quality than a bank filtrate or surface water ressources (Ventullo and Larson, 1985; Melioris et al., 1986; Matthess et al., 1988). For this reason, especially in some rural areas, groundwater has been used as a drinking water without any pretreatment. Yet, groundwater is predominantly derived and permanently recharged from atmospheric precipitations and surface water that percolate into the subsurface through differently composed soil layers. The percolates obviously collect widely spread over atmospheric, terrestrial and aquatic environments due to different anthropogenic activities. In addition, accidental contaminations of pristine groundwater aquifers also occur. Thus, a public concern is growing as to the health hazard caused by contaminated groundwater.

In the last years, huge amounts of money have been spent in the EU and USA on remediation of soil and water resources affected by contamination, and different attempts towards bioremediation technologies have been undertaken (Smith et al., 1998; Kasamas et al., 1998; Bardos et al., 2000; Gatchett et al., 2000; Vega et al., 2000). Now, experts recognize that a clean-up of contaminated soil and groundwater by applying sophisticated technologies is hardly achievable at reasonable costs in many areas. Therefore, natural attenuation has been repeatedly considered as an alternative (Tonnaer et al., 1998; Harris et al., 2000; Teutsch and Rügner, 2000; McCarthy and Ellis, 2002; Reible and Demnerova, 2002). In course of long-term natural processes, biodegradation of organics and stabilization of inorganics should provide substantial remedies of contaminated sites. An essential condition for success to be achieved is an adequate resistance of microorganisms autochthonous to groundwater against occasionally high concentration of chemical contaminants, i.e., growth of microorganisms and their enzymatic activities must not be strongly inhibited by pollutants. This is because metabolic active microorganisms are by far the most important agents naturally affecting fate of pollutants in subsurface materials and waters (SCS Engineers, 1979; Filip and Milde, 1988; Hall, 1988). In order to determine microbial resistance to pollutants we tested in laboratory the influence of different organic chemicals, well known as groundwater pollutants, on the growth and metabolic activities of microorganisms obtained from a pristine groundwater aquifer.

2. Material and Methods

2.1. GROUNDWATER SAMPLING

Groundwater was collected from a deep waterworks well (31.8 m) in environs of Eppertshausen (Hesse, Germany). The local aquifer is covered by a thick clay layer (2.3 m), and thus widely protected from anthropogenic contamination. Basically, simple procedures can be used if sampling groundwater for microbiological analyses (Phelps and Fredrickson, 2002). We used a straightforward method by filling clean, sterile glass bottles with groundwater directly from a well tubing. Prior to sampling, however, water was pumped for 3 h to make sure samples to originate from a pristine aquifer. The fresh filled bottles were kept at an ambient temperature (ca. 10°C) and transported to the laboratory without delay.

2.2. ENRICHMENT OF MICROORGANISMS AND INCUBATION CONDITIONS

A PYGV medium (Stanley, 1968) was used which allows growth of a broad spectrum of groundwater bacteria (Hirsch and Rades-Rohkohl, 1983). In portions (250 ml) of a 1:4 diluted sterile medium 250 ml of groundwater was added, and the cultures were incubated for 12 days on a rotary shaker (ca. 100 rpm) at 10°C. After incubation the microbial biomass was separated from the liquid by centrifugation, and freeze dried. Analyses made by courtesy of the Hygiene Institute of the Technical University Berlin (Germany) indicated the presence of *Arthrobacter, Pseudomonas, Flavobacterium*, and *Alcaligenes* species as components of the enriched microbial biomass. For the individual tests fresh PYGV medium in test tubes (4 ml; dilution 1:8) was inoculated with a small portion of the biomass, and the cultures were incubated on a rotary shaker for 7 days at 10°C. Afterwards, the cell density of microbial cultures was adjusted to an extinction value 0.01 at 650 nm, and the incubation of five parallel cultures with chemicals added was continued for 24 h (1 d). In some experiments, the groundwater microorganisms were exposed to selected chemicals for six weeks (42 d). In this case a PYGV medium (1:100) was inoculated with groundwater (25 ml) without any pretreatment, and stationary cultures were incubated in triplicate at 10°C in the dark.

2.3. CHEMICALS UNDER TESTING

Organic chemicals serving as agents affecting microorganisms are listed in Table 1. They were used in four to five different concentrations. In some cases saturated solutions of the individual chemicals were also used (marked with * in the tables).

2.4. MICROBIOLOGICAL AND BIOCHEMICAL ANALYSES

The microbial biomass was estimated as ATP (Adenosinetriphosphate) using a method of Stutz et al. (1986). A Lumac Inc. NRB reagent was used for the ATP extraction, and a Lumac/3M Biocounter M 2010 for the ATP concentration measurements. A method by Liu (1981) was used for the colorimetric estimation of the dehydrogenase activity. Microbial respiration (uptake of oxygen) was measured by a L2-Method according to German Standard Methods of Water Testing (DEV).

Results of all analyses were evaluated statistically using a “t-Test”. For all data presented in the respective tables a value p d” 0.05 was obtained. The Minimum Effect Concentrations, i.e., MEC (1 d) or MEC (42d) values reflect 50 % inhibition (EC_{50}) obtained in the most sensitive test an caused by individual chemicals. Usually, ATP measurement and dehydrogenase activity were most sensitive tests.

TABLE 1. List of potential groundwater contaminants used in tests.

Nonhalogenated Aromatics

Benzene; Toluene; o-Xylene; m-Xylene; p-Xylene; Ethylbenzene; 1,3,5-Trimethylbenzene; Isopropylbenzene; Styrol

Chlorinated or Nitrated Aromatics

Chlorobenzene; 1,2-Dichlorobenzene; 1,3-Dichlorobenzene; 1,4-Dichlorobenzene; 1,2,4-Trichlorobenzene; Hexachlorobenzene; 2-Chlorotoluene; 2,4-Dichlorotoluene; Nitrobenzene; Trinitrotoluene

Chlorinate Aliphatics

Dichloromethane; Trichloromethane; Tetrachloromethane; 1,1,1,-Trichloroethane;

1,1,2-Trichlorotrifluoroethane; 1,2-trans-Dichloroethane; Trichlotoethene; Tetrachloroethene;

1,2-Dichloropropane; 1,3- Dichloropropane; Hexachlorobutadiene; á-Hexachlorocyclohexane;

â-Hexachlorocyclohexane; ã-Hexachlorocyclohexane;

Polycyclic Aromatics

Anthracene; Fluoranthene; Phenanthrene

Anilines

N-Methylaniline; N,N-Dimethylaniline; 2,4-Dimethylaniline

Phenoles

Phenol ; 2,4-Dichlorophenol ; 2,4,5-Trichlorophenol ; Pentachlorophenol

Ethers

Methoxybenzene ; 1,3-Dimethoxybenzene ; Diphenylether ; 1,4-Dioxane

Softeners

n-Dibutylphtalate ; Benzyldibutylphtalate; bis-2-Ethylhexylphtalate; Tributylphosphate

Other Chemicals

Acetone; Atrazine; Ethylparathione; 2-Ethyl-1-Hexanole; Thiophene

3. Results and discussion

3.1. NONHALOGENATED AROMATIC HYDROCARBONS

Nonhalogenated aromatics are relative less stable in the subsurface but accidentally, they appear in elevated concentrations in groundwater; for some of them a cancerogenic potential is well known (Schleyer and Kerndorff, 1992). Table 2 shows MEC values for the respective compounds.

TABLE 2. Effects of nonhalogenated aromatics on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 d)	MEC (42 d)
Benzene	1770	1100[a*]	1000
Toluene	470	n.e.	290
o-Xylene	175	110[a*]	100
m-Xylene	130	81[a*]	
p-Xylene	200	n.e.	
1,3,5-Trimethylbenzene	20	n.e.	
Styrene	280	170[a*]	
Ethylbenzene	140	88[a,b*]	
Isopropylbenzene	50	31[a*]	

a = Value obtained in ATP test; b = Value obtained in dehydrogenase test; n.e. = no effect;
* = see Material and Methods (2.3)

A decrease in toxicity was sometimes related to increasing water solubility of the individual compounds. Ortho-xylene, e.g. inhibited groundwater bacteria at a concentration of 110 ppm while toluene did not show effect. A high concentration of benzene was tolerated in both short-term and long-term tests. Correspondingly, based on modeling the fate and transport of similar compounds (BTEX), Battermann and Meier-Löhr (2000) concluded that a monitored natural attenuation should be considered as a reliable remediation action for containment of a BTEX-plume in the subsurface.

3.2. CHLORINATED OR NITRATED AROMATIC HYDROCARBONS

Basically, chlorinated but nitrated aromatics such as monochlorobenzene, o- or p-dichlorobenzene, 1,2,3-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene, could be degraded by natural consortia of groundwater microorganisms (Riis et al., 2000). In our experiments, 3-nitrotoluene, and especially nitrobenzene showed toxic effects on microbial biomass and dehydrogenase activity already at low concentrations, while for similar effects with chlorinated aromatics concentrations near to full degree of saturation should be used (Table 3).

TABLE 3. Effects of chlorinated or nitrated aromatics on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 d)	MEC (42 d)
Chlorobenzene	500	310[a,b*]	300
1,2-Dichlorobenzene	100	62[a*]	62
1,3-Dichlorobenzene	120	77[a,b*]	
1,4-Dichlorobenzene	49	n.e.	
1,2,4-Trichlorobenzene	36	3[b]	
Hexachlorobenzene	0.006	0.0038[b*]	n.e.
2-Chlorotoluene	47	n.e.	
2,4-Dichlorotoluene	<100	3[a,b]	
Nitrobenzene	1900	10[b]	10
3-Nitrotoluene	500	30[a]	<100

For symbols see Table 1.

3.3. CHLORINATED ALIPHATIC HYDROCARBONS

Chlorinated aliphatic hydrocarbons are common contaminants of groundwater aquifers (Wilson, 1988; Schleyer and Kerndorff, 1992). From data in Table 4 one can recognize that in most cases high concentrations of the individual compounds were required in order to detect an inhibition of groundwater microorganisms under experimental conditions. Both short- and long-term tests delivered similar results.

Biodegradation of aliphatic halogenated hydrocarbons usually requires dechlorination under anaerobic conditions which is followed by an oxidative destruction of the residual metabolites. Indications exist that natural attenuation in aerated aquifers is not sufficiently effective to prevent these pollutants from spreading in the subsurface (Holmes et al., 1998; Bosma et al., 1998).

3.4. POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) represent an important group of hydrophobic organic contaminants especially in industrially polluted soils

TABLE 4. Effects of chlorinated aliphatic hydrocarbons on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 d)	MEC (42 d)
Dichloromethane	16000	3000[a]	
Trichloromethane	9000	300[a]	1000
Tetrachloromethane	800	500[a,b*]	
1,1,1-Trichloroethane	500	310[a*]	
1,1,2-Trichlorotrifluoroethane	170	n.e.	n.e.
1,2-trans-Dichloroethene	600	370[a,b*]	n.e.
Trichloroethene	1100	300[a]	300
Tetrachloroethene	150	94[a,b*]	94
1,2-Dichloropropane	2700	1700[a*]	
1,3-Dichloropropene	2700	100[a]	100
Hexachlorobutadien	2	1[b]	
α-Hexachlorocyclohexane	1.4	n.e.	
β-Hexachlorocyclohexane	0.24	0.15[b*]	
γ-Hexachlorocyclohexane	1.9	n.e.	

For symbols see Table 1.

but because of their low water solubility and hydrogeochemical mobility they do not play important role as groundwater contaminants (Schleyer and Kerndorff, 1992; MacLeod and Semple, 2000). In our experiments saturated solutions of anthracene, fluoranthene and phenanthrene did not affect the biomass, i.e., ATP concentration of groundwater microorganisms, and the activity of dehydrogenase was slightly decreased only in samples contaminated with anthracene. Thus, it was redundant to present individual experimental results in a table. In soil samples contaminated with PAHs and heavy metals (Me), Maliszewska-Kordybach and Smreczak (2000) established a significant decrease of dehydrogenase activity in the order: control>PAHs>Me>PAHsMe.

3.5. ANILINES AND PHENOLS

Data in Table 5 show that some anilines exerted toxic effects on groundwater microorganisms already by concentration as low as 1% of a full saturation. Even more, trichlorophenol and pentachlorophenol exhibited in a short-term test the strongest toxicity of all chemicals under testing.

TABLE 5. Effects of anilines and phenols on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 d)	MEC (42d)
N-Methylanline	30000	300[a]	<30
N,N-Dimethylaniline	1000	620[a,b*]	620
2,4-Dimethylaniline	1000	100[a,b]	
Phenol	82000	30[a]	
2,4-Dichlorophenol	4500	10[b]	
2,4,5-Trichlorophenol	2000	0.3[a]	>3
Pentachlorophenol	2000	0.3[b]	3

For symbols see Table 1.

However, results obtained in long-term test (42 d) indicate that in course of time, adaptation of microorganisms to elevated concentration of phenols may occur. Safronov et al. (2000) were able to enrich a microbial assemblage from wastewater that could be adapted to 2-3 g l^{-1} of phenol.

3.6. ETHERS

As shown in Table 6, methoxybenzenes exerted toxic effects on groundwater microorganisms at concentrations between 100 – 300 ppm. The toxicity of diphenylether was measured at concentration near to the point of total solubility. A water miscible dioxane exerted toxic effects at concentrations of 3 % and 1% in short-term and long-term tests, respectively.

TABLE 6. Effects of ethers on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 d)	MEC (42 d)
Methoxybenzene	1500	300[a]	
1,3-Dimethoxybenzene	800	100[a]	
Diphenylether	21	13[a]	
1,4-Dioxane	miscible	30000[a]	>10000

For symbols see Table 1.

3.7. SOFTENERS AND OTHER CHEMICALS

In short-time tests, softeners (see Table 1) did not exert any inhibition effects on groundwater microorganisms. In a long-term test tributylphosphate in a concentration of 100 ppm caused a 30% decrease in microbial biomass (ATP). These results are not presented in a table.

From other chemicals under testing, a high concentration of acetone (10 %) was needed to obtain a strong decrease in biomass and dehydrogenase activity. Different pesticides inhibited groundwater microorganisms only at concentrations near to a full saturation (Table 7).

TABLE 7. Effects of some other chemicals on groundwater microorganisms (values in ppm).

Compound	Solubility	MEC (1 d)	MEC (42 d)
Acetone	miscible	10000[a]	
Atrazine	30	n.e.	
2-Ethyl-1-hexanole	1000	620[a,b]	620
Ethyl-parathione	2.4	n.e.	
Thiophene	3600	1000[b]	

For symbols see Table 1.

Using a respiratory test five chemicals recognized as common groundwater contaminants, e.g., by Milde and Kerndorff (1987), were also tested in mixtures for possible effect on groundwater microorganisms. The following concentrations were used: Dichloromethane 660 ppm; Trichloromethane 300 ppm; Tetrachloromethane 30 ppm; Tetrachloroethene 5ppm; 1,2,4-Tchlorobenzene 1.3 ppm. No significant inhibition of the microbial respiration activity was observed in these experiments.

In the absence of acute environmental risk, natural attenuation might represent a cost-effective alternative for the bioremediation of contaminated groundwater aquifers. However, this type of remediation strategy requires the identification and quantification of different natural mechanisms and limits. Hollender et al. (2000) performed microcosm studies, and in inhibition tests they used *Daphnia magna* which, however, may not represent groundwater organisms. In our experiments a mixed population of autochthonous groundwater microorganisms was used and our experimental conditions such as nutrient level and temperature might rather correspond with those usually existing in the subsurface. On the other hand, we applied chemicals in higher concentrations than those usually found in contaminated groundwater aquifers (Milde and Kerndorff, 1987; Schleyer and Kerndorff, 1992), i.e., a worst case situation was simulated in our experiments. In despite of this, groundwater microorganisms demonstrated a high degree of resistance against majority of the chemicals used. Even most effective chemicals such as chlorophenols, nitrated aromatic hydrocarbons, and anilines had to be used in rather high concentrations to achieve a significant inhibition of microbial biomass and activity.

4. Conclusions

Natural attenuation in a contaminated site is affected by a complex of environmental factors. Thus, a comprehensive examination of the chemical, physical, biological, and hydrogeological conditions on site should be made before making final decision for applying or not of this type of remediation. Our results indicate that even high concentration of different chemicals need not necessarily prevent natural attenuation to control and eventually remediate groundwater contaminated by chemical pollutants.

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6. References

Bardos, R.P., Mariotti, C., Marot, F. and Sullivan, T., 2000 Decision support for contaminated land in Europe and North America (Output from CLARINET and

NATO/CCMS pilot study on remedial action technologies for contaminated soil and groundwater. In: *Contaminated Soil 2000,* Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 337-344.

Battermann, G. and Meier-Löhr, M., 2000 Modeling and evaluation of natural attenuation at a JP4 contaminated site. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 2, Thomas Telford Publ., London, pp. 761-762.

Bosma, N.P., van Aalst-van Leuven, M.A., Gerritse, J. And van Heiningen, E. 1998 Intrinsic dechlorination of 1,2-dichloroethane at an industrial site. In: *Contaminated Soil ´98*, Proc. 6th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 197-202.

Coates, J.D. and Achenbach, L.A. 2002 The biogeochemistry of aquifer systems. In: *Manual of Environmental Microbiology*, 2nd Edition, Ch.J. Hurst (Ed. in Chief), ASM Press Washington, D.C., pp. 719-727.

DEV - *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung*. 4. Lieferung (1966), Verlag Chemie, Weinheim/Bergstrasse.

Filip, Z. and Milde, G. 1988 Biotechnologische Prinzipien und Umwelthygienische Aspekte von In Situ-Sanierungsmaßnahmen im Boden- und Grundwasserbereich. In: *Biotechnologische In-situ-Sanierung kontaminierter Standorte,* Z. Filip (Hrsg.), Schr.-Reihe Verein WaBoLu 80, Gustav Fischer Verlag, Stuttgart, pp. 11-37.

Gatchett, A., Rabelt, V., Steffens, K., Argus, R. 2000 United States/Germany technical bilateral agreement: Past, present & future. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 587-590.

Hall, C.V. 1988 Research for ground-water quality management with an emphasis on in situ biorestoration. In:

Biotechnologische In-situ-Sanierung kontaminierter Standorte, Z. Filip (Hrsg.), Schr.-Reihe Verein WaBoLu 80, Gustav Fischer Verlag, Stuttgart, pp. 261-271.

Harris, B., Smith, J., Finnamore, J., Carey, M., Morrey, M. and Marsland, T. 2000 Adopting monitored natural attenuation as an option for the remediation of polluted groundwater in the UK. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 474-477.

Hirsch, P. and Rades-Rohkohl, E. 1983 Microbial diversity in a groundwater aquifer in Northern Germany. *Dev. Int. Microbiol.* 24 : 183-200.

Hollender, J., Althof, K., Mundt, M. and Dott, W. 2000 Microcosm studies to assess the potential for natural attenuation. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 2, Thomas Telford Publ., London, pp. 713-719.

Holmes, M.W., Morgan, P., Klecka, G.M., Klier, N.J., West, R.J., Davies, J.W., Ellis, D.E., Lutz, E.J., Odam, J.M., Ei, T.A., Chapelle, F.H., Major, D.W., Salvo, J.J. and Bell, M.J. 1998 The natural attenuation of chlorinated ethenes at Dover Air Force Base, Delaware, USA. In: *Contaminated Soil ´98*, Proc. 6th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 143-152.

Kasamas, H., Franzius, V. and Ferguson, C. 1998 Concerted action on risk assessment for contaminated sites in the European Union – CARACAS. In: *Contaminated Soil ´98*, Proc. 6th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 19-24.

Liu, D. 1981 A rapid biochemical test for measuring chemical toxicity. *Bull. Environ. Contam. Toxicol.* 26 : 145-149.

MacLeod, C.J.A. and Semple, K.T. 2000 A comparison of single and multiple addition of pyrene on soil microbial processes. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 2, Thomas Telford Publ., London, pp. 807-810.

Maliszewska-Kordybach, B. and Smreczak, B. 2000 Synergistic effect of polycyklic aromatic hydrocarbons (PAHs) and heavy metals on soil enzymatic activity. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 2, Thomas Telford Publ., London, pp. 908-909.

Matthess, G., Pegdeger, A. and Schroeter, J. 1988 Persistence and transport of bacteria and viruses in groundwater – a conceptual evaluation. *J. Contam. Hydrol.* 2: 171-188.

McCarty, P.L. and Ellis, D.E. 2002 Natural attenuation. In: *Innovative Approaches to the On-Site Assessment and Remediation of Contaminated Sites*, D. Reible and K. Demnerova (Eds.), Kluwer Acad. Publ., Dordrecht, pp. 141-181.

Melioris, L., Mucha, I. And Pospisil, P. 1986 *Groundwater – Research and Investigation Methods*. ALFA Bratislava / SNTL Praha, 429 pp. (in Slovak).

Milde, G. and Kerndorff, H. 1987 Die Altlasten und das Grundwasser. *Entsorgungspraxis* 12/1987: 598-604.

Phelps, T.J. and Fredrickson, J.L. 2002 Drilling, coring, and sampling subsurface environments. In: *Manual of Environmental Microbiology*, 2nd Edition, Ch.J. Hurst (Ed. in Chief), ASM Press, Washington, D.C., pp. 679-695.

Reible, D. and Demnerova, K. 2002 Introduction. In: *Innovative Approaches to the On-Site Assessment and Remediation of Contaminated Sites*, D. Reible and K. Demnerova (Eds.), Kluwer Acad. Publ., Dordrecht, pp. xxxi-xxxii.

Riis, V., Simon, D. and Babel, W. 2000 degradation potential of the autochthonous microorganisms in the groundwater of a waste dump for organo-chlorines. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. nn Contaminated Soil, Vol. 2, Thomas Telford Publ., London, pp. 789-790.

Safronov, V., Bagrova, Ch. And Kouznetsov, Y. 2000 High intensive low-waste and low-discharge microbiological system of phenol destruction. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 2, Thomas Telford Publ., London, pp. 1483-1484.

Schleyer, R. and Kerndorff, H. 1992 *Die Grundwasserqualität westdeutscher Trinkwasserressources.* VCH Verlag, Weinheim, 249 pp.

SCS Engineers 1979 *Selected Biodegradation Techniques for Treatment and/or Ultimate Disposal of Organic Materials.* US EPA-600/2-79-006, Cincinnati, Ohio, 358 pp.

Smith, M.A, James; S.C. and Kovalick, W.W. 1998 Comparative international study of soil and groundwater remediation technologies. In: *Contaminated Soil ´98*, Proc. 6th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 9-18.

Stanley, J.T. 1968 Prosthecomicrobium and Ancalomicrobium, new prosthecate freshwater bacteria. *J. Bacteriol.* 95: 1921-1942.

Stetzenbach, L.D., Kelley, L.M. and Sinclair, N.A. 1986 Isolation, identificaton, and growth of well-water bacteria. *Ground Water* 24: 6-10.

Stutz, W.G., Leki, G. and Lopez-Pila, J.M. 1986 Die ATP-Konzentration von Trinkwasser im Vergleich zur Koloniezahl. *Zbl. Bakt. Hyg.* B 182: 421-429.

Teutsch, G. and Rügner, H. 2000 Natural attenuation as a remediation approach. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 468-473.

Tonnaer, H., Otten, A., Alphenaar, A., and Roovers, C. 1998 Natural attenuation: A basis for developing extensive remediation concepts. In: *Contaminated Soil ´98*, Proc. 6th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 191-196.

Vega, A., Argus, R., Heuel-Fabianek, B. and Siebert, J. 2000 Evaluating treatment technologies – QA approaches in the USA and Germany. In: *Contaminated Soil 2000*, Proc. 7th Int. FZK/TNO Conf. on Contaminated Soil, Vol. 1, Thomas Telford Publ., London, pp. 571-574.

Ventullo, R.M. and Larson, R.J. 1985 Microbial diversity and activity of heterotrophic bacteria in ground water. *Environ. Toxicol. Chem.* 4 : 759-771.

Wilson, J. 1988 Some critical points of the microbial restoration of underground sites polluted by the volatile chlorinated hydrocarbons. In: *Biotechnologische In-situ-Sanierung kontaminierter Standorte,* Z. Filip (Hrsg.), Schr.-Reihe Verein WaBoLu 80, Gustav Fischer Verlag, Stuttgart, pp. 367-377.

SPECIFIC BIOLOGICAL THREATS IN WESTERN MEDITERRANEAN REGION

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Abstract

This paper relates the occurrences of Harmful Algae Blooms episodes in Western Mediterranean countries. This phenomenon appears to have increased in frequency, intensity and geographic distribution. The impacts of such events have reached whole countries maritime borderers' in this region, by the proliferation of numerous harmful algae species producing various type of marine biotoxins and probably the azaspiracid (AZP) that start to make one's appearance in Ireland the last few years.

Keywords: Western Mediterranean countries/ Harmful Algae Blooms/ marine biotoxins/

1. Introduction

Proliferations of microalgae in marine and brackish waters can cause different kinds of effects that are perceived as harmful from the human point view. Such events could entrained massive fish kills, contaminate seafood with toxins, and deteriorate enclosed ecosystems in the world posing a threat to human health, exports of shellfish, development of aquaculture practices, and tourist exploitations.

The reported world–wide increase in biological threat has also involved the western Mediterranean sea, where there have been numerous blooms of harmful algae during the last decades. Toxicity caused by the accumulation

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of algal toxins in marine organisms caused important socio-economic problems due to the harvesting ban in the affected areas. Indeed the harmful algae are a completely natural phenomena, four explanations has been suggested for this apparent increase devolves upon a scientific awareness of toxic species, stimulation of plankton blooms by cultural eutrophication and/ or unusual climatic conditions, geographical dispersion due to the transport of cyst in ballast water or to movement of molluscs stock from an area to another or a development of aquaculture in coastal water (Hallegraeff, 1995).

The phytoplankton strains of *Alxandrium*, *Dinophysis*, *Gymnodinium, linguidinium* are supposed to be the principal toxins producers in the western Mediterranean region. Due to the recurrent bloom of those harmful species, almost all countries have established the monitoring networks for early warning at the time of the apparition of this phenomenon. The proliferation of the later species, always accompanied with the detection of toxins level surpassing the safety threshold, lead to the ban of marine organism harvesting for a long time causing substantial economic losses.

2. Paralytic shellfish poisoning producers species (PSP)

Numerous species of toxic dinoflagellates, namely *Gymnodinium catenatum* and various genus of *Alexandrium*, that produce “Paralytic Shellfish Poisoning” (PSP) toxins, are well widespread in western Mediterranean region.

Gymnodinium catenatum is a naked chain-forming dinoflagellate causing Paralytic Shellfish Poisoning (PSP) event in western Mediterranean Sea. The occurrence of *G.catenatum* in the region has been reported from the South coast of Iberian Peninsula, from Malaga waters in southern Spain and from Fusaro Lagoon In southern Italy (Franca and Almeida, 1989; Bravo et al., 1990; Fraga, 1996) the north side of Morocco and seems to be related with Atlantic surface water flowing into the Mediterranean through the Gibraltar strait (Fraga et al., 1988, Tahri, 1998; Taleb et al., 1998, 2001). This dinoflagellatedd is widespread from the Alboran Sea, the body of water shared by Morocco and Southeast Spain, to Algerian basin and Sardinia channel (Gomez and Claustre, 2001). In 1994 an enormous bloom of this species has occurred at a large scale reaching the northern Atlantic from Cape Finisterre (Galicia, Spain) until the Essaouira, in Morocco (Taleb et al., 2003). This phenomenon was fatal particularly in Morocco where four persons died and almost seventy persons hospitalised after shellfish consumption.

Alexandrium strains are the toxic species most widespread in the western Mediterranean Sea. Four species of *Alexandrium* have been frequently cited as responsible for PSP toxic incidence in this region, namely *A. minutum*, *A. catenella, A. lusitanicum* and *A. tamarense*.

A. minutum is the most widespread toxic microalgae in the Western Mediterranean region. This strain is one of the main agents of PSP outbreaks and water discolorations. The last decade, recurrent blooms of this organism have been described causing in this region the substantial economic loses. This dinoflagellate has been identified in Galician waters as well as in the harbour of Palma de Mallorca and Arenys de Mar harbours in Mediterranean waters of in Spain (Forteza et al., 1998; Garcés et al., 1998) in the north Adriatic Sea (Honsell, 1993; Cabrini et al., 1996) and in Morocco (Tahri, 1998; Taleb et al., 2003).

A. catenella is widely distributed in cold temperate waters. This dinoflagellate was first detected in Barcelona harbour in 1996. Since then, there has been growing and evidence of an increase in abundance and extension in the close coastal waters. In late spring 1998, the first toxic event was described in Catalonia (NE Spain), not only in harbours but also in open sea waters (Vila et al., 2000) and in Thau Lagoon at the French Mediterranean coast (Laâbir et al., 2002).

A. lusitanicum has been identified in the north Mediterranean coasts of Portugal (Franca and Almeida, 1989), Spain (Franco et al., 1995) and Italy (Cabrini et al., 2000) but never in the southern side. Its proliferation seemed to be restricted to the cold temperate waters.

A. tamarense: The identification of this species has been confirmed in North Adriatic Sea (Cabrini et al., 2000) and the Thau lagoon of France Mediterranean coast (Lassus et al., 1999). Whereas, its presence is suspected in Nador lagoon in Morocco, following an obtained characteristic PSP toxin profile in mussel (Taleb et al., 2004).

3. Diarrheic shellfish poisoning producers (DSP)

Dinophysis is one of the largest genera of dinoflagellates with more than 200 species described responsible for outbreaks of DSP worldwide. Various Genus of this dinoflagellate such as *D. acuminata, D. sacculus, D. caudata and D. fortii D. acuta, D. tripos* cause troubles in all European countries of western Mediterranean Sea, namely Spain (Bravo, 1995; Mariòo et al., 1998; Delgado et al., 1996), Portugal (Palma et al., 1998); French (Marcaillou-Le Baut and Masselin, 1990) and Italy (Draisci et al., 1998). Although there is little information from the opposite side, some or all those strains of *Dinophysis* are most likely to be responsible for the presence of DSP toxins detected in the shellfish beds of Northern Africa.

Lingulodinium polyedrum is responsible for recurrent blooms in north Adriatic Sea (Tubaro et al., 1998) and Portugal (Amorim et al., 2000). Its apparition has never been confirmed in the Mediterranean side of North Africa countries, but has been involved in recent blooms at a large scale covering the Atlantic shore of Morocco (Taleb and Hummert, 2000).

4. Amnesic shellfish poisoning producers

Amnesic shellfish poisoning (ASP) is caused by diatom species of genus *Pseudo-nitzschia*. At least eight species of diatom genus of *Pseudo-nitzschia* were reported, but only three are involving in the production of DA and derivatives (Bates et al., 1998).

Since the first report of the mortal incidence caused by ASP toxins in Canada in 1987 (Bates et al., 1989), their presence has been confirmed in Western Mediterranean countries including Spain (Miguez et al., 1996), Portugal (Vale and Sampayo, 2002), France (Le Doux et al., 1996), Italy and Morocco (Taleb, no published data). However, the levels detected were very low and never reached the safety threshold.

5. References

Amorim, A., Palma, A.S., Sampayo, M.A., Moita, M.T., 2000. On a *Lingulodinium polyedrum* bloom in Setúbal bay, Portugal. In: Hallegraeff, G.M., Blackburn, S.I., Bolch, C.J., Lewis, R.J. (eds.), H A.B. 2000. IOC of UNESCO, pp.22-25.

Bates, S.S., Garrison, D.L., Horner, R.A., 1998. Bloom dynamics and physiology of domoiacid-producing *Pseudo-nitzschia* species. In NATO AS1 Series**,** G 41, pp. 267-292.

Bates, S.S., Bird, C.J., deFreitas, A.S.W., Foxall, R., Gilgan, M., Hanic, L.A., Johnson, G.R. McCulloch, A.W., Odense, P., Pocklington, R., Quilliam, M.A., Sim, P.G., Smith, J.C., Subba Rao, D.V., Todd, E.C.D., Walter, J.A. and Wright, J.L.C. 1989. Pennate diatom *Nitzschia pungens* as the primary source of domoic acid, a toxin in shellfish from eastern Prince Edward Island, Canada. *Can. J. Fish. Aquat. Sci.* 46:1203-1215.

Bravo, I., Reguera, B., Fraga, S., 1995. Description of different morphotypes of *Dinophysis acuminate* complex in the Galician Rias Baixas in 1991. In Harmful Marine Algae Blooms, Lassus, P., Arzul, G., Erand, E., Gentien, P., and Marcaillou-Le-Baut, eds. (Lavoisier, Paris), pp. 21-26.

Bravo, I., Reguera, B., Martinez, A. Fraga, S., 1990. First report of *Gymnodinium catenatum* on the Spanish Mediterranean coast. In: Graneli, E., Sundstrom, B., Edler, L. and Anderson, D.M. (Eds.), *Toxic Marine Phytoplankton.* Elsevier, New York, pp. 449-452.

Cabrini M., Cok S., Pecchiar I., Beran A., Predonzani S., 2000. *Alexandrium* distribution and toxicity in the Gulf of Trieste (Northern Adriatic Sea). In: Hallegraeff, G.M., Blackburn, S.I., Bolch, C.J., Lewis, R.J.(eds.), HAB 2000. IOC - UNESCO, pp.22-25.

Cabrini M., Chiurco R., Cok S., Martecchini E., Pecchiar I., Ganis P., 1996. The occurence of *Alexandrium* spp. Along the Northern Adriatic coasts. In: Yasumoto, T., Oshima, Y. and Fukuyo, Y.(eds) Harmful and Toxic Algal Blooms. I.O.C. of UNESCO, pp.81-84.

Delgado, M., Garcés, E., Camp, J. 1996. Growth and behaviour of *Dinophysis sacculus* from NW Mediterranean. In: Yasumoto, T., Oshima, Y. and Fukuyo, Y. (eds.), *Harmful and Toxic Algal Blooms*. I.O.C. of UNESCO, pp.261-264.

Draisci, R., Lucentini, L., Giannetti, L., Marchiafava, C., James, K.J. and Kelly, S.S. 1998. Diarrhoeic shellfish toxin profiles in phytoplankton and mussels from Italy and Ireland as determined by LC-MS and LC-MS-MS. In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T.(eds.) Harmful Algae. Xunta de Galicia and IOC-UNESCO, Spain, pp.495-498.

Forteza V., Quetglas G., Delgado M., Reyero M.I., Fraga S., Franco J.M, Cacho E., 1998. Toxic *Alexandrium minutum* bloom in Palma de Mallorca harbour, (Balearic Islands, Western Mediterranean). In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T.(eds.) Harmful Algae. Xunta de Galicia and IOC-UNESCO, Spain, pp.58-59.

Fraga, S., 1996. Wintering of *Gymnodinium catenatum* Graham in Iberian waters. In: Yasumoto, T., Oshima, Y. and Fukuyo, Y. (eds), *Harmful and Toxic Algal Blooms*. I.O.C. - UNESCO, pp. 211-214.

Fraga, S., D.M. Anderson, I. Bravo, B. Reguera, K.A. Steidinger, C.M. Yentsch., 1988. Influence of upwelling relaxation on dinoflagellates and shellfish toxicity in Ria de Vigo, Spain. *Estuar. Coast. Shelf Sci*., 27: 349-361.

Franca, S., Almeida. J. F. 1989. Red tides: Biology, Environmental Science, and Toxicology.

Okaichi, T., Anderson, D.M., Nemoto. T.(eds). Elsevier Science Publishing. pp. 93-96.

Franco, J.M., Fraga, S., Zapata, M., Bravo, I., Fernandez, P. and Ramilo, I. 1995. in: Harmful Marine Algae Blooms, Lassus, P., Arzul, G., Erand, E., Gentien, P., and Marcaillou-Le-Baut (eds.) (Lavoisier, Paris), pp.53-58.

Garcés, E., Delgado, M., Vila, M. and Camp, J. 1998. An A*lexandrium minutum* bloom: *Isitu* growth or accumulation? In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T. (eds.) Harmful Algae. Xunta de Galicia and IOC of UNESCO, Spain, pp.167-170.

Gomez F., Claustre H., 2001. Spreading of *Gymnodinium catenatum* Graham in the western Mediterranean Sea. *Harmful Algae News*, 22, 1-2.

Hallegraeff G.M. 1995. Harmful algal blooms: A global overview. In: Hallegraeff, G.M., Anderson, D.M., Cembella, A.D. (eds.), Manual on Harmful Marine Microalgae. IOC Manuels and Guides N°33. UNESCO, pp.1-22.

Honsell, G., in: 1993. Smayda, T.J. and Shimizu, Y.(eds.), Toxic Phytoplancton Blooms in the Sea, Elsevier, Amsterdam, pp. 77-80.

Laabir, M., Génovési-Giunti, N., Barré, N., Vaquer, A., Collos, Y., Erard Le Denn, E., Pons, V., Bident, B. 2002. The resting cyst of the red-tide dinoflagellate *Alexandrium catenella* (Dinophycea) from Thau Lagoon (Western French Mediterranean coast).X HAB 2002 proceeding (in press).

Lassus, P., Abadie E., Amzil, Z., Belin, C., Comps, M.A., Elzière-Papayanni. P., Le Bec M., Marcaillou-Le Baut C., Nézan E., Poggi R., 1999. Contamination de l'étang de Thau par *Alexandrium Tamarense.* Bilans et prospectives, Ed. Ifremer, 44p.

Le Doux, M., Belin, C., Lotfi, Y., Lassus, P., Fremy, J.M. 1996. Domoic acid: state of contamination of shellfish in France. Preliminary study. In: Yasumoto, T., Oshima, Y., Fukuyo, Y. (eds) *Harmful and Toxic Algal Blooms*. I.O.C. - UNESCO, pp.135-137.

Marcaillou-Le Baut, C., Massellin P., 1990. Recent data on Diarrhetic Shellfish Poisoning in France. In: Toxic Marine Phytoplancton, Graneli, E., Sundstrom, B., Edler, L. and Anderson, D.M., eds. (Elsevier, New York), pp. 487-492.

Mariòo, J., Maneiro, J. and Blanco, J. 1998. The harmful algae monitoring programme of Galicia: Good value for money. In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T. (eds.) Harmful Algae. Xunta de Galicia and IOC - UNESCO, Spain, pp.229-232.

Miguez, A., Fernández, M.L., Fraga, S., 1996. First detection of domoic acid in Galicia (NW of Spain). In: Yasumoto, T., Oshima, Y. and Fukuyo, Y. (Eds.), Harmful and Toxic Algal Blooms. I.O.C. - UNESCO, pp.143-145.

Palma, A.S., Vilarinho, M.G., Moita, M.T. 1998. Interannual trends in the longshore Distribution of *Dinophysis* off the Portuguese coast. In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T. (eds.) Harmful Algae. Xunta de Galicia and IOC of UNESCO, Spain, pp.124-127.

Tahri, J.L., 1998. *Gymnodinium catenatum* Graham blooms on Morocccan waters. In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T. (Eds.), *Harmful Algae*. Xunta de Galicia and IOC of UNESCO, Spain, pp. 66-67.

Taleb H., Reqia Sagou, Rachid Amanhir, 2004. Decontamination rates of PSP toxins in mussel (*Mytilus galoprovinciallis*) and oyster (*Crassostrea gigas*). Procedding of the 5th Int. Conf. on Molluscan Shellfish Safety", June, Galway, Irlande (in press).

Taleb H., Vale P., Blaghen M., 2003. Spatial and temporal evolution of PSP toxins along the Atlantic shore of Morocco. *Toxicon*, 41 : 199-205.

Taleb, H., Vale, P., Jaime, E., Blaghen, M., 2001. Study of paralytic shellfish poisoning toxin profile in shellfish from the Mediterranean shore of Morocco. *Toxicon*, 39 (12), 1855-1861.

Taleb H., Hummert C., 2000. Okadaïc Acid and dinophysistoxin-2 in Morocco. Abstracts of 9th Inter. Conf. on Harmful Algae Bloom, Tasmania.

Taleb, H., Idrissi, H., Blaghen, M., 1998. Seasonality of PSP toxicity in shellfish from the Atlantic and Mediterranean coasts of Morocco. In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T. (eds.) Harmful Algae. Xunta de Galicia and IOC of UNESCO, Spain, pp. 68-69.

Tubaro, A., Sidari, L., Loggia, R.D., Yasumoto, T. 1998. Occurrence of yessotoxin-like toxins in phytoplancton and mussels from Northern Adriatic Sea. In: Reguera, B., Blanco, J., Fernández, M.L., Wyatt, T. (Eds.), *Harmful Algae*. Xunta de Galicia and IOC of UNESCO, Spain, pp. 470-472.

Vale, P. and Sampayo, M.A.M., 2002. Evaluation of extraction methods for domoic acid analysis in naturally contaminated shellfish from Portugal. *Harmful Algae*, 19: 1-9.

Vale P., Sampayo M.A.M., 1996. DTX-2 in Potuguese bivalve. In : In: Yasumoto, T., Oshima, Y. and Fukuyo, Y. (Eds), Harmful and Toxic Algal Blooms. IOC of UNESCO, Paris, pp. 539-542.

Vila M., Delgado M., Camp J., 2000. First detection of widespread toxic events caused by *Alexandrium catenella* in the Mediterranean Sea. In: Hallegraeff, G.M., Blackburn, S.I., Bolch, C.J., Lewis, R.J. (eds.) HAB 2000. IOC of UNESCO, pp. 8-11.

IS ENVIRONMENTAL POLLUTION WITH POLYCHLORINATED BIPHENYLS A PROBLEM FOR BULGARIA

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Abstract

Analysis of the pollution sources and levels of polychlorinated biphenyls (PCBs) in Bulgaria and other countries is performed. Acceptable limits in different media are compared with the existing levels. At present PCBs are a problem more as by-products of different combustion processes. The need for additional studies is underlined concerning the environmental and health long term effects.

Key words: polychlorinated biphenils /PCBs/ limits/pollution sources/ levels/cancer/aquatic life.

1. Introduction

Polychlorinated biphenyls (PCBs) are one of the groups of persistent organic compounds (POPs) identified by the UNEP Coverning Council Decision 19/13 adopted in February 1997. The following factors are of primary interest for the classification: persistence in water, soil and sediments, bioaccumulation, toxicity, volatility, long-rang transport and bioavailability

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 137–150.

(Maelstrom 2000). The group of PCBs incorporates a class of synthetic organic compounds used for more than 50 years as additives to oils in electric equipment, as dielectric fluids – transformers, capacitors in hydraulic machines and in other apparatuses as heat carriers where chemical stability is required in view of safety and durability. Besides that they are input in paints and inks as solvents, they are applied in pesticide and herbicide production, in plastics production as plastificators, etc. PCBs have some 60 trade names of which arochlor, clofen, canechlor, santovak, phenochlor, pyranol, inertin, sibanol, pyralen, sovol, sovtol, delor are the most popular. In 1991 the global production of PCBs amounts up to 1.5 thousand tons (Kurlyandski 1998). PCBs have been applied in almost all countries and in a number of fields. This is due to their specific properties, namely chemical inertness and resistance to heating and environmental factors. The above properties place PCBs among the most popular environmental pollutants. They are listed in UNEP list of persistent organic pollutants (POPs) which have to be globally banned.

2. Basic data

The common formula of PCBs is C12H(10-n)Cln, where the number of chlorine atoms varies from 1 to 10. This chemical class includes two benzene nuclei bound together and chlorinated to a different extent.

Thus it is theoretically possible to have 209 individual, yet similar compounds. The trade product contains usually 50 to 130 compounds. Barro et al. (2004) identified PCB's using combination of sorbent enrichment and ultrasound-assisted solvent extraction has been used to determine polychlorinated biphenyls in air. Analytes were sampled by pumping a known volume of air through a porous polymer (Tenax TA). The enriched adsorbent was transferred into a glass vial, and ultrasound-assisted extraction of the analytes was then performed in n-hexane. Quantification was carried out by using gas chromatography coupled to tandem mass spectrometry. Breakthrough volume of the sampling step was studied, indicating that 10 cubic meters of air could be processed without losses of the most volatile compounds. Good recoveries (75-96%) were obtained, and limits of detection at the sub ng/ cubic meter were achieved for all the analytes. The proposed method is very simple and fast, avoiding the use of large solvent volumes and time-consuming preconcentration steps. PCBs are fire-resistant, with low conductivity and high resistance to heating to 1500ºC. Some of them are chemically inert and resistant to oxidizers and other chemical compounds.

They are water insoluble but easily soluble in fats. These positive technological properties make them extremely hazardous for environment and human health as they accumulate in the environment and disseminate through water and air with the dust, and they also cumulate in the adipose tissue of humans and animals (Fiedler 1997). The acute lethal *per os* dose of PCBs is 1 to 11 g/kg depending on their composition. They also penetrate through the skin and the respiratory ways. PCBs cumulate in the organism.

Their effect on humans can be acute at high exposure, expressed in skin and mucous membranes irritations, liver and immune disturbances, and nervous symptoms. The chronic effects are more hazardous. They are characterized by disturbed reproduction and fetus development, and malignant neoplasms.

3. New data on mechanism of action and health effects

3.1. ENVIRONMENTAL BEHAVIOR AND MECHANISM OF ACTION

The microbial degradation of polychlorinated biphenyls (PCBs) has been extensively studied in recent years Pieper (2004) The genetic organization of biphenyl catabolic genes has been elucidated in various groups of microorganisms, their structures have been analyzed with respect to their evolutionary relationships, and new information on mobile elements has become available. Key enzymes, specifically biphenyl 2,3-dioxygenases, have been intensively characterized, structure/sequence relationships have been determined and enzymes optimized for PCB transformation. However, due to the complex metabolic network responsible for PCBs degradation, optimizing degradation by single bacterial species is necessarily limited. Hydroxylated PCBs appear to bind with higher selectivity to transthyretin relative to other serum proteins and in so doing inhibit amyloid fibril formation. (Van Vranken 2004). The results of Madia et al (2004) suggest that PBDE-99 and Aroclor 1254 exert differential cytotoxic effects on human astroglial cells.

3.1.1. Endocrine disruption

Arulmozhiraja et al. (2004) studied the estrogenic and thyroid activities of PCBs. Ninty one monohydroxylated PCBs were measured with two-hybrid assays using yeast cells containing the human estrogen receptor ERalpha or human thyroid receptor TRalpha. Estrogenic activity of 30 of the 91 compounds, including all compounds active in the yeast two-hybrid assay, were also measured by a reporter gene assay employing Chinese hamster ovary cells. Haraguchi (2004) study was performed to compare the metabolite profiles of polychlorinated biphenyls (PCB's) in the liver and serum of rats, hamsters and guinea pigs after exposure to a PCB mixture, Kanechlor 500 (100 mg/kg, ip). The percentage contribution of major PCB residues in the liver five days after exposure indicated that non-planar PCBs with 2,4- or 2,3,4-chlorine substitution were more abundant in the liver in the order: rats (43% of total PCBs) > hamsters (20%) > guinea pigs (11%), whereas coplanar PCB's with 4-, 3,4- or 3,4,5-chlorine substitution were predominant in guinea pigs (61%), followed by hamsters and rats (both 26%). The hepatic concentrations of methylsulfonyl metabolites (MeSO2-CBs) were higher in the order: guinea pigs > rats > hamsters. Mi and Zhang (2005) studied the toxic and hormonal effects of polychlorinated biphenyls on cultured testicular germ cells of embryonic chickens. The results indicated that A1254 exposure imposed both toxic and hormonal effects on embryonic testicular germ cell proliferation, which may cause reproductive disorder and even infertility at adulthood.

3.2. PCB'S AND AQUATIC LIFE

Polychlorinated biphenyls (PCBs) are the second greatest cause of fish advisories, and are often the greatest contributors to dioxin-like toxic equivalency (TEQ) in fish and seafood (Judd et al. 2004). Because fish consumption is associated with both contaminant risks and health benefits, incremental health risks from PCBs in fish should be considered within the context of overall TEQ associated dietary risk to enable consumers to make informed decisions about choosing diet.

The enantiomeric composition of seven chiral PCB's congeners was measured in the Lake Superior aquatic food web sampled in 1998, to determine the extent of enantioselective biotransformation in aquatic biota. Wong et al. (2004).This study highlights the potential of chiral analysis to study biotransformation processes in food webs. Research continues to support the theory of endocrine disruption. Endocrine disruption is defined as the ability of a chemical contaminating the workplace or the environment to interfere with homeostasis, development, reproduction and/or behavior in a living organism or its offspring. Certain classes of environmentally persistent chemicals such as polychlorinated biphenyls (PCBs), can adversely affect the endocrine systems of aquatic life and terrestrial wildlife (Whaley 2003). When PCBs concentrations exceed recommended criteria for aquatic life safety they appear as a primary cause of environment degradation and reduced species richness. An uptake model, FGETS (Food and Gill Exchange of Toxic Substances) was used to analyze fish biodiversity and distribution in the two streams in relation to bioaccumulation of PCB congeners 1254 and 1260. (Marchettini 2001) Water and sediment samples were collected in the lower Parana delta at four sites with different levels of exposure to pollution to evaluate the anthropogenic impact through chemical analyses and mortality bioassays. Individual polychlorinated biphenyls, metals were measured in waters, porewaters and sediments. (Cataldo et al. 2001). Concentrations were above levels recommended for the protection of aquatic life. Evaluation of the potential cancer risk to adults from ingesting polychlorinated biphenyls (PCBs) in fish and shellfish using an equilibrium partitioning model of PCB bioaccumulation in the aquatic animal was performed (Barron et al. 1994). Estimated potential cancer risk to humans increased exponentially with increasing hydrophobicity of the PCBs. Risk assessment using toxic equivalency factors predicted substantially greater potential risk for specific congeners than for PCB mixtures. Compared with data from the National Pesticide Monitoring Program and criteria recommended for the protection of aquatic life, residue concentrations were moderately high in the Apalachicola River (Winger et al., 1978). Relationships among chemical structure, aquatic toxicity, and bioconcentration potential were examined for several classes of organic compounds (Birge et al. 1983). Structure-toxicity correlations were based largely on median lethal concentrations (LC50) and toxicant threshold concentrations (LC1) determined in mini-chronic tests with early life stages of fish and amphibians. Exposure was initiated at fertilization and maintained through 4 days posthatching. Bioconcentration potential was assessed using n-octanol/water partition coefficients (log P). In tests with polychlorinated biphenyls (PCB's), acute and chronic toxicity generally increased with percent chlorination. In addition, toxicity of specific PCB's appeared to be affected by the ratio of less chlorinated to more highly chlorinated isomers.

3.3. PCBs AND CANCER

PCBs have been classified by the International Agency for Research on Cancer (IARC) as possible human carcinogens. The no-observed-adverse-effect-level (NOAEL) for rats is 5 - 0.05 , for mice 1.25 - 0.5, for monkeys 0.08 - 0.007 mg/kg weight (Niemeyer 2000a). Recent epidemiologic studies have suggested that genetic polymorphisms in the cytochrome P-450 1A1 gene (CYP1A1) may affect the relation between environmental exposure to polychlorinated biphenyls (PCBs) and breast cancer risk. Zhang et al. (2004) report results from a case-control study. The CYP1A1 m2 genetic polymorphism was associated with increased risk of female breast cancer. Rusiecki et al. (2004) confirmed previous findings in the literature of no positive association between environmental exposure to PCBs and risk of breast cancer. It has been hypothesized that endocrine-active chemicals (EACs) may be responsible for the increased incidence of breast cancer and disorders of the male reproductive tract. Synthetic chemicals with estrogenic activity (xenoestrogen) and the organochlorine environmental contaminants polychlorinated biphenyls (PCBs) have been the prime etiologic suspects. However, results of extensive research on PCBs does not show a correlation between PCB exposure and development of breast cancer (Safe et al. 2004). An increasing incidence of testicular cancer has been reported from several western countries during the last decades. According to current hypothesis testicular cancer is initiated during the fetal period and exposure to endocrine disruptors such as some persistent organic pollutants has been of concern. No significant differences were found among cases and controls. However, case mothers had significantly increased concentrations of a number of PCB congeners. These data further elucidate the role of foetal exposure to different PCB congeners in the aetiology of testicular cancer (Hardell et al. 2004). Charlier et al. (2004) studied PCBs contamination in women suffering from breast cancer with presumably healthy women. The results suggest that environmental exposure to PCBs may contribute to multifactorial pathogenesis of breast cancer. A mortality study of workers employed between 1944 and 1977 at an electrical capacitor manufacturing plant where polychlorinated biphenyls (PCBs),(Mallin et al. 2004) Age,gender, and calendar year-adjusted standardized mortality ratios (SMRs) were calculated for 2885 white workers. Total mortality and all-cancer mortality were similar to expected in both males and females. Females employed 10 or more years had a significantly elevated SMR of 6.2 for liver/biliary cancer. Intestinal cancer was significantly elevated in females employed 5 or more years after PCB's were introduced (SMR = 2.2). In males, stomach cancer (SMR = 2.2) and thyroid cancer (SMR = 15.2) were significantly elevated. Although individual exposure assessment was limited, PCB's alone or in combination with other chemicals could be associated with increased risks for liver/biliary, stomach, intestinal, and thyroid cancer. Kimbrough et al. (2003) studied human exposure to polychlorinated biphenyls and health effects. In occupational mortality studies, exposures were much higher. In some studies, various specific cancers were elevated. However, these appear to be chance observations resulting from multiple comparisons since the increase of specific cancers was not consistent between studies and was no longer present in some cohorts when studies were repeated at a later date with longer follow-up. Overall, the data fail to demonstrate conclusive adverse health effects of PCBs at concentrations encountered with human exposures.

4. Limits

USA. The daily admissible dose is 1 mg /kg human body weight.

Bulgaria (Annual bulletin 2001)

- soils total PCBs:
  - referent background values 0.005 mg/kg
    - precautionary levels 0.02 mg/kg
    - maximal admissible concentrations 0.2 mg/kg
    - intervention levels 1 mg/kg

Germany (Fidler,1997)

- in waste – the total of 6 most frequently found compounds 1 mg/kg dry matter and 0.2 mg/kg of each compound /PCB 28; 52; 101; 138; 153; 180/
- in foods, milk, meat, fish, eggs 0.04-0.05 mg/kg adipose tissue for each individual compounds, multiplied by 6
- indoor air 300 to 3000 ng/m^3. The analysis is preformed on 6 compounds and their sum is multiplied by 5
- drinking water 0.0001 mg/l for an individual compound and 0.0005 mg/l for the total sum.

Russia (Kurljansky ed. 1998)

MAC for workplace air 1 mg/m^3

Water, including drinking water 0.001 mg/l

Soils -0.06 mg/êg

Other countries **–** average shift concentration at the workplace - 0.01 to 0.5 mg/m^3 and MAC from 0.03 to 10 mg/m^3.

Foods of animal origin 0.008 - 2 mg/kg.

Natural waters *European community* MAC 0.5 mg/l.

5. Preliminary data on possible sources of pollution with PCBs in Bulgaria

Polychlorinated biphenyls were introduced in limited amounts in Bulgaria mainly in closed systems as different transformers, capacitators, vacuum pumps, voltage regulators, electric switches, hydraulic fluids, etc. for all types of industrial processes, for mining, transport and construction.

The analysis reviewing possible PCB-containing waste shows that they are disseminated all over the country. Thus the transformers in the Metallurgy plant in Pernik contribute about 100 tons of PCBs, and the Wire plant in Burgas has provided some 20 tons. Large amounts of capacitator batteries, imported mainly from Kazakhstan have been used in chemical, metallurgical and refinery industry in Vratza (6 tons), Varna, Burgas and Pleven. It is also possible that PCB-containing details have been imported for furnishing plants, hotels, etc. It is expected that by 2010 the solid waste containing PCBs and polychlorinated paraffin will reach 8000 tons according to the plan for elimination of equipment containing PCB's (IVECOL 1997).

Andreev et al. (1996) present an evaluation of possible emissions of PCBs and other persistent chlorinated hydrocarbons. They have applied the method EMER/CORINAIR-94, according to the convention for trans-boundary air pollution at great distance.

In relation to the implemented method open pollution sources were studied. The data are based on calculations. No measurement of real amounts or concentrations has been done.

The emissions by types of activities in 1990/95 in kg PCBs are:

Thermal power plants using lignite - 52.29/50.802

Incineration processes in settlements - 87.201/344.2

Industry – boilers, turbines, etc. - 9.557/7.553

Road transport - 89.374/72.38

Other types of transport - 15.1/7.1

Solid waste - 0.811/0.151

Total 1990 - 258.44 kg

Total 1995 - 382.284 kg

The emissions in the different regions in 1990/1995 were:

Spot sources:

Haskovo - 45.569/43.665

Sofia city - 3.379/4.9

Sofia region - 4.643/5.6

Non-spot sources:

Haskovo - 72.11/86.0

Sofia - 28.970/46.6
Total for the country - 1995 - spot sources - 55.341
Total for the country - 1995 – non-spot sources - 326.8
Total for the country from both source types - 382.189
The main spot sources in 1990/1995 generated PCBs (kg):
Thermal power plants:
Maritza I - 7.8/4.937
Maritza II - 2-20.12/22.609
Maritza III - 15.595/15.326
Bobov dol - 3.4/5.223
Kremikovtzi – Metallurgical plants:
Agglomeration - 1.416/1.838
Blast furnaces - 1.942/3.052

Expertise analyses of the National Center of Hygiene, Medical Ecology and Nutrition

Port Varna – 1999 – soil concentrations of PCBs in mg/kg -
PCB -118 up to 2.0
PCB -153 up to 2.340
PCB -138 up to 2.900
PCB -180 up to 0.746

The Environmental Executive Agency to the Ministry of Environment and Waters has been regularly examining 6 substances of the PCB's group in soils in Bulgaria since 1997. The 1999 data based on 95 soil samples are within the background values (0.005 mg/kg for the sum of examined PCBs) (Annual Bulletin 2001).

Asphalt is included in UNEP list for outdoor application of PCBs. There are some 50 asphalt plants in Bulgaria where occupational exposure and environmental pollution can be expected.

PCBs analysis of food products have been performed. In ng/100 g product they are: in yogourt- 558; in milk-24 to 2888; in cheese 205 to 11896; in meat- 412 to 2760; in fish-257 to 4027. (T.Rizov, personal communication).

6. Other countries' data

Vietnam reports soil concentrations in mg/kg as follows: 392 around transformer facilities, 1426 in urban waste, around electric plants 18,810 (UNEP 2000)

Dyke (1997) presents data on PCBs emissions in the environment in England:

Waste waters release in the air 99 kg/year, in soils - 280 , in water - 40.

Coal releases in the air 260, and in soil 30 kg/year.

Steel production generates respectively 410 and 40, leakages provide 4500 and 2000 and breakages - 240 and 15000 respectively.

In Germany in office air were found maximal total concentrations (multiplied by 6) up to 1251 ng/m^3(Benthe et al. 1992 cit.by Fiedler 1997). The emissions from open sources in 1998 were 12 tons yearly (Neumeir, 2000b).

Similar data for emissions from large sectors in Hungary are presented by Adamis and Kovacs (1998). The emissions from thermal plants have the greatest values. In the period 1980 - 1996 they are in the range 49-68 kg/ year. Other sectors providing significant emissions are the industrial - 12-37 kg, communal - 11.6-30 êã and transport - 7-10 êã.

Holoubek (2000) reports the following data for PCBs content in the air of Koshice (Czech Republic) in pg/m^3:

Compound	Concentrations
28-	0.001-0.084
52-	0.001-0.072
101-	0.002-0.079
118-	<0.001-0.013
138-	0.008-0.101
153-	0.009-0.101
186-	0.005-0.117.

The maximal sum is 0.45 ng/m^3.

The comparison of the literature data with the scarce data for Bulgaria does not reveal significant differences.

7. Conclusions

PCBs are insufficiently studied in Bulgaria. At present they are a problem more as by-products of different combustion processes.

The environmental pollution around Thermal Power Plant “Maritza 1-3” during the 40-year commissioning of these facilities should be studied in details in relation to emissions propagation to different distance from the plant.

Asphalt preparation and application can also be a source of exposure for workers and the environment.

8. References

Andreev V. 1996. Responsible researcher and editor. Studying pollution with PCBs related to anthropogenic activity in Bulgaria. Bulgarian Academy of Science, National Institute of Meteorology and Hydrology. Contract 239, 1691/06.12.1996, Ministry of Environment.

Adamis S. and G. Kovacs, 2000 . POPs related Situation relevant to Hungary.II Monitoring releases of POP's by G. Kovacs. In Proceedings of the subregional awareness raising workshop on Persistent Organic Pollutants (POP's). Kranjska Gora, Slovenia, 11-14 May 1998, IOMC 210-222.

Annual Bulletin 2001. State of the environment in Bulgaria. Executive Environmental Agency to the Ministry of Environment and waters, Sofia, 1999.

IVECOL. Analysis and perspectives for implementation of PCBs in Bulgaria in 1900-2-10. Sofia, May 1997.

Arulmozhiraja S., Shiraishi F., Okumura T., Iida M., Takigami H., Edmonds J.S., Morita M. 2004. Structural Requirements for the Interaction of 91 Hydroxylated Polychlorinated Biphenyls with Estrogen and Thyroid Hormone Receptors. Toxicol Sci. Dec 15;

Barro R., Ares S., Garcia-Jares C., Llompart M., Cela R. 2004 A simple and fast micromethod for the analysis of polychlorinated biphenyls in air by sorbent enrichment and ultrasound-assisted solvent extraction. Anal Bioanal Chem Dec 9;

Barron M.G., Yurk J.J., Crothers D.B. 1994. Assessment of Potential Cancer Risk from Consumption of PCBs Bioaccumulated in Fish and Shellfish. Environ Health Perspect. 1994 Jun;102(6-7):562-7.

Birge W.J., Cassidy R.A. 1983. Structure-activity relationships in aquatic toxicology. Fundam Appl Toxicol. Sep-Oct;3(5):359-68.

Cataldo D., Colombo J.C., Boltovskoy D., Bilos C., Landoni P. 2001 Environmental toxicity assessment in the ParanÃ¡ river delta (Argentina): simultaneous evaluation of selected pollutants and mortality rates of Corbicula fluminea (Bivalvia) early juveniles Environ Pollut; 112(3):379-89.

Charlier C.J., Albert A.I., Zhang L., Dubois N.G., Plomteux G.J. 2004 Polychlorinated biphenyls contamination in women with breast cancer. Clin Chim Acta. Sep; 347(1-2):177-81.

Dyke P., 1999. Inventories for Persistent By-products of Industrial and Combustion Processes. In Regional Based Assessment of Persistent Toxic Substances. Workshop Reports from GEF project. UNEP/Chemicals September 167-173.

Fidler K., 1997. Safe management of PCB and case studies. In Proceedings of the Subregional Meeting on Identification and Assessment of Releases of Persistent Organic Pollutants (POP,s) St. Petersburg , Russian Federation, IOMC; 1-4 July 129-138

Judd N., Griffith W.C., Faustman E.M. 2004 Contribution of PCB exposure from fish consumption to total dioxin-like dietary exposure Regul Toxicol PharmacolOct;40(2):125-35.

Haraguchi K., Koga N., Kato Y. 2004. Comparative metabolism of polychlorinated biphenyls and tissue distribution of persistent metabolites in rats, hamsters and guinea pigs. Drug Metab Dispos. Dec 17;

Hardell L., Van Bavel B., Lindstrom G., Carlberg M., Eriksson M., Dreifaldt A.C., Wijkstrom H., Starkhammar H., Hallquist A., Kolmert T. 2004 Concentrations of polychlorinated biphenyls in blood and the risk for testicular cancer. Int J Androl Oct;27(5):282-90.

Holoubek I. 2000. Persistent Organic Pollutants in Czech Republic : sources, inventories, levels, risks and management.In Proceedings of the subregional awareness raising workshop on Persistent Organic Pollutants (POP's). Kranjska Gora, Slovenia, 11-14 May 1998, IOMC 80-90.

Kimbrough R.D., Krouskas C.A. 2003. Human exposure to polychlorinated biphenyls and health effects: a critical synopsis Toxicol Rev.;22(4):217-33.

Kurlyandski B.A. ed. 1998. Model of a national strategy and plan of action for reduction and elimination of POP's releases Annex II ,1-52 in Proceed. of the Subregional Meeting on National Strategy and action plan for reducing/elimination POP's Releases Moscow, Russian Federation 14-17 July UN IOMC

Madia F., Giordano G., Fattori V., Vitalone A., Branchi I., Capone F., Costa L.G. 2004 Differential in vitro neurotoxicity of the flame retardant PBDE-99 and of the PCB Aroclor 1254 in human astrocytoma cells. Toxicol Lett. Dec 1;154(1-2):11-21.

Mallin K., McCann K., D'Aloisio A., Freels S., Piorkowski J., Dimos J., Persky V. 2004 Cohort mortality study of capacitor manufacturing workers, 1944-2000. J Occup Environ MedJun;46(6):565-76.

Marchettini N., Panzieri M., Tiezzi E.B. 2001.Effects of bioaccumulation of PCBs on biodiversity and distribution of fish in two creeks in east Tennessee (USA). Ann Chim. Jul-Aug;91(7-8):435-43.

Mi Y., Zhang C. 2005. Toxic and hormonal effects of polychlorinated biphenyls on cultured testicular germ cells of embryonic chickens. Toxicol Lett. Feb 15;155(2):297-305.

Neumier G. 2000a Toxicology and health impact of PCB's. In Proceedings of the subregional awareness raising workshop on Persistent Organic Pollutants (POP's). Kranjska Gora, Slovenia, 11-14 May 1998, IOMC 108-116.

Neumier G. 2000b. The technical life-cycle of PCB's (Case study in Germany). In Proceedings of the subregional awareness raising workshop on Persistent Organic Pollutants (POP's). Kranjska Gora, Slovenia, 11-14 May 1998, IOMC 117-123.

Pieper DH. 2004. Aerobic degradation of polychlorinated biphenyls. Appl Microbiol Biotechnol. Dec 22;

Rusiecki J.A., Holford T.R., Zahm S.H., Zheng T. 2004Polychlorinated biphenyls and breast cancer risk by combined estrogen and progesterone receptor status. Eur J Epidemiol.;19(8):793-801

Safe S. 2004. Endocrine disruptors and human health: is there a problem. Toxicology. Dec 1;205(1-2):3-10.

UNEP Chemicals. 2000. Country Case Studies on Persistent Organic Pollutants (POP's)
IOMC,March.

Van Vranken D.L. 2004. Polychlorinated biphenyls inhibit amyloid fibril formation. Chem Biol Dec;11(12):1604-6.

Whaley D.A., Keyes D., Khorrami B. 2001. Incorporation of endocrine disruption into chemical hazard scoring for pollutionprevention and current list of endocrine disrupting chemicals. Drug Chem Toxicol. Nov;24(4):359-420.

Wahlstrom. Bo. 2000. Criteria for identifying persistent organic pollutants. In Proceedings of the subregional awareness raising workshop on Persistent Organic Pollutants (POP's). Kranjska Gora, Slovenia, 11-14 May 1998, IOMC.103-7.

Winger P.V., Sieckman C., May T.W., Johnson W.W. 1978. Residues of organochlorine insecticides, polychlorinated biphenyls, and heavy metals in biota from Apalachicola River, Florida, J Assoc Off Anal Chem. 1984 Mar-Apr;67(2):325-33.

Wong C.S., Mabury S.A., Whittle D.M., Backus S.M., Teixeira C., DeVault D.S., Bronte C.R., Muir D.C. 2004 Organochlorine compounds in Lake Superior: chiral polychlorinated biphenyls and biotransformation in the aquatic food web. Environ Sci Technol. Jan 1;38(1):84-92.

DOES SURFACE WATER TREATMENT NEED SPECIAL MEASURES IN THE CZECH REPUBLIC?

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Abstract

Water quality in Czech watercourses has improved significantly in the last decade.

A noteworthy problem still consists in continuous microbial pollution important particularly for use of surface water as a source to produce drinking water and for recreation.

Pollution with specific organic substances e.g. polyhalogenated and polycyclic aromatic hydrocarbons and locally by heavy metals namely mercury, cadmium and lead still remains a problem. There are substantial differences in various regions depending on population density and the local industry structure, proportion of wastewater treated, agriculture and its intensity in pertinent rivers' watersheds.

A subject of an emerging interests are potential health risks due to presence of organochlorines in chlorinated drinking water and rising concentration of endocrine disrupters in the main watercourses used for production of drinking water.

Keywords: Surface water quality/ drinking water/ wastewater treatment/ endocrine disrupters / polyhalogenated hydrocarbons / organochlorines/ polycyclic hydrocarbons / arsenic/ mercury/ human health/ risk assessment.

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1. Introduction and general comments

Water quality in Czech watercourses has improved significantly in the last decade. Data from the national network that monitors water quality show that stage 5 of water quality (very significantly polluted water) was eliminated both in the main watercourses and most of the large tributaries. These main watercourses usually have stage 3 (polluted water), only some limited sections still contain water of stage 4 (significantly polluted water).

As far as purity is concerned, there are still problems with watercourses that have less water and high accumulation of pollution sources.

A serious problem still consists in continuous microbial pollution of Czech rivers. It comes mainly from municipal sources lacking wastewater treatment plants in many settlements, especially with population equivalent between 2.000 and 10.000.

The level of microbial pollution is important particularly for use of surface water as a source to produce drinking water and for recreation. Most watercourses that are important in terms of water management are considered unsuitable for recreation because of their high microbial pollution. In this context, there are also difficulties with direct diversion of water from some watercourses for drinking-water purposes.

Pollution with specific organic substances still remains a problem. The situation should get better with implementation of the EU legislation - this concerns both the scope of the substances involved and the necessary measures to prevent their release into the environment. (EU, 2003) .Somewhere the situation has improved substantially - e.g. concentration of mercury in the most polluted local watercourse Bílina has been reduced by two orders since the beginning of 1990s. However, higher concentrations of cadmium, lead and nickel were found out in some watercourses. In several watercourses, higher burden with halogenated organic compounds from chemical industry is still detected.

Also water from most individual wells, unfortunately, does not meet the standards for drinking water, especially in terms of nitrates and microbial pollution.

Water quality is influenced especially by point sources of pollution (towns, villages, industrial and agricultural estates) and area sources (agriculture, erosion, atmospheric deposition). With decreasing pollution from point sources, the area sources are gaining importance. This is clear predominantly in case of nitrates, less significant in case of phosphorus compounds. There are substantial differences in various regions depending on population density, proportion of wastewater treated, methods used in agriculture and its intensity and also on the level of atmospheric deposition. In case of main watercourses (the Labe (Elbe), Vltava and others), concentrations of the total phosphorus have dropped in the last decade. The decrease is caused by a decreased number of cattle bred, lower content of phosphorus in washing powders in comparison with the past and also by decreased use of industrial fertilisers in these rivers' watersheds. However, concentrations of total phosphorus in watercourses are still high which is also caused by the fact that vast majority of wastewater treatment plants is not equipped with the third treatment stage that is able to remove inorganic nitrogen and phosphorus from wastewater.

2. Waste water treatment

In the last decades, organic pollution discharged (expressed as BOD (5) and COD (Cr)) and pollution with suspended solids and dissolved inorganic salts in the Czech Republic have decreased by 70% in average.

In 2001, 570.7 million m^3 wastewater were discharged into public sewerage. Out of this amount, 95.5% was treated, at least mechanically. In 2001, the share of public sewers in the total amount of wastewater discharged into watercourses was 32% (in 2000 it was 48.9%). Volume of wastewater discharged into rivers without any treatment is therefore decreasing significantly.

The quality of wastewater treatment still does not meet standards that are desirable in developed countries because the stages 1 and 2, i.e. mechanical and biological treatment, still prevail. There is lack of treatment plants equipped with stage 3 of wastewater treatment, i.e. removal of nitrogen and phosphorus. However, the situation will always depend very much on the polluters' behaviour (it is better to prevent pollution) because in the wastewater treatment plants that are used most frequently, i.e. plants employing biological processes, the content of phosphorus can only be reduced by 20-40% theoretically.

Conventional wastewater treatment is widely applied in industrialised countries, have traditionally focused on the removal of suspended solids and pollutants that require oxygen in the receiving waters to decompose (BOD) but not on the reduction of nutrients – dissolved phosphates and nitrates. Tertiary treatments must be added to effectively reduce nutrient levels.

These dissolved salts are responsible for impairing the quality of river water by increasing the risk of water flower, especially in summer.

In the past, we tried to resolve this problem by intensive carp-and-duck-breeding on ponds added to current municipal wastewater treatment facilities as the third stage of biological treatment. This type of process guaranteed by means of water plankton, a not negligible reduction of nitrates and phosphates, enabled biotransformation of them into fish meat and duck eggs and meat. About two decades later, the breeds became heavily infested with *Salmonellae*. Following liquidation of the above-mentioned carp-and-duck-breeds the fish species grasscarp (white amur) and (tolstolobik) *Hypophtalmichthys molitrix* were placed in the ponds. Both fish species, which were imported from Siberia, are herbivorous. They literally gorge themselves with water plants profiting from higher nitrate and phosphate content in the cleaned, treated residential sewage water.

In 1990s, existing wastewater treatment plants were intensified and enlarged (333 new municipal wastewater treatment plants were put into operation between the years 1990 and 1999), suburbs were involved into public sewerage network and practically all industrial wastewater was brought to a basic treatment. As a result of changes in legislation, small treatment plants were built for family houses and seasonal recreation estates in places where there was no central sewerage. This resulted in a higher proportion of inhabitants whose homes are connected to sewerage and a better quality of water in watercourses. It is also linked with constructions of municipal wastewater treatment plants in smaller towns and villages, leading to improvement of water quality in smaller streams (protection of larger recipients), protection of soil and groundwater. In comparison with Central and East European countries, the Czech Republic is on a relatively good level - three quarters of all inhabitants (i.e. approx. 7.7 million people) live in houses that are connected to public sewerage and only 5% wastewater is not treated. In connection with adoption of the EU legislation, however, it will be very difficult to meet the requirement to build sewer systems and wastewater treatment plants in towns with population equivalent 2000 - 10000 (below -mentioned transition period till the year 2010 is valid in this case). At present, the problem is not solved in more than 5000 small villages with population equivalent less than 100. In villages where it is not cost-efficient to build wastewater treatment plants it will be necessary to promote and support alternative treatment methods, e.g. reed-bed systems

Pre-treatment of wastewater before discharge into sewerage is now common for industrial plants that are connected to municipal sewerage.

In connection with our accession to the EU, the Czech Republic has the transition period in the area of water protection (by the end of the year 2010) to meet some requirements of Directive 91/271/EEC on municipal wastewater treatment. The transition period is intended for building of sewer systems and municipal wastewater treatment plants in towns with population equivalent between 2000 and 10000 and for intensification (removal of nitro-gen and phosphorus) of wastewater treatment plants that serve for more than 10000 population equivalent in so called sensitive areas. In this context, the Czech Republic has declared its intention to include the whole of the country's territory into one sensitive area.

3. Water consumption

In the last decade, intakes of surface water and groundwater are constantly decreasing, as well as wastewater discharge. Total consumption of water has gone down by approximately 50% since 1990. From the beginning of 1990s, intake of water from public water mains has also been decreasing while the number of inhabitants supplied from public water mains was growing. Reduction of the specific consumption of water (i.e. number of litres consumed in average by one inhabitant per one day) is also a positive trend.

In 1995 - 2001, water consumption divided according to different sectors has dropped by approx. 25%. There are substantial differences among the single sectors concerning water supply. At present, most water is drawn off by public water mains but the industry and energy sectors are also demanding as far as water supply is concerned. Intake of water for agriculture is relatively low because in the Czech Republic it is almost not necessary to irrigate due to favourable weather conditions. For wastewater discharge, the proportions are similar to those for intake. As well as for materials and energy, it is also necessary to increase eco-efficiency in case of using water within each sector. This should be reached mainly through introduction of new technologies that do not need much water to enter the production process and that focus on consistent recycling of water.

In the Czech Republic, 10.8% of the total amount available was drawn off in 2001, which is an average value for OECD countries. Thus the Czech Republic ranges from the low to slight water stress. Total amount of water available includes the surface and groundwater (basic) runoff with the present available technologies being used.

The fact that *loss in water mains* is being reduced is quite positive (in Prague water mains, for instance, about 50% drinking water produced is lost before it reaches the consumers) although the improvement should rather be put down to overall reduction of water consumption. Decrease of water consumption that is justified by reduced industrial production and saving water in households is, however, gradually coming to end. Lower intakes of water are connected with higher concentrations of pollution in wastewater (pollution is not "diluted"). This fact results in a higher proportion of pollution in waste sludge and the possibility to use the sludge in agriculture can be therefore reduced at some instances.

4. Chemical and microbiological pollution

4.1. FERTILISERS AND PESTICIDES USE

Since early 1990s, consumption of industrial fertilisers has dropped by almost 50%. In 2001, however, it increased in comparison with the previous year while the amount of nutrients getting into land from organic fertilisers remained unchanged. Consumption of pesticides has also dropped substantially in 1990 - 1993. Since that time, the consumption has been stable or slightly growing. But we should keep in mind that since early 1990s, efficiency of the active components in pesticides has multiplied and it is not necessary to consume so much pesticide per one hectare. A positive result of these changes consists in the fact that, within austerity measures, there is not massive eutrophication of water caused by excessive fertilising anymore. This may change, however, because in the last two years the amount of fertilisers used is going up again, especially in case of nitrogen fertilisers.

In international comparison, consumption of pesticides (per 1 hectare) in the Czech Republic is lower than the EU and OECD averages. Nevertheless, it is necessary to continue reducing the consumption and to take advantage of the pests' natural enemies (biological protection of crop). The optimal approach available now is integrated protection.

4.2. VERY HAZARDOUS AND HAZARDOUS SUBSTANCES

The most important substances in this group are considered to be particularly organohalogen and other compounds, mercury, cadmium, nickel and lead. EC legislation is greatly concerned with the subject of hazardous substances in the aquatic environment, in relation both to the range of monitored substances and to the necessity of preventing their escape into the aquatic environment. Work was completed in 2002 on project VaV/650/3/00 - the occurrence and movement of hazardous substances in the hydrosphere in CR, which contributed significantly to evaluation of substances that are relevant for watercourses in CR.

The target pollution level standard for pollution characterised by the summary indicator AOX (adsorbable organic halogens) is 30 $mg.l^{-1}$ (Annex No.3 of Government Regulation No. 61/2002 Coll.) AOX concentrations of hundreds of $mg.l^{-1}$ were found just exceptionally in a most heavily polluted part of the Bílina River. Temporary increases were found in AOX values during the floods in August 2002 in the Labe (Elbe) as a result of the accidental escape of chlorine from Spolana Neratovice.

Chlorinated organic compounds (1,2,-dichloroethane, trichloramethane, trichloroethene, tetrachloroethene and hexachlorobenzene) originate mostly from the chemical industry through discharge of wastewaters into the Bílina or directly into the Labe (Elbe), or from burdens from the past.

On an average in 2002, the concentration of hexachlorobenzene in the Bílina in the Ústí nad Labem profile exceeded the EU quality target (30 $ng.l^{-1}$); this contamination should be decreased substantially as a consequence of connection of Spolchemie, a.s. to the WWTP in Ústí nad Labem.

Polychlorinated biphenyls (PCBs) and DDT originate from environmental burdens from the past. They continued to be monitored, mostly in formerly identified polluted sections of watercourses. Contamination by DDT at the confluence of the Bílina with the Labe is caused by polluted soils from the premises of the Spolchemia, a.s., in Ústí nad Labem. Pollution by polycyclic aromatic hydrocarbons (PAH), the most important of which are fluoranthene and benzo(a)pyrene, originates from coal mining, the coke industry, and some production processes, such as impregnation of wood with creosote oil (railway ties, poles), and also from the operation of automobiles.

The mercury content in the Bílina, which was quite unsatisfactory in the lower stream in the past, has decreased substantially, by two orders of magnitude, since 1991, through measures introduced at Spolchemia, a.s., Ustí nad Labem. The EU quality target (1 $mg.l^{-1}$ as an annual average) was met in the Bílina - Ústí nad Labem profile; the average concentration in the Bílina - Ústí nad Labem profile in 2002 was 0.3 $mg.l^{-1}$ Spolchemie, a.s., which is the company using most mercury in this country, has long implemented measures to decrease all emissions; however, extreme escapes still occurred in 2002; onAugust 1, 2002,avalue of 1.43 $mg.l^{-1}$wasrecorded in the Bílina - Ústí nad Labem profile. Elevated cadmium concentrations were found in the Ostrava area in the Olše, the Ostravice and the Odra, derived primarily from industrial sources in the Ostrava agglomeration.

Elevated lead concentrations were found in the local watercourses (metallurgical works, old burdens, mine water), where elevated concentrations of nickel, copper and zinc were also found.

4.3. SURFACE WATER POLLUTION

Surface water quality is affected mainly by *point pollution sources* (cities and municipa-lities, industrial plants and concentrated agricultural animal production units). In 2002, 7. 9 million inhabitants were living in residences connected to public sewer systems, i.e., 77.4% of the inhabitants of the Czech Republic (CR). The connection of inhabitants to sewer systems in CR is above the average for the European OECD countries, equal to about 62%. A total of 576.3 mil. m^3 of wastewater was discharged into public sewer systems, 92.6% of which was treated (mainly in mechanical-biological waste water treatment facilities).

The quality of surface and ground waters is significantly affected by *diffusive pollution sources*, especially pollution from agricultural activities, atmospheric deposition and erosion run-off. The importance of diffusive pollution is increasing with the continuing decrease in pollution from point sources. It makes a considerable contribution especially for nitrates and acidification and less for phosphorus and varies in different areas of CR in dependence on population densities, the degree of treatment of discharged wastewaters, the intensity and manner of agricultural management and the level of atmospheric deposition. The five year R&D task "Reduction of diffuse pollution of surface and ground waters in CR" was completed in 2002 at the T.G.M. Water Management Research Institute, yielding, amongst other things, designation of areas vulnerable to nitrates, phosphorus and acidification. On the basis of outputs from this project, Government Regulation No. 103/2003 Coll., on designation of vulnerable areas and on the use and storage of fertilizers and barnyard fertilizers, alternation of crops and implementation of anti-erosion measures in those areas in which vulnerable areas were designated pursuant to Council Directive 91/676/EEC (the Nitrate Directive) and a list of binding measures for vulnerable areas were issued.

4.4. MICROBIAL POLLUTION

Microbial pollution of watercourses is a significant factor particularly in the treatment of surface waters as drinking water and in the use of surface waters for bathing. Evaluation of microbial indicators in the profiles of the state network indicates that the microbial pollution of watercourses in CR remains high, and is derived primarily from municipal sources of pollution. Important water courses (except for reservoirs) are mostly not considered to be suitable for bathing. In cooperation with ME, MA has prepared the draft wording of a Decree stipulating surface waters used for bathing, to implement § 34 of Act No. 254/2001 Coll., on waters and amending some other Acts (the Water Act); these are mostly locations at water reservoirs and recreational ponds. If the surface water at these locations does not correspond to the requirements on water quality for bathing, suitable measures will be adopted. Following the floods in 2002, there was a temporary increase in microbial levels in the affected watercourses, especially below the affected WWTPs.

4.5. FLOODS AND IMPACT ON THE ENVIRONMENT

The catastrophic August floods occurred in two waves, on August 5-7 and August 11-18, 2002. It was caused by the progress of two deep low-pressure areas and the related frontal systems across central Europe in a short time interval. The sector with the heaviest rainfall in both systems occurred over the Czech Republic. In addition, both systems moved slowly, prolonging the period of constant precipitation over the territory of CR. The greatest amount of precipitation exceeded 400 mm in the Novohradské Mts. on the border with Austria. Precipitation of more than 300 mm occurred over a substantial part of Šumava and the Novohradské Mts. and in their foothills, and also in the eastern part of the upper sections of the Krušné Mts. and Jizerské Mts.

The Vltava in Prague culminated at 12'clock on August 14 at a flow rate of 5160 $m^3.s^{-1}$, corresponding to 500-year levels. This was the highest evaluated flow rate on the Vltava in Prague in the history of standard observations.

A significant temporary increase in discharged pollution occurred mainly because of the floods. As a consequence of flooding and damage to the equipment in 2002, a number of important WWTPs in the watershed of the Vltava were shut down for several months and, in the best cases, only the mechanical stage of water treatment was in operation at a number of WWTPs. In the Vltava watershed, discharged pollution increased in 2002 compared to 2001 by 211 % in terms of BOD_5, by 108% in terns of COD_{Cr} and by 230% in terms of SS. All the WWTPs affected by the floods were fully in operation by the end of 2002. In the other watersheds, the discharged pollution decreased by 0.9% in terms of BOD_5, by 7.6% in terms of COD_{Cr} and by 2.4% in terms of SS as a consequence of operation of new and reconstruction of older

WWTPs completed in 2001 or 2002, intensification of older WWTPs and connection of parts of the public sewers to WWTPs. The discharged pollution was also decreased when chemical precipitation of phosphorus was employed in some WWTPs, leading to reduction of discharged organic pollution characterized by the BOD_5 and COD_{Cr} indicators. (Quoted from the Report of Ministry of the Environment of the Czech Republic, 2003)

The *extreme flood* affected the watercourses in the watersheds of the Vltava, Ohøe and Labe below the confluence with the Vltava. As a consequence of the high water levels, WWTPs were flooded, taking 120 WWTPs out of operation, 29 of which were large with a capacity of over 10 000 EI and treatment of waste water was interrupted. The operation of WWTPs was gradually renewed, mostly within 6 weeks after the floods and others by the end of 2002. Of flooded industrial enterprises, the greatest impact on the water quality in the Labe was exerted by escape of chlorine and ammonium sulphate from Spolana Neratovice but the water quality in the Labe was not endangered by escapes of dioxins from this plant. The interruption of the operation of WWTPs and escapes of substances from industrial companies had only a temporary effect on the water quality in water courses and did not have a long-term effect on the overall favourable state and trends in water quality in water courses.

4.5.1. Accidental pollution and floods

Accidental pollution is another factor that detrimentally affects the quality of surface and ground waters. In 2002, the Czech Environment Inspection (CEI) recorded 246 cases of accidental contamination or endangering of water quality in the territory of CR, of which groundwater was involved in 12 cases.

5. Chlorination of drinking water

A most critical characteristic of water for human health is its microbiology. The microbiological quality of drinking water can be controlled effectively by disinfection, which normally involves the use of *chemical oxidants*. Chemicals used on a substantial scale as disinfectants are chlorine, hypochlorite, chloramine, chlorine dioxide and ozone. *Chlorination* is almost universally accepted as the *method of choice* for purifying/disinfection drinking water supplied. It was first used on a continuous basis for this purpose at the beginning of the twentieth century. Since some water suppliers have difficulty in maintaining acceptable water quality, particularly with regard to taste and odour, chlorine may be used in combination with *ozone, chlorine dioxide, ammonia* and *activated charcoal*. These treatments are sometimes followed by dechlorination, for example with sulfur dioxide.

5.1. CHLORINATION BY-PRODUCTS

Chlorination/disinfection by-products in water are formed when chlorine-based disin-fectants react with the organic matter available in water. As many as 500 chlorination by- products have been identified, including *trihalomethanes* (THMs), and *halogenated acids* and *aldehydes* (HAAS), some of which are carcinogenic to experimental animals. Water in which these compounds and other trace contaminants are present is a very *complex mixture*. Formation and occurrence of the by-products is dependent on a number of factors, including the method of disinfection, the level and content of organic matter, pH, temperature and duration of treatment. THMs and HAAS are generally the most prevalent by-products; others occur at lower levels, but current knowledge on them is limited due to the small number of studies. Little is known about how various by-products are corre-lated; they may differ by region due to differences in determinants of their formation. *THMs* have regularly been used as a *marker for the mixture* of by-products in water, because they are *measured routinely*, but little is known as to whether they are a good marker for individual by-products such as chloral hydrate, trichloroacetic acid, dichloro-acetic acid and MX ('mutagen X', 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-fura-none). Only a small fraction of the chlorination by-products that have been identified in drinking water have been tested for carcinogenicity.

5.1.1. Potential health risks

Chlorinated drinking water has been reported to be associated with the development of some human cancers, most particularly cancer of the urinary bladder. (Table 1).

TABLE 1. Evaluations of chlorinated drinking water, some chemicals used in the chlorination of drinking water and some chlorination by-products, (*IARC, 84).*

Agent	Degree of evidence[a] of carcinogenicity		Overall evaluation of carcinogenicity to humans
	Human	Animal	
Chlorinated drinking-water	I	I	3
Some chemicals used in the chlorination of drinking-water			
Sodium chlorite	ND	I	3
Hypochlorite salts	ND	I	3
Chlorination by-products			
Bromodichloromethane	I	S	2B
Bromoform	I	L	3
Chlorodibromomethane	I	L	3
Halogenated acetonitriles			
Bromochloroacetonitrile	ND	I	3
Chloroacetonitrile	ND	I	3
Dibromoacetonitrile	ND	I	3
Dichloroacetonitrile	ND	I	3
Trichloroacetonitrile	ND	I	3

[a] I, inadequate evidence; S, sufficient evidence; L, limited evidence; ND, no data.

The epidemio-logical studies have examined exposure to chlorinated drinking water rather than to specific disinfection by-products, like chloramine, chloral hydrate, dichloroacetic acid, trichloroacetic acid and MX. It is important to recognize that none of the disinfectant by-products can be considered individually as the plausible causes for the cancers observed in human studies. When the potency of the by-products that have been evaluated is viewed in the context of their concentrations in drinking -water, it appears that these are at least three orders of magnitude too low to account for the risks implied. In most circumstances, however, the *toxicity of a mixture* cannot be assessed solely by evaluating individual compounds identified in this mixture. This is particularly the case for chlorinated drinking water that contains hundreds of disinfection by-products, none of which dominates the toxicity of the mixture. (IARC 2004).

The investigation of possible risks for cancer from consuming chlorinated drinking water in human populations is difficult, and *hindered by a number of methodo-logical obstacles*. Chlorination may produce quite different profiles of chemical by-products in different areas. Characterization of a person's water consumption is complicated by the fact that, in many parts of the world, people change residence from time to time, and the nature of their source of domestic water changes as a consequence. Furthermore, people may consume water not only at home but also at work and elsewhere, and may drink not only chlorinated water but also unchlorinated water, bottled water, boiled water and other liquids, which will greatly influence their exposure to chlorination by-products. Exposure to constituents of water other than by ingestion - by inhalation or skin absorption - may also occur. Even if associations between human cancer risk and exposure to residential chlorinated water supplies can be demonstrated, they may be due to other constituents of the water that is chlorinated or to particular (e.g. genetic) characteristics of the populations who live in areas served by such water supplies.

6. Chemicals released into the environment

In the last decade, emissions of heavy metals and persistent organic pollutants (e.g. polyhalogenated and polycyclic aromatic hydrocarbons) into the environment have decreased. However, e.g. mercury still remains a problematic substance. Regardless of reduction of its emission in Europe, high contents of mercury are still found in animal and human tissues in the Arctic. Despite of success concerning reduced emissions of different chemicals into the environment, a number of the substances exceed determined limits and thus they are potentially hazardous e.g. for pregnant women and breastfed children (Bencko et al. 2004). High contents of dioxins and mercury in fish are just two examples. There is a number of *new pollutants* released into the environment that are *not monitored* but can be hazardous for both human health and environment.

7. Conclusions

Water is essential to life, and the maintenance of an adequate supply of unpolluted water and especially safe drinking water is an essential requirement for both human health and good environmental quality. Human demands upon the earth's water are great. Water is taken for human use, irrigation and industry and is returned to environment as industrial discharge, agri-cultural run-off and microbiologically contaminated, treated or untreated sewage. Water quality varies according to these discharges, the season and the geology of an area.

I order to improve checking of chemical substances released into the environment including the water compartment it is necessary to develop, along with the present conventional monitoring methods focusing mainly on the atmosphere, water and soil, new approaches enriched with monitoring of the overall flows of chemicals into and through the environment and monitoring of pollutants also in biological materials and wastes from the technosphere. Having in mind the precautionary principle the *integrated assessment* of the impacts on health and the environment should cover the *complete life cycle of the products*, with respect to significant properties of chemical substances such as the ability to accumulate in living tissues or resistance to decomposition and long life in the environment characteristic for *persistent environmental pollutants* including e.g. endocrine disrupters family (Bencko, 2003; ATSDR 2002; NATO CMS, 1991).

There are substantial and *irrefutable benefits of disinfection* of water supplies by chemical methods, including chlorination. Any major change to these programmes would need to be evaluated fully as to its costs and benefits with regard not only to the need to *maintain microbiological safety* but also to the possible long-term adverse effects of alter-natives to chlorination.

8. Acknowledgement

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9. References

ATSDR Tox Profiles, Atlanta, 2002, http://www.atsdr.cdc.gov.

Bencko V. 2003. Risk assessment and human exposure to endocrines disrupters. In: Jedrychovski, W.A., Petera, F.P., Maugeri, U. (Eds.) Molecular Epidemiology in Preventive Medicine. International Center for Studies and Research in Biomedicine in Luxembourg, pp.315-327.

Bencko V., Èerná M., Jech L., Šmíd J. 2004. Exposure of breast-fed children in

the Czech Republic to PCDDs, PCDFs, and dioxin-like PCBs, Environmental Toxicology and Pharmacology, Vol.18, pp.83-90.

EC ,2003. Europe's environment: the third assessment. Copenhagen.

IARC ,1991. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans,* Vol. 52, *Chlorinated Drinking-water; Chlorination Byproducts; Some Other Halogenated Com-pounds; Cobalt and Cobalt Compounds,* Lyon, IARCPress

IARC, 1995 *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans,* Vol. 63, *Dry Cleaning, Some Chlorinated Solvents and Other Industrial Chemicals,* Lyon, IARCPress

IARC, 2004. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans,* Vol. 84, Some Drinking-water Disinfectants and Contaminants, including Arsenic, Lyon, IARCPress

Ministry of the Environment, 2003 Report on the Environment in the Czech Republic 2003, ISBN 80-7212-277-0.

NATO CMS 1991. Dioxin Perspectives. A pilot study on International Information Exchange on Dioxins and Related Compounds, Vol.16.

WATER MANAGEMENT IN REPUBLIC OF MOLDOVA. PRINCIPAL THREATS

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Abstract

Water management and impact of water related hazards on health were investigated. Although some aspects of water quality and supply have improved over the last decade, progress has been variable. Anthropogenic pressure on water resources affect health and water born diseases occur throughout country. The rural and socially excluded populations are especially vulnerable to water related hazards. To improve the situation with regard to water resources, the following issues need to be addressed: (a) the overall poor quality of water resources, (b) the supply of drinking water to the rural population in accordance with established standards and (c) watershed protection.

Keywords: Republic of Moldova / aquatic resources / water management / mineralization / nitrates / fluoride / hydrogen sulfite / bacterial hazards / health

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1. Aquatic resources

1.1 SURFACE WATERS

The water resources of a country are determined by a number of factors, including the amount of water received from precipitation, inflow and outflow in rivers and the amount lost by evaporation and transpiration (Water and Health in Europe 2003) Republic of Moldova, which area is 33,7 thousand km^2, is located in South-East of Europe, in a region of insufficient precipitation, limited water resources, with temperate climate and relatively limited humidity (Environmental performance reviews 1998). About 1,32 billion m^3 of water are formed in its territory every year. There are not uniform and regular precipitations in Moldova. In its northeast part (Briceni, Ocnita, Soroca, Camenca) and in the central part of the country (Sraseni, Calaras) it falls 550-600 mm of precipitations yearly. This value is decreasing gradually from northwest to southeast, reaching 370-400 mm in Taraclia and Ciadir-Lunga. As a rule precipitations fall as downpour in the warm period of year and approximately 10% from whole its quantity is in form of snowfall (Ropot, 2002). Tremendous downfalls are characteristic for Republic of Moldova. It can occur that in a short time the precipitations constitute more then 200 mm per day. In 1991-1996 years such rains in many localities provoked a number of human victims and enormity of economic losses. There are also many droughts in this territory.

Three years from every ten are drought-afflicted here. The hydrographic network is quite pronounced (16000 km total length of rivers). It includes 3621 rivers and rivulets, 57 lakes with a total area of 62.2 km^2 and about 3000 ponds (Ropot, 2002; Starea mediului, 2004). Moldova is mostly located between two large rivers: Dniester and Prut. River Dniester, with a basin covering 57% of the Moldovan territory and an average annual discharge of 10 billion m^3, separates the Republic of Moldova from Ukraine. River Prut, with a catchment covering 24% of country's territory and a yearly discharge of 2.4 billion m^3, delimits Moldova from Romania. The largest natural lakes are situated in the lower part of river Prut and river Dniester. The largest water reservoirs are Costesti-Stinca - on river Prut (735 million m^3) and Dubasari - on river Dniester (490 million m^3) (Starea mediului, 2004).

The river water resources are classified in 4 categories: natural resources (14,82 billion m^3), generated by the specific climatic conditions of the territory; real resources (14,36 billion m^3), collected from the entire river catchment, modified by human activity; ecological resources (4,58 billion m^3), necessary to maintain the ecologic balance of the river and available resources (9,78 billion m^3), which can be used for industrial, agricultural and household purposes (Ropot, 1998).

1.2. UNDERGROUND WATERS

About 1,1 billion m^3 of underground water are formed in Republic of Moldova every year. From the total underground water reserves (3,173,000 m^3/day), 2,602,000 m^3/day are potable water reserves and 573,000 m^3/day are technical water reserves (Starea mediului, 2004; Ropot, 2002).

By the purpose of use, the underground waters can be potable, mineral, industrial and thermal. All these types of groundwater occur on the entire territory of Republic of Moldova.

The underground waters constitute 32-35% of the total water used for centralized water supply in Moldova. For this purpose 6600 artesian wells across the country with the depth above 60m were in use at the beginning of nineteenth (Ropot, 2002). Because of the high general mineralization or high content of fluorine, hydrogen sulphide (H_2S), hydrocarbons, etc., many artesian wells do not meet the national requirements for drinking water. Because of these conditions approximately 2000 from the whole number were authorized to be used as sources of drinking water. Nevertheless, because of the absence of alternative, some of the wells were authorized as sources for centralized water supply in spite of some fluorine or hydrogen sulphide excess.

Due to different circumstances during 1997 were functioning 5600 (Ropot, 1998) and during 2000 - 4000 (Ropot, 2002). During 2002 only 3100 of them were estimated to be operational. The rest of them were abandoned and at present they do not belong to any legal owner ((Starea mediului, 2003).

Phreatic waters are spread in all country areas but with different profundities. There are 38,9 thousand m^3 of local phreatic waters per 1 km^2. The reserves of shallow phreatic waters have not been estimated yet, but it is known that some 50,000 m^3 of them are used every day. Such waters are easy for access. They are used for local water supply and the share of phreatic waters in rural area reach 95% from all water used. More often the water is drag out from the handmade shallow wells or catchments of phreatic waters. There are more than 132 thousand of such local sources of drinking water across the country (Ropot, 2002).

Mineral waters, which extracted out from depressions, are categorized as potable and curative waters. Mineral waters are spread all over the country. The most commonly known are: Varnita, Balti, Chisinau, Soroca, Camenca, Hîrjauca, etc. The water mineralization is between 1.0-10.0 g/dm^3. Curative mineral waters mostly occur in the south and northeast of the country. They contain hydrogen sulphate (30,0-80,0 mg/dm^3), iodine (17,0-26,0 mg/dm^3), bromine (132,0-139,0 mg/dm^3) and other chemical elements (lithium, radon, strontium, boron) (Starea mediului, 2004). Industrial groundwater contains rare chemical elements, which can be extracted. Waters containing iodine (1-60 mg/dm^3), bromine (20-250 mg/dm^3), helium (up to 15.0 ml/dm^3) and boron are prevailing. Thermal waters occur in the Prut river floodplain and in the south of Moldova. The temperature of the water is 20-80^{0}C and the yield, 10-100 m^3/day.

2. Environmental management of water issues

In the last decade Moldova made significant efforts to improve and adjust the legislative framework in the problem of management of water issues. There are about 20 legislative acts and 30 normative acts, as well as strategy, concepts, programs and action plans have been adopted until now. To ensure the implementation of this legislation different instruments are used. The most important strategic documents on environment and public health protection are as follows: National Program for Household and Industry Wastes Management (2000), Republic of Moldova Environmental Policy Concept (2001), National Action Plan in Environment Health (2001), Republic of Moldova Water Supply and Sewerage Program (2001), Concept of Socio-Hygienic Monitoring System in Republic of Moldova (2002), National Ecological Security Program (2003), National Strategy and National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants (2004), etc. The proper institutional system was established in this field at the national, municipality/town and district level. In the water sector four different State Bodies deal with various aspects of environment management: Department for Environment Protection of Ministry of Ecology and Natural Resources; Ministry of Health; Ministry of Agriculture and Food Processing; and Association Geology of Moldova (Ageom).

Since 1991 Moldova has been involved in the process of international, regional and bilateral cooperation, signing 18 and ratifying 17 international conventions including Convention for Control of Transboundary Transportation of Dangerous Wastes and Their Neutralization (Basel), Convention on Transboundary Air Pollution in the Long Ranges (Geneva), Convention for Protection and Use of Transboundary Water Courses and International Lakes (Helsinki), Convention on Persistent Organic Pollutants (Stockholm) and others showing thus its adhesion to sustainable development principles and its wish to cooperate in this field.

In 2002 year 83,2 million m^3 of wastewater were treated in 106 wastewater treatment plants (WWTPs). 94% of this quantity were discharged into the watercourses of the Dniester basin, 4% - into the Prut basin, 1% - into the Danube basin and 1% - into the Black Sea catchments. In most WWTPs, due to frequent power cuts or to improper operation, the biological step is not working properly or at all and consequently the effluents are not treated to the expected degree (Starea mediului, 2004; Ropot, 1998). Most of the villages and small enterprises, factories and works in rural area have not WWTPs. Quite near 3.5 million m^3 were discharged in 2003 year without any treatment in small rivulets? (Starea mediului, 2004).

The change of the economic system brought significant changes to the livestock breeding sector. Most big animal complexes have been dismantled and the animal herd has been moved to the private households. Consequently, the pollution sources became very diffused and practically unmanageable. The diffuse pollution, which originates from the filtration fields of the sugar refineries, drainage waters from agriculture fields, as well as the remaining 36 big animal breeding farms is not monitored (Ropot, 1998). According the data provided by the State Ecological Inspectorate, the existing livestock every year produces approximately 15 million m^3 of manure. A roughly estimation denoted that at least 3-4 million m^3 is used in agriculture as manure. The rest quantity remains within villages being mineralized. Soluble chemical compounds derived from the mineralization such as nitrates, chlorides, sulphates etc., are conveyed with precipitations (soil water) in the soil deepness and afterwards arrive at the water-bearing strata (subsoil or phreatic water) used for local potable water supply.

3. Chemical and bacterial hazards occurring in water

The poor water quality in small internal rivers is an issue of permanent concern. The hydrobiological assessment of the water quality indicated that all small river courses are largely degraded. The concentrations of organics, ammonium, nitrites, phenols, copper regularly exceed maximal admitted concentrations. The water quality of the Raut River corresponds to III-IV quality class, moderately polluted to very polluted. The river Bac falls into

IV category, with pollution maximum in summer. All these small rivers have low flows and a poor natural self-purification capacity, therefore their water quality is easily affected by urban waste water discharges: the Bac river – from Chisinau; Lunga river – from the town of Ceadir- Lunga; Raut river – from the city of Balti; Cogilnic river – from the town of Hincesti. In such a way, the small rivers to a certain extent determine level of pollution both Dniester and Prut rivers.

Generally the chemical water quality of the Prut and Dniester rivers is actually classified as clean or moderately polluted (II-III quality class) (Ropot,1998). Dniestr and Prut water has begun to possess satisfactory chemical composition and good organoleptical properties in the last years. Its general mineralization consists 248–473 mg/dm^3 for Dniester and 232-644 mg/dm^3 for Prut, the highest values being denoted in summer months (Ropot,1998; Starea mediului, 2003). The water quality of the Prut and Dniester rivers show an improvement of the chemical water quality as compared to the 1980-1990s: the nitrate content decreased 2-3 times; the content of nitrite (up to 0.2-0.3 mg/dm^3) and phosphate (up to 0.08-0.1 mg/dm^3) is quite low. The oxygen regime is satisfactory. For example, the content of some elements in the Dniester river is as follows: Mn -3.2-32.6 µg/dm^3, Pb – 1.8-3.7 µg/dm^3, Al – 12.8-42.1 µg/dm^3, Ti – 1.1-3.5 µg/dm^3, Mo - 1.7-2.8 µg/dm^3, Ni - 2.4-4.2 µg/dm^3, V - 1.6-2.7µg/dm^3, Cu -1.9-18.9µg/dm^3, Zn - 18.8-178µg/dm^3, Cd - 0.9-4.1µg/dm^3, Cr - 0.3-1.7 µg/dm^3. The highest concentrations are recorded downstream of the confluence with river Bac (carrying the waste water from the capital city Chisinau) and upstream the cities of Soroca, Tighina and Tiraspol (Starea mediului, 2003) So in both Dniester and Prut rivers the concentrations of heavy metals, nitrogen and phosphorus in 98% of analyzed water samples are at an acceptable level, which did not affect the normal biological processes.

The saprobe index for Dniester and Prut also generally corresponds to moderately polluted water (III class) (Republic of Moldova Environmental Health Report 2003). According to the investigations of the National Centre for Preventative Medicine, the number of total coliforms in Dniester and Prut is usually 10^3-10^6 per dm^3, faecal coliforms, 10^2-10^3 per dm^3. The most high bacteriological contamination of Dniester and Prut water is characteristic for season of snow thawing.

In such a way, only Dniester and Prut rivers water can be used for drinking-water supply, but after purification, using methods based on decantation, filtration, coagulation, and disinfection.

Shallow groundwater layers are extremely vulnerable to anthropogenic impact and the pollution of groundwater is a growing concern in Moldova.

The major source of pollution with nitrogen is livestock and human waste. The chemical groundwater quality is the worst in all part of the country while in terms of microbiological pollution the eastern and central parts are most affected, where the number of polluted wells exceeds 10%. In 2001-2002, only 20% of checked shallow water sources complied with sanitary and hygienic standards (Calitatea mediului, 1999; Starea mediului si sanitarea, 2002; Starea mediului si sanitarea, 2003).The spectrum of parameters exceeding the norms is very wide: nitrogen compounds, fluoride, chloride, sulphates etc. Deep groundwater layers often show high mineralization, high content of fluoride, hydrogen sulfite (H_2S), ammonia, hydrocarbons, while shallow groundwater is increasingly polluted with nitrate. It is not unusual to find in many shallow wells concentrations of nitrate of hundreds of mg/l. The incidence of standard exceedings reaches 70% of the whole number of shallow wells. Both natural and anthropogenic factors are at the origin of this situation (Ropot, 1998; 2002; Republic of Moldova Environmental Health Report 2003; Salaru, 2001). In many localities the values of total dissolved solids and hardness exceed 2-3 times the international drinking water quality standards. There is a significant bacterial pollution of local water sources due to anthropogenic factors (Starea mediului, 2004).

4. Impact on quality of life and health

Access to a sufficient supply of safe water is essential in maintaining public health. Situations with inadequate water supply directly and indirectly affect life quality and human health, increase the likelihood of person-to-person disease transmission (Opopol, 2002). Main water supply sources of the Republic of Moldova are Nistru River, which covers 54% of the total water used, Prut River contributing 16%, other surface water sources – 7% and ground water – 23%. Only 83% of urban population and 17% of rural inhabitants has access to drinking water supply through centralized system. Because of the economic deficiencies water has become an increasingly deficient commodity in many towns being delivered with irregularity. Excepting Chisinau and Belts towns, drinking water from the water pipe is served with the intermittence of 8-12 hours per day. The rest of consumer is supplied from local noncentralised water resources, reaching in some regions 95-100%.

According Ministry of Health data, consumption of drinking water causes 35-40% of diarrheas. Thus the incidence of acute diarrhea is higher than general value in the regions with bacteriological samples, which do not comply with allowed standards. In 2003 it was registered 2 breaking out of dysentery (133 cases in Comrat and 8 cases in Crihana Veche), while in 2002 – 6 breaking out. The biggest breaking out of 2002 year was represented by viral hepatitis A (177 cases in Straseni).

Poor hygiene caused by the lack of water has an evident impact on human life quality (Sanatatea copiilor, 2004).

Concentrations of nitrates, which frequent exceed maximum admissible concentrations, influence about 1,5 million inhabitants. Vast epidemiological investigations done in Republic of Moldova (Opopol, 2002) denoted a pronounced impact of high concentrations of water nitrates on human health. They suppress the tissue respiration enzymes, affect liver function and both hempoiesis and immunopoiesis. Children suffer from both biological and physical development retardation. The integrated assessment of health has shown an evident worsening of children health indexes. The general morbidity among children living in the water-polluted areas is 3.9 times higher in comparison with the children living in non-polluted areas (general incidence is 733.1 and 189.9 per 1000 children). Now the situation is changing for the worse due to the continuous increasing of the drinking water pollution. High concentrations of hydrogen sulfite affect both the organoleptic properties (taste, smell, turbidity) of water and consumer health due to alkaline medium of such water. Fluorosis is wide spread among children in localities were people use drinking water with the content of fluorine above 1,5 mg/dm^3. In Floresti, Cornesti and other towns high fluorine concentration is associated with artesian water and there 4-11% of schoolchildren suffer from dental fluorosis.

5. Conclusions and proposals

Republic of Moldova water management authorities try to sustain considerable effort to design and to have an infrastructure that corresponds to the market economy and public health needs. In conditions when the economy is going through transition and recession the task is truly enormous and it has to proceed in stages. The current objective is to assure the maintenance and operating costs of the existing water-supply facilities. The objective more or less is achieved in some towns (Chisinau, Belts, etc.). Most of rural residents have no access to satisfactory quantity of qualitative drinking water. Chemical and bacterial hazards occurring in phreatic waters significantly affect health of people in the whole rural area of the country.

In general to improve the situation with regard to water resources the following issues need to be addressed: (a) the overall poor quality of water resources; (b) the supply of drinking water to the rural population in accordance with established standards (Guidelines for drinking water Quality, 2004); (c) watershed protection.

6. References

Calitatea mediului ºi sãnãtatea populaþiei în Republica Moldova, 1999. Primul Raport naþional al Republicii Moldova prezentat la Conferinþa III minesterialã Mediul ºi Sãnãtatea, Londra, 16-18 iunie 1999 (The State of Environment and Population's Health in the Republic of Moldova. First National Report for the Third Ministerial Conference on Environment and Health, London, June 16-18, 1999). Chisinau, 40p.

Environment Performance Reviews. Republic of Moldova, 1998. United Nations. New York and Geneva. P. 67-72.

Guidelines for Drinking-water Quality, 2004. Third edition. World Health Organization, 2004. V.1. http://www.who.int/water_sanitation_health/publications/en/

Opopol, N. Environment, 2002. Health, and Sustainable Development in Transition Countries / Social Sciences and Political Change. Promoting Innovative Research in Post-Socialist Countries. Philosiphy & Politics Series No 9. Cassling R.&Fragniere G. P.I.E.-Peter Lang. Bruxels-Bern-Berlin-Frankfurt/M-New York-Oxford-Wien. P 257-266.

Opopol, N. 1990, Hygiene Estimation of Total Amount of Incorporated Nitrates with Foods and Water in Human Body in Russian), 376 p.

Republic of Moldova Environmental Health Report, 2003. (Unpublished report presented to WHO. 2003. 19 p.

Ropot, V. 1998. Probleme privind calitatea, folosirea ºi protecþia apelor in Republica Moldova (Aspects concerning quantity, utilization and protection of waters in Republic of Moldova) // Rezumatele comunicarilor celei de a treia Conferinte Internationale stiintifico-practice "Apele Moldovei", 25-26 februarie 1998. Chisinau, P.28-33.

Ropot, V. 2002. Resursele de apa, cantitatea, calitatea, utilizarea ºi protecþia lor (Resourses of water, their quantity, utilization and protection) // Studii si comunicari practice privind managementul resurselor de apa in conditiile unui mediu vulnerabil (materialele seminarului din 20-23 noiembrie 2001). Chisinãu, Editura “Universul”. P.16-31.

Salaru, I., 2004. Sãnãtatea populaþiei în dependenþã de calitatea apei folosite în scopuri potabile (Human health in relation with the drinking water quality) // Studii si comunicari practice privind managementul resurselor de apa in conditiile unui mediu vulnerabil (materialele seminarului din 20-23 noiembrie 2001). Chisinãu, Editura “Universul”. P.60-63.

Sãnãtatea copiilor în relaþie cu mediului, 2004. Raport naþional (Children’s Health and Environment. National Report). Chiºinãu, 2004, 52 p.

Starea mediului în Republica Moldova în anul 2002; 2003. Raport naþional (State of Environment in Republic of Moldova; National Report) (2003). Ministerul Ecologiei, Construcþiilor ºi Dezvoltãrii Teritoriului al Republicii Moldova / Institutul Naþional de Ecologie. Chiºinãu, 144 pag.

Starea mediului în Republica Moldova în anul 2003; 2004. Raport naþional (State of Environment in Republic of Moldova; National Report) (2004). Ministerul Ecologiei ºi Resurselor Naturale a Republicii Moldova / Institutul Naþional de Ecologie. Chiºinãu, 130 pag.

Starea sanitaro-igienicã ºi epidemiologicã, indicii de activitate a serviciului sanitaro-epidemiologic de stat (SSES) conform raportelor statistice a organelor ºi instituþiilor SSES pe a.2001; 2002. (Sanitary-hygienic and epidemiological condition, state sanitary-epidemiological service (SSES) activity indicies according the statistical reports of 2001 year), Chisinau, 2002.

Starea sanitaro-igienicã ºi epidemiologicã, indicii de activitate a serviciului sanitaro-epidemiologic de stat conform raportelor statistice a organelor ºi instituþiilor pe a.2002; 2003. (Sanitary-hygienic and epidemiological condition, state sanitary-epidemiological service activity indicies according the statistical reports of 2002 year), Chisinau, 2003.

Water and Health in Europe, 2003. A joint report from the European Environment Agency and the WHO Regional Office for Europe. WHO Regional Publications European Series, No.93. 222 p.

WATER MANAGEMENT IN MOROCCO

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Abstract

Morocco faces a serious challenge in terms of water resources management over the near- and medium-terms, both in terms of quantity and quality. The quality of superficial and groundwater resources are currently affected by i.) pollution from rejected domestic and industrial wastewater, ii.) leakage of fertilizers and phytosanitary products and iii.) soils erosion and transport of sediments. A new water law has been promulgated in 1995. It provides a comprehensive framework for integrated water management. This new law constitutes an efficient juridical tool to develop more considerable efforts for water use and mobilization in order to make them compatible with aspirations of socio-economic development of Morocco in the 21 century.

Key words: moroccan water resources/ mobilization and uses/ pollution sources/ fertilizers/ transport of sediments/ efficient juridical tool/

1. Introduction

Morocco is known for its water resources that are limited and irregular in time and space. Due to the semi-arid to arid climate that reign in the major part of the territory, precipitation remains weak compared to the bordering countries of the North of the Mediterranean. With episodically dryness, the water resources undergo a deterioration of their quality by the various pollutant emissions, the domestic and industrial wastewater. In the other hand, these resources are increasingly scarce due to a continued growth in demand,

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 177–180.

an improvement of life standards, as well as some industrial and agricultural developments.

In addition to the cyclical droughts that hinder water resources mobilization, the pollution of rivers and underground water reserves increasingly threatens water usage and drinking water production, in particular. In fact, the lower the quality of raw water, the more its treatment is complicated and costly.

2. Mobilization and uses of the water resources

Except in the north–west areas and Atlas mountains, the rainfall in Morocco remains low in comparison to the north Mediterranean countries. The mean annual rainfall varies between 500 to 2000 mm in the northwest of Morocco, to less than 100 mm in the southeast region of the country. A century rainfall data analysis shows that the climate of Morocco is principally characterized by drought. In general, the annual mean of total rainfall in Morocco is estimated to about 150 billion cubic meters, among these 121 billion cubic meters are lost by evaporation / transpiration and about 29 billion cubic meters reach superficial stream and ground water. The surface water flow estimated to 20 billion cubic meters are closely linked to rainfall and evaporation conditions. About 65% of available surface water resources of Morocco are located in the north and the center of Atlantic basins. Three big basins, namely Sebou, Bou-regreg and Oum Rbia, hold alone more of the 2/3 of the hydraulic potential of the country. Mobilized water reaches 56 % of the potential (Blaghen, 2002; Mandi, 2002).

The potential of groundwater resources is estimated to 4 billion cubic meters per year, with more than 50% located in the center and the north of Morocco. Groundwater resources constitute an important quantity of the national hydraulic heritage and represent the only water resource of desert area.

All these resources are submitted to extremely cyclic variations. Sharped cycles of drought have important consequences on the national economy particularly in agriculture. Water resources are also affected by continuous increase of water needs due to the fast evolution of the population, improvement standards of living, urban and industrial development and extension of modern agriculture. The consequences of these pressures are an increased deterioration of the Moroccan water resources quality.

The population growth (11,626 millions in 1960; 26.074 millions in 1994 and about 30 millions at present) and the social and economic development increased water needs in drinking water, industry agriculture and energy. These water needs were partially satisfied through increased mobilization of surface and groundwater resources with high cost of investment (Mandi, 2002).

The irrigation is the principal user of water in Morocco with nearly 90% of the total request, whereas the remainder is used for the provisioning of the population with drinking water and for the industrial sector. Industry and all confused sectors consumes 1.088 billion cubic meters of water including: 81% sea water, 14% comes from surface waters, 4 % of drinking water and 1% of underground water. The demand for drinking water mobilizes currently more than 700 million cubic meter per year. The rate of service road is 80% in urban environment and 30% in rural medium, where 70% of the population consumes less than 20 litters/day/habitant, which represent nearly 1/6 of the daily consumption of a townsman.

3. Water management

Morocco has a surface of 447.000 km², a population of 28 million in 1999 and an average population growth of 1.8 % annually over the period from 1990 to 1999. Almost 55 percent of the total population of the country was urban. The access to clean water increased from 32 % of the total population between 1982 and 1985 to 52 % by 1990 to 1996 (World Bank, 2000; Tortajada, 2003).

In 1995, the Moroccan government emphasized in its National Environmental Strategy that the priorities in term of environmental management would be on water, air, solid waste and soil-related issues. In term of water management, the lack of industrial and domestic wastewater treatment facilities represent a serious threat to the quality sources in the country, and thus the health of the population and ecosystems. Approximately, only 5 percent of all urban wastewater produced is properly treated. The current municipal wastewater market is estimated at 5 Billion US$ (World Bank, 1995).

Morocco faces a serious challenge in terms of water resources management over the near- and medium-terms, both in terms of quantity and quality. Considering the importance of water to economy and social and environmental conditions of the country, it is absolutely critical that water resources should be managed efficiently and equitably for both the current and the future generations. At present, the mobilizable water resources are exploited at 65%. The elaborated hydraulic balance sheet shows that water deficit situation is already registered at some basins in Morocco (Mandi, 2002).

The quality of superficial and groundwater resources are currently affected by: i) pollution from rejected domestic and industrial wastewater, ii) leakage of fertilizers and phytosanitary products and iii) soils erosion and transport of sediments (Ministère de l'Aménagement du Territoire, de l'Urbanisme, de l'Habitat et de l'Environnement, 2001).

To meet the challenges posed by the growing water scarcity, Morocco has adopted an integrated approach to water resources management through mutually reinforcing policy and institutional reforms. A new water law has been promulgated in 1995. It provides a comprehensive framework for integrated water management. This new law constitutes an efficient juridical tool to develop more considerable efforts for water use and mobilization in order to make them compatible with aspirations of socio-economic development of Morocco in the 21 century (Echihabi, 2002; Rafik, 2002).

4. References

Blaghen M., 2002, in Applied research in water quality intended for drinking water supply in Morocco. Workshop on Integrated Management of water limited resources. Marrakech, May.

Echihabi L., 2002,in Applied research in water quality intended for drinking water supply in Morocco. Worksho-+p on Integrated Management of water limited resources. Marrakech, May.

Mandi L., 2002, in Applied research in water quality intended for drinking water supply in Morocco. Workshop on Integrated Management of water limited resources. Marrakech, May.

Ministère de l'Aménagement du Territoire, de l'Urbanisme, de l'Habitat et de l'Environnement, 2001. Rapport sur l'Etat de l'Environnement du Maroc, Département de l'Environnement, October.

Rafik M., 2002 in Applied research in water quality intended for drinking water supply in Morocco. Workshop on Integrated Management of water limited resources. Marrakech, May.

Tortajada C., 2003. Professional Women and Water management: Case study from Morocco. IWRA, Water International, Volume 28, Number 4, Pages 532-539.

World Bank, 1995. "Middle East and North Africa. Environment Strategy, Towards Sustainable Development, Middle East and North Africa Region." Report N°. 1360.1-MNA. Washington, D.C.: The World Bank.

World Bank, 2000. "World Development Report 2000/2001. Attacking Poverty." Washington, D.C.: The World Bank.

THE ROMANIAN NATIONAL ACCIDENTAL AND INTENTIONAL POLLUTED WATER MANAGEMENT SYSTEM

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Abstract

In Romania, the specificity of water resources, namely, the fact that not all the quantity used in the production processes is actually consumed, results in the return of an important part to the source, with damaged quality parameters, which in its turn is the water source for downstream users. The management of industrial and urban wastewaters is far from satisfactory, and require rehabilitation and development measures, while less than 50% of the population is connected to the public sewage system.
Key words: Romanian waters/ characteristics/ accidental pollution/ intentional pollution/ measures/ management /sustainable development

In Romania, especially due to the multi-functionality and multiple uses of the water, to the inconsistency between distribution in time and space of water resources and requirements, as well as due to the water recycling phenomenon along watercourses, coordination of the activities of management and use of water resources proved to be highly necessary. At the same time, due to the uneven distribution of inner rivers within the territory and the minimized use of the Danube waters, because of its peripheral position along the southern boundary of the territory, it was necessary to carry out works for development of hydrographical basins. This led to the setting up

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 181–184.

of storage lakes, of a total volume of more than 13 billion m^3, equipped with all works related to the complex activities of water development, by-pass galleries and channels for the transfer of the water resource from overflow basins into deficit basins or within the same hydrographic basin.

Fighting floods in hydrographic basins requires performance of river damming and regulation works, as well as harnessing of floods or forestation for protection of water resources.

As shown by the "Romanian Waters" National Authority (2004), the total water demand increased from 1.4 million m^3 in 1950 to more than 20 million m^3 in 1989, due to population increase and development of industry and agriculture. The main trend recorded after 1989 was an important decrease of unused water flows. Today, water takeoffs decreased from 20.4 billon m^3 to 7.24 billon m^3 due to: reduced economic activity, reduced water consumption in technological processes, reduced losses, implementation of the economic system in water management.

All hydrographic basins include more than 1,000 industrial sights, agricultural and stock raising units and localities with a major impact on water resources. Almost half of these sights are equipped with water purification plants operating improperly, and approximately 20% of them are not equipped with water purification plants, the result being both pollution sources and losses of substances, which are discharged along with wastewaters. All these activities may have a devastating impact on water ecosystems, with damage of the natural ecological cycle, on humid areas, on the proper performance of overall economic activities, if such activities are not properly planned and managed.

In Romania approximately 25% of waste waters are discharged directly (without being purified) in the recipient waters, 19% are purified only mechanically, 56% are purified by the secondary biological stage, and at present there is no advanced biological purification (tertiary) process.

More than 67% of urban water purification plants are over 15 years old, many sewage systems have been neglected in the last decades, and repair and maintenance works are necessary to avoid pollution of surface and underground water. The resulting mud is stored mostly in a dry state on available lands, in contradiction with the modern methods of wastewater management. Priority must be given to improvement of the purification degree for the current level of sewage systems. The problems caused by industrial wastewaters must be solved by an integrated pollution preventing strategy, based on latest generation non-pollutant technologies, as states the National Strategy for Sustainable Development of Romania (Governul Romaniei, 1999). The prevention principle for the control of pollutants, with higher risk for the human health will have to be largely used. The development of an integrated strategy (in point of both quality and quantity) by hydrographic basins is highly important, requiring an effective control of pollution sources in agriculture (diffused). Under these circumstances, water management must cope with the new problems by adopting an adequate approach in the analysis of policies and options in order to contribute to a correct decision making process concerning resource management according to Romania's specific conditions.

For an integrated water resource management, the Ministry of the Environment and Water Management as well as the "Romanian Waters" (Apele Romane, 2004) National Authority, took technical, economic, legal, organizational and social measures, at central level and at the level of hydrographical basins, the undividable geographical entities on which water resource management is carried out. Mention must be made that development and regular updating of the frame schemes of water development and management by hydrographical basins, in order to establish the fundamental orientations concerning a sustainable, unitary, balanced and complex water resource management. From a legal point of view, the Law on Waters No. 107 / 1996 creates the legal framework necessary for a sustainable water resource development.

As a country located downstream within the Danube's hydrographic basin, Romania cooperates on a bi- or multilateral basis within international agreements or conventions, in order to apply the principles and achieve the goals agreed by signing Agenda 21 at the International Conference in Rio de Janeiro. Thus, Romania is a signatory country to two important conventions, namely the Convention regarding the use of cross-border watercourses and international lakes and the Convention regarding cooperation for the protection and sustainable use of the Danube , being among the first counties, which ratified these conventions.

At present, Romania is one of the EU associated countries, which channels all its efforts to become a member country of this community. In this context, the environmental and particularly water management policy has become a cross-sector policy whose performance strategy must be applied in a responsible way to the other sectors (considered until now as main or potential pollutants) such as agriculture, industry and transport.

References

Apele Romane" Compania Nationala " [*"Romanian Waters" National Authority*], 2004, internal report of the "Romanian Waters" National Company, Bucharest.

Guvernul Romaniei, 1999, Strategia Nationala pentru Dezvoltare Durabila [*National Strategy for Sustainable Development of Romania*], Bucharest, pp. 29-32.

RISK FOR PREGNANT WOMEN DUE TO BIOLOGICAL AND CHEMICAL POLLUTION OF DRINKING WATER

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Abstract

Recently acts of terrorism are directed against the peace population, and for this purpose are used explosive, poison gases, there was more accessible a biological and chemical weapon. This problem to become more actual in conditions of the terrorism connected to an opportunity of use for these drinking of water sources. Especially vulnerable group are pregnant women. In conditions falling of birth rate and high death rate in Russia the problem of protection of reproductive health of the population is the major direction of the state policy determining national safety.

Key words: drinking water/ terrorism/ health/ reproduction impairment/ MAC values.

1. Influence of terrorism at deliberate pollution of potable water on an organism of the pregnant woman

One of possible ways of committing terrorist act is drinking water, one of the most vulnerable targets which living things and human beings feel vital necessity for. However, though drinking water is regularly controlled, a chance of direct immediate action aimed at destruction, further causing acute or chronic pathologies in the population is real Of great vulnerability are group

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 185–191.

due to deliberate poisoning of drinking water are pregnant women and feeding mothers (Sivochalova., Feytshans., Denisov., and Golovaneva, 1999).

In figure 1. possible mechanisms of development of complications of pregnancy from influence of biological and chemical agents (Saveleva., 2000). The sensitiveness of vessels to the vessel-active substances.

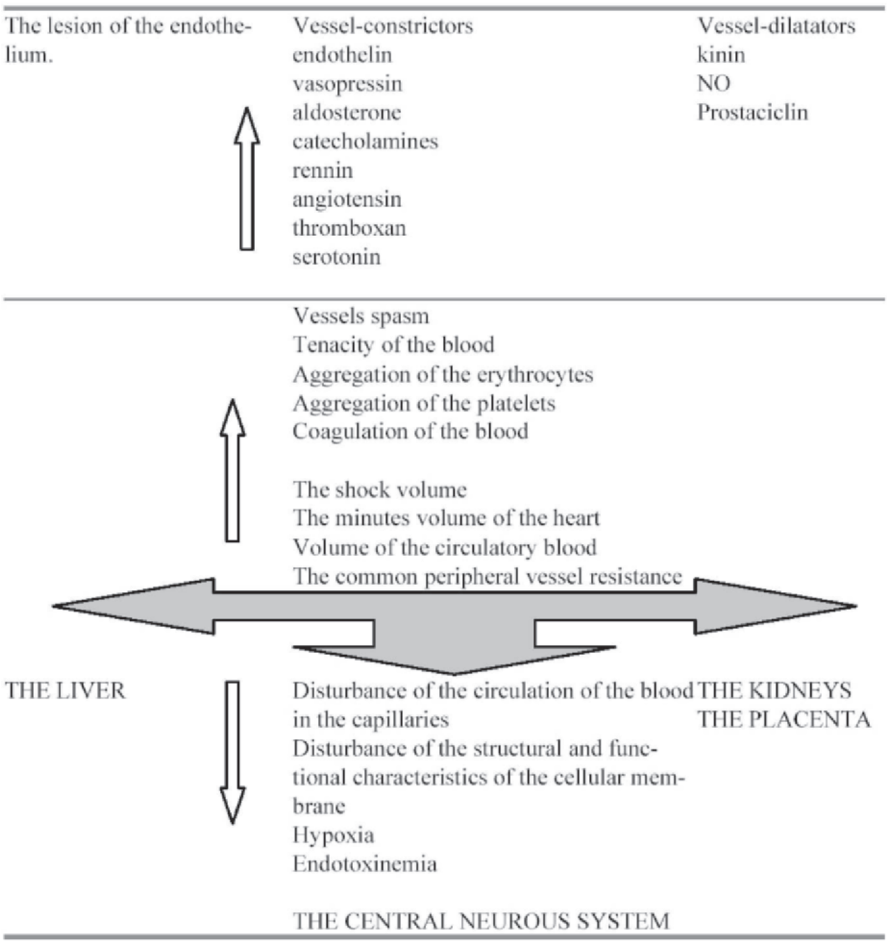

Figure 1. The mechanism of the rise pregnancy complications by the influence agents (biological, chemical).

2. Risk for pregnant women developed due to pollution by biological agents of drinking water

The main source of biological danger to drinking water to which pregnant women can be exposed are microorganisms as they represent the most extensive, diversified and least investigated part of all alive world. Bio-danger can be defined as health hazard for human life, and at pregnancy the threat is growing with regard to health and life of a mother and her posterity. One of the basic sources of biological danger is biological terrorism in all its forms including deliberate pollution of drinking water. Bio-risk is defined by concentration of an agent and is expressed as a flash of epidemic or bio-accident. To biological agents that can be used by terrorists, according to classification proposed by RAMS Academician A.A.Vorobjeva, activators of smallpox, plague, Siberian ulcer, botulism, Venezuelan horses encephalitis, rabbit-fever, q-fevers, illnesses of Marburg, influenza, glanders and typhus should be attributed to. First of all, it is connected with high contagiousness of given diseases, by transfer of the activator, high pathogenicity for a person and a number of other factors. Clinical diagnosis of particularly dangerous infections for pregnant women represents significant difficulties as the majority of doctors are familiar with these diseases only theoretically. Besides during last epidemics many infections proceeded atypically, were characterized by change of semiology and display of complications not peculiar to classical picture, that especially is at a loss current of the pregnancy having the symptoms and complications, sometimes similar to infections. It is necessary to note also that treatment of extremely dangerous infections for pregnant women in many respects has empirical character (Shuvalov, 1999). The estimation of separate medical products and methods of therapy cannot be carried out according to principles of demonstrative medicine as the least dangerous the preparation is necessary for a fetus. Besides there is one more problem of therapy quickly developing resistance of activators to antibacterial and antiviral preparations that have been promoted by their irrational application, and also physiological condition of a woman. Pregnancy aggravates decision-making with regard to existing treatment alternatives The data of epidemiological researches indicate, that at pregnancy infection risk increases. Risk of developing a pathology at the pregnant woman is great, also owing to decrease in the levels of factors of immunological protection (factor of the phagocytic protection, mechanisms of specific immune potential and an opportunity of influence of microorganisms with lower prick - index. It is true that infection affecting a pregnant woman, may trigger development of pregnancy complications such as threat of interruption, eclampsy, spontaneous abortions and also influence intra-uterine development of a fetus to cause congenital developmental anomalies, delays of intra-uterine development, fetus hypoxia.

Preventive measures directed to disinfection of drinking water not always have positive character. For example, increase in concentration due to chlorination of drinking water can evoke the mechanism of negative deliberate influence on a human body. Chlorine-containing mixtures are one of the basic reagents used at water-purifying stations for disinfection of water. Basic agents of adverse influence on human organism are chlororganic substances, which are formed during disinfection of drinking water by chlorine. During two-level technology of water-preparation mutation of water considerably increases, leading factors thus are the processes lowering oxygenation and chromaticity, and also high contents of free active chlorine. In a planting network mutagen activity of water, as a rule, increases during transportation in the summer period bring particularly high. Leading factors thus are technological processes http://www.bibalex.org/Einstein2005/lowering parameters turbidity, oxygenation and ðÍ. The factors promoting increase mutation of water during transportation through planting network are, high levels of active free chlorine, low values ðÍ and alkalinity. Statistically significant positive factors of correlation between parameters of pollution of drinking water products of chlorination and level of spontaneous abortions and frequency of mutations in somatic cells of children in 12 Russian cities have been revealed. It agrees to the aforesaid of a measure of preventive maintenance directed on prevention of biological pollution of drinking water should be under the constant control of public health services as it can be used by terrorists.

3. Risk for pregnant women because of chemical pollution of drinking water

Poison gases in drinking water can be various chemicals. As to toxicity level all chemical compounds can be divided into 6 groups.

- Extremely toxic and highly toxic substances are:
- Some compounds of heavy metals (mercury, lead, cadmium, selenium, nickel, zinc);
- Compounds containing cyanic group (a hydrocyanic acid and its salts);
- Compounds of phosphorus and phosphorus-organic chemicals;
- Halogens (chlorine, bromine);
- Phosgene. Very toxic substances:

- Mineral and organic acids (sulfuric, nitric, acetic, phosphoric and others);
- Alkalis (ammonia, caustic potassium and others);
- Compounds of sulfur;
- Chloride and brome methyl;
- Some spirits and aldehydes of acids;
- Organic and inorganic amino compounds (aniline, three benzene, nitro toluene, phenols and their derivatives).

Influences on an organism of a pregnant woman due to poisoning of drinking water with extremely toxic, very toxic and moderately toxic substances can lead to a lethal outcome for the woman and a fetus or seriously impairs health of a woman and a fetus (for the woman to become the reason of development eclampsy as consequences of infringement neuro-endocrine interactions, spontaneous abortion; for a fetus: congenital developmental anomalies, with damage of structure of the hereditary device, hypoxia a fetus, placenta insufficiency. On table 1 chemical substances which can be used at a deliberate poisoning of potable water, and their influence on the pregnant woman are submitted.

4. Measures of preventive maintenance (Izmerov et al. 2001)

Measures of preventive maintenance of pollution of potable water which are necessary for carrying out the most pregnant woman feeding with mother:

- Always it is necessary to remember, that potential pollutions potable water can become the reason of acute or chronic problems with health, and sometimes and death;
- It is necessary to use only checked up by the centers of sanitary protection water and to have a necessary stock;
- At impossibility of check to use water-purifying filters; At impossibility of check, sense organs can serve as the tool for definition of quality of potable water.

TABLE 1. Possible failures of influence of conditionally toxic chemical substances on an organism of pregnant women.

Substance	Influence on current of pregnancy	Influence on a fetus and newborn	Influence on a lactation
Fluorine	It is not found out	Intra-uterine defeat of a fetus, congenital developmental anomalies of a bone skeleton	It is not found out
Trichlorethylene	Pregnancy with abortive outcome, premature birth and complications in sorts	It is not found out	It is not found out
Gasoline	Complications of pregnancy, sorts, infringement of hormonal function of a placenta	Stillbirth, hypotrophia fetus	Infringement of a lactation
Chloroethylene	Pregnancy with abortive outcome	Stillbirth, congenital developmental anomalies	It is not found out
Arsenic	Complications of pregnancy, sorts, pregnancy with abortive outcome	A delay of intra-uterine development, congenital developmental anomalies of bone, nervous, urinogenital system	Infringement of a lactation
Cadmium	Pregnancy with abortive outcome, premature birth	Congenital developmental anomalies of a structure of an obverse skull, stillbirth	It is not found out
Mercury	Pregnancy with abortive outcome, premature birth, functional insufficiency of a placenta, pathological current of sorts	A delay of intra-uterine development, congenital developmental anomalies	Infringement of a lactation
Lead	Pregnancy with abortive outcome, premature birth	It is not found out	It is not found out
Heptochlorine	Pregnancy with abortive outcome, premature birth	It is not found out	Infringement of a lactation
Manganese	Pregnancy with abortive outcome, premature birth, eclampsy, complication of sorts	A delay of intra-uterine development	It is not found out
Toluene	Premature birth	A delay of intra-uterine development, congenital developmental anomalies	It is not found out
Selenium	It is not found out	Congenital developmental anomalies	It is not found out
Chloroform	Pregnancy with abortive outcome, premature birth, eclampsy	It is not found out	It is not found out
Pesticides	Complications of pregnancy, sorts, intra-uterine destruction of a fetus	Congenital developmental anomalies, stillbirth, hypotrophia fetus	Penetration into milk

5. References

Sivochalova O.V., Feytshans I.L., Denisov E.I., and Golovaneva G.V., 1999. The right of workers on reproductive health: priorities today and in the 21st century. Human rights in Russia: declarations, norms and life. Proceeding to the International Conference. M. pp. 214-217.

Saveleva G.M., 2000. Obstetrics. Ì. pp.408-409.

Shuvalov Å.Â., 1999. Infectious diseases. Ì. p.654.

Izmerov N.F., Sivochalova O.V., Denisov E.I. 2001., Medical and social problems of reproductive protection and decision making in this field. Actual problems of reproductive health in conditions of anthropogenous pollution. Proceedings to the International Symposium. Kazan, pp. 5-13.

CHEMICAL TERRORISM: THREATS TO WATER SUPPLIES

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Abstract

Although for practical reasons, terrorist attacks on water systems are considered less likely than on other targets, threats to drinking water cannot be ignored. A large-scale chemical sabotage of drinking water, even insufficient to cause casualties, could still have disastrous socio-economical consequences. There is therefore a need to maintain a high-level of security around water treatment and distribution facilities, especially those supplying critical infrastructures, and to develop emergency preparedness programs at both the local and national levels.

Keywords: chemical terrorism/ targets/detection/ warning system/ risk assessment.

1. Introduction

In the wake of 11th September 2001 and the anthrax incidents, potential terrorist attacks on the drinking water supply systems have become an important matter of concern and have been debated in different arenas (Meinhardt 2004; American dietetic association 2003; Sallem 2003). Although for practical reasons, terrorist attacks on water systems are considered less likely than on other targets, threats to drinking water cannot be ignored and several governments and agencies have already taken actions to prevent and

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 193–199.

mitigate the risks of such deliberate contamination. Among the most likely candidate biological agents for terrorist actions, only a few are effectively transmissible via drinking water and in most cases the likelihood of major public health impact is limited by standard water treatment inactivating most water-borne pathogens. By contrast, toxic chemicals appear a much more serious threat since some of them are much more readily accessible, are less likely to be removed during water treatment and if properly handled, may not harm the terrorists themselves. Some important key issues concerning both the evaluation and prevention of terrorist threats to drinking water, and more specifically threats that are chemical in nature will be addressed here.

2. Chemicals treats, their targets and detection

In theory there is a plethora of deadly chemicals agents which can be added in drinking water with a view to contaminating entire populations. Fortunately, not all of them are suitable for terrorist attacks on water supplies, as this would require the chemicals to be soluble and stable in water, to resist to standard water treatment such as chlorination and to be undetectable by taste, color or odor at harmful levels. This already excludes a whole range of organic chemicals that are almost insoluble in water such as dioxins, PCBs or the organochlorine compounds. In practice, the spectrum of candidate poisons is further narrowed by the sheer volume of the water tanks or reservoirs to contaminate, which is usually so large that it requires a huge dose of chemicals. A chemical sabotage by classical inorganic poisons (arsenic, cyanide, ricin,) of a large water reservoir would indeed require, in order to cause fatalities, very large amounts which can be difficult to obtain or to handle. However, a range of extremely toxic chemicals such as those used in chemical warfare do exist, but most of them are either very difficult to obtain as they cannot be purchased and their production requires a high level of scientific and technological expertise. A more readily available source of poisonous substances is represented by the dual use chemicals which are produced in large volumes for peaceful purposes (pesticides, precursors or intermediates in the chemical or pharmaceutical industry) but might be deviated from their habitual use. Many of these chemicals are cheap and can therefore be bought in large quantities, if not simply stolen from remote or insufficiently protected industrial sites. However, the possibility of ecoterrorism cannot be excluded, the terrorists deciding to use doses that are too low to cause casualties but sufficient to create a large scale panic and a disruption of water supply affecting a given civilian population or infrastructure. Good candidates for such a scenario could be for example radioactive chemicals, long-lived radioisotopes in particular, some water-soluble potent carcinogenic or neurotoxic agents.

Threats to drinking water supply include threats to drinking water sources, treatment, distribution systems as well as drinking water storage facilities. Large reservoirs and dams represent in theory the most vulnerable targets of terrorist assaults requiring thus a high level of protection. These sources of water are indeed more difficult to protect and the water stored in these facilities is usually of such quality that it requires limited treatment prior to general distribution. By contrast, water facilities using surface water should be less vulnerable as the water undergoes extensive treatment and controls prior to its distribution. This usually takes place in enclosed facilities, which are easier to secure than open air water reservoirs. However, as by definition terrorist capabilities and targets are largely unpredictable, any water system, even the smallest one, could be targeted, provided a climate of terror disrupting normal economic and social life can be generated. In fact, the target could even simply be bottled water or drinks produced with drinking water from any source, throwing suspicion on a given type of drink or trademark. The impact of such an attack should not be underestimated, as highlighted by the Coca-Cola incident in Belgium in 1999 (Nemery et al. 2002). To get an idea of the number of possible targets, it is important to bear in mind that in the US alone, there are more than 150,000 public water treatment and distribution facilities.

The major difficulty with intentional chemical water contamination lies in its detection and warning system. The procedure for chemical contamination of drinking water would not usually require the use of explosive or spraying systems so that the contamination could easily remain silent for several days or weeks, as long as there is no outbreak of water-related poisoning emerging from the normal disease-pattern. It could even pass unnoticed if the water surveillance systems are not designed to detect the specific chemical type or else are scheduled to operate at regular intervals which do not coincide with the contamination incident. The ability to detect rapidly an incident will therefore largely depend on the utility management of water surveillance systems, especially its analytical capacity and frequency of control measurements. In view of the wide variety of potential water contaminants and the difficulty of implementing real-time monitoring for most of these, the weakest link in the safeguarding of drinking water certainly lies in the limited detection capacity of current monitoring systems.

3. Risk assessment and management

There are several parameters which need to be considered when evaluating the potential impact of a chemical attack on water supplies. The first thing to determine is the exact nature of the contamination. It is important to know whether the contamination is due to a single compound, or a mixture of chemicals or whether the contaminants can be associated with toxic breakdown products. The transmissibility of the chemical along the water distribution is another important issue, since, depending on the physico-chemical properties of the contaminant and the water treatment technologies in application, the contaminants can either be activated or completely eliminated by precipitation, adsorption or inactivation before reaching the consumers. Organic contaminants for instance will be efficiently removed by activated charcoal filters while chlorination will inactivate some toxins (see Table 1) and techniques such as reverse osmosis and distillation eliminate most hazardous chemicals.

TABLE 1. Examples of potential chemical threats to water supplies.

Chemical warfare	Toxins
BZ	
GA	anatoxin A
GB	botulinum
HC	nicotine
HD	microcystins*
Lewisite	ricin*
LSD	saxitoxin*
VX	solanine
	T-2 mycotoxins*

* resistant to 1-5 ppm active chlorine (adapted from Sallem 2003)

This indicates that the point of entry of the contaminant in the water supply system is a critical determinant. Since the total amount of chemicals added is usually unknown, risk assessment should be based on actual chemical measurements in drinking water, from which the risk of acute and long-term health effects can be estimated. Key aspects are of course the time scale of the incident as well as the size of the affected populations. As indicated above, unless the terrorists had access to large amounts of extremely toxic chemicals, the risk of acute poisoning by toxic chemicals added to water supplies appears limited, its impact being mainly psychological and socio-economical. As to the possibility of serious long-term health consequences, which might be feared from cumulative or carcinogenic chemicals, they are likely to be significant only for those incidents which would affect large populations and would not be too limited in time.

For those contaminants which are regulated in drinking water, a rapid risk assessment can be made by referring to current guidelines, but it is then essential to take the time factor into consideration as these guidelines are indeed designed to protect public health during lifetime. Most of these guidelines are derived from critical exposure levels (NOAELs or LOAELs) after the application of uncertainty factors taking into account differences in sensitivity between individuals or species. In practice, this means that after taking into account the duration of exposure, for a majority of regulated contaminants, a very large exceedance of the drinking water guidelines or standards would be necessary for the intake over a short period of time to reach levels causing adverse effects.

In case of chemical warfare agents, a rapid assessment of the likelihood of acute effects on public health can be made by referring to the standards for military drinking water published by the US National Research Council. These guidelines provide the concentrations in drinking water that should not cause acute adverse effects nor degradation of military performance following a consumption for 7 days of 5 to 15 liters of water. For instance, for a consumption of two liters of water per day, the guideline ranges from 15 μg/l for an extremely toxic compound like GD up to 15,000 μg/l for cyanide (National Research Council 1995).

In order to be really helpful and provide sound guidelines, risk assessment in the context of a chemical attack on water supply systems must meet several criteria. First, the risk assessment must be performed by an authoritative public health institution with all guarantees of competence and independence. It is also essential that risk assessment be done under transparent conditions with rapid communications to the public and to the medical community concerning prevention, damage limitations, diagnosis or treatment. The worst case scenario is that of a complete silence on the part of the authorities, leaving the place for dissemination of wrong messages, anxiety for those who have consumed contaminated water and an unnecessary level of scare. Risk assessment must be communicated in clear and quantitative terms. It is counterproductive to reduce the risk communication to a listing of the potential health hazards of the contaminants without clearly indicating the exposure conditions with may actually lead to acute or chronic health effects. Finally, the risk assessment must also be practical, i.e. provide clear guidance for those who might have consumed the water, and about the permissible usage of water in addition to drinking (bathing, showering, cleaning, washing, cooking, etc.) and the possible water treatments for sanitation purposes.

4. Safeguarding measures and preparedness programs

Even if terrorist threats have no yet targeted water supplies, the possibility of sabotaging drinking water with chemical agents must be borne in mind. Several actions can be taken at different levels to minimize or mitigate the potential health risks and socio-economical impact.

- Safeguarding the water facilities. The first line of defense against acts of sabotage certainly lies at the level of water facilities. This implies several initiatives, such as vulnerability assessment, security enhancement, reinforced protection and surveillance.

- Increasing the efficacy of water monitoring and warning systems for the rapid detection of chemical threats. In contrast to most direct terrorist activities, drinking water contamination can be much more difficult to detect. In particularly critical areas (large reservoirs or infrastructures), water quality monitoring systems could be improved to cover a broader range of chemical agents including specific bacterial toxins and radioactive materials.

- Increasing the efficacy of water treatment systems in order to incorporate processes inactivating or removing chemical and/or biological agents. The potential of terrorist attacks should be integrated into the design and performance levels of drinking water facilities. A variety of water treatment technologies such as UV, ultrafiltration, activated charcoal filters, reverse osmosis can indeed provide efficient barriers against many hazardous agents. Reverse osmosis and activated charcoals currently represent the best technologies used by the US army.

- Increasing the emergency preparedness at local, national and international levels. This would require the implementation of rapid alert systems, the elaboration of emergency response plans, the storage of equipment and reagents for detection and neutralization of specific chemical, biological or radioactive agents.

- Strengthening international collaboration in the following areas: identification of terrorist activities, the production, sale and use of chemical warfare and dual agents, the development of technologies to combat terrorism and the networking of intelligence services.

5. Conclusions

In comparison with other types of terrorist threats, chemical threats to water supplies appear relatively limited because of the very large amounts of agents needed to contaminate drinking water supplies. However, a large-scale chemical sabotage of drinking water, even insufficient to cause casualties, could have a mighty social and economical impact which cannot be underestimated. There is therefore a need to maintain a high-level of security around water treatment and distribution facilities, especially those supplying critical infrastructures, and to develop emergency preparedness programs at both the local and national levels.

6. References

American Dietetic association. 2003. Position of the American Dietetic Association: Food and water safety. *J Am Dietetic Association* 103, 1203-1216.

Meinhardt, P. 2004, Physician Preparedness for Acts of Water Terrorism. Available from URL: http://www.waterhealthconnection.org/bt/index.asp

National Research Council. 1995. Guidelines for chemical agents in military field drinking water. Washington, DC: National Academy Press.

Nemery B., Fischler B., Boogaerts M., Lison D., Willems J. 2002. The Coca-Cola incident in Belgium, June 1999. *Food Chem Toxicol* 40, 1657-1667.

Sallem, H. 2003. Issues in chemical and biological terrorism. *Int J Toxicol*. 22, 465-471.

WATER FRAME DIRECTIVE – AN EFFECTIVE APPROACH FOR POLLUTION PREVENTION OF WATER SOURCES IN CASE OF EMERGENCIES AT RIVER BASIN LEVEL

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Abstract

The Drought in the period 1982-1994 had its natural influence on the amount of water resources in Bulgaria. The negative consequences of this process influenced all spheres of the social and economical life in the country, including those important for the Public Health, especially drinking water supply. Bulgaria is a country with limited water resources, which requires a clever management and balance of the available water reserve. The lack of professional management approach during the dry period, led to an abrupt and large-scaled collapse in the water supply system in the country.

Water Frame Directive - WFD 2000/60/EC suggest a new philosophy for integrated management and pragmatic strategy for protection of the quantity and quality of all categories natural waters at a level “river basin”, with stress on the drinking water sources and water reserves.

Key words: Water quantity/ quality/ drought/ dam/ management/ regime/ new approach

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 201–209.

1. Introduction and overview of the critical period

The first signs of the impending crises in Bulgaria chronologically appeared in 1982, when the precipitation and river runoff under the norm were observed. The drought had a local character and affected only the territory of Northern Bulgaria. It began in May-June and the driest months were September and October.

In the following years 1983-1985 the tendency gradually progressed. The precipitation and the river runoff decreased respectively to 85% and 70% of the normal. The temperatures were extremely high. The yields were low and the more and more frequent fires in the forests caused considerable damage.

In 1986-1990 the precipitation decreased to 77% of the normal values and the river run off down to 46% 1990 was extremely dry.

A great number of the regions in the country were caught in the crisis with the quantity of water. The number of settlements under regime of drinking water progressive increased. On the background of the political changes, the sporadic warnings of professionals in the water field about the impending crisis in water supply did not meet an adequate response.

The drought reached its peak in the period 1993-1994. These are the driest years in the history of the country, with precipitation of 72% of the normal and decrease in the river run off to 41%. The temperatures are record-breaking. The withering of forests and the numerous forest fires, spreading over enormous areas, caused irreparable damage. Very hard are the consequences for the agriculture. During this period the lowest yields of wheat and corn were observed. The water supply of the biggest cities was also disturbed. A number of dams were fully depleted and the quality of the drinking water got worse (Fig. 1). The drought assumed threatening size and grew into an unavoidable disaster, spread over the whole country. The average water demand in the country for basic purposes decreased to one third of that in 1989.

The dynamics of the water amount stored in dam "Iskar" during the dry period 1982-1994 are shown in Table 1. Most dramatically were the changes recorded in the last two years 1993-1994.

The dam is the main drinking water source of the capital Sofia, serving a population of 1 113 674 people in the critical years 1993-1994. The dam was almost fully depleted when the necessity aroused to allocate water for the industrial purposes and production of electricity. The available water volume was only 66 million cubic meters; this is less than the "dead volume" of 90 million cubic meters set by the design documents of the dam. The decision to apply water regime in Sofia, taken in May, was imposed in September, and the water supply of the residential districts of the city was drastically limited to one of every three days. During the regime from September 1994 to April 1995 about 65% of the water in the dam passed through a Drinking Water Purification Plant (DWPP) before being directed to water supply net. The rest of it and the small amounts of mountain water from the mountains Vitosha and Rilla were not purified and they were directed in the net only after chlorine disinfection (Bardarska and Dobrev, 2003).

According to the systemized data from the monitoring of drinking water, compared with the period before the regime, there were an increased number of samples deviating in quality from the normal in characteristics such as colour, iron, and manganese. With normal value for iron of 0.2 mg/l, the samples varied in the range 0.15-1.5 mg/l. With norm for manganese of 0.05 mg/l, the measured values were from 0.1 to 0.97 mg/l. The colour and turbidity of water, to a large extent, deviated from the usual. The observed abnormalities were a direct result of decreased quality of the row water in the dam during the regime period because of the fact decrease of the storage water amount in the dam (Gopina and Vasilev, 1998).

During the regime the microbiological water quality did not change considerably. However, there was found a presence of "faecal coli forms" in the raw water, and of some opportunistic pathogen bacteria (such as Pseudomonas aeruginosa, Pseudomonas fluorescens and Pseudomonas species) in the no-treated water and in water samples by the consumer. The opportunistic pathogenic microflora is usually isolated from the raw water. In this case, the diagnostics of samples from the water supply net had an indicative function by the complicated conditions. That was a result of aroused problems in the water treatment process (purification and disinfection), which are connected with the achievement of the necessary effectiveness and process-management by conditions of a water supply regime and a limited water quantity. The dynamics of the percentage of abnormal microbiological samples during the regime period shows that it was more than 10% and surpassed the admissible 5% agreed by WHO (WHO, 1996). This circumstance, the worsened hygiene conditions of living in a settlement with dense population of more than one million people, the numerous closed groups (universities, hospitals, military institutions etc.), the use of not properly investigated and/or controlled water sources create conditions for a more complicated epidemic situation and risk of waterborne diseases. The reason for the fact that there was no increase in the frequency of morbidity from the most common gastro-intestinal infection diseases, such as Hepatite A and Shigellosis, is large-scaled media preventive campaign of the hygiene and epidemiological services in Sofia (Gopina et al., 2003).

The objective analysis of the situation with the critical depletion of the "Iskar" dam and the water regime in Sofia coincides with that of the regions in the country with traditional perennial regime and their main water sources.

Table 2 represents the condition of water supply in the administrative centers in Bulgaria with the largest percentage of population on water regime.

As shown by Hristov et al. (2003), the water losses during the period 1982-1994 increased from 17% to 46,5%(2,6 times), and in 1995 they were more than 50%. The authors state that the reasons for the considerable losses are the amortized water supply net and the type of materials (80% asbestos-cement pipes), the poor management of the water supply systems, the lack of control over the use of water and the observance of the admissible limits, the lack of mechanisms for the participation of society in the management of water, the inadequate normative organization, etc.

The data from tables 1 and 2 confirm the lack of effective planning and management of the water supply sphere, including the years of the drought's peak.

The potentialities of the powerful system of water sources, built around the capital, several times surpass the needs of the population. On the other hand, for the large number of reserve water sources, including mineral, there was a lack of the enough data of water quality observation, necessary before to be used them by the population.

If an ingenious integrated management is carried out, having as a priority the drinking water supply, then Sofia, having an overall need of 180 million m^3, should not reach such a catastrophic lack of drinking water.

2. The new preventive approach

The Water Frame Directive (WFD 2000/60/EC) reforms EU water legislation by introducing a new model for water management. From an environmental point of view, the aim of this directive is the preventing from further deterioration and the achieving "good status" in all kind of waters. The WFD´s managerial approach – integrated water management at the river basin level - aims at ensuring overall coordination of water policy in the EU. Because of this fact the implementation of the WFD is strongly recommended as the best tool for protecting the quality and managing the quantity of the river waters and generally of all water resources.

The integrated river water management should be carried out as the following 6-step process:

- Set up River Basin Districts (RBDs)

- Catalogue the characteristics of the area RBD (different for the surface and the ground waters)
- Identify the environmental stresses (impact of the human activity and water use)
- Design and implement “basic” and ”additional” measures:
  “Basic” – pollution controls, controls on abstraction and losses, etc.
  “Additional” – to be used when the “basic” are not sufficient to achieve “good status”
- Monitor progress
- Revise the measures (if necessary) on the basis of such progress

The first set of “basic” measures according the 4-th step needs to be established by 2009, be fully operational by 2012 and up for review by 2015, and every 6 year thereafter. The measures have to be coordinated for the whole RBD and included in the River Basin Management Plans (RBMPs) to be produced for every RBD. The RBMPs will also contain the information derived from steps 1-6 and may be supplemented by the production of more detailed programs and management plans for sub-basin, sector, issue or water type, to deal with particular aspects of water management. At present Bulgaria is divided in four RBD – Black Sea RBD, Danube RBD, West-Aegean RBD and East-Aegean RBD and is finishing the preliminary frame for preparing the RBMPs.

3. Conclusion

The new approach WFD 2000/60/EC turns out to be, at present, the most effective and realistic strategy of preventing and minimizing of the negative consequences of expected or/and unexpected emergencies, connected with enough quantity and safety quality of drinking water for population.

The harmonization of the Bulgarian national legislation with the European Directives in the field of the water was in progress during the last ten years. The first basic document, which was passing by the Bulgarian National Assembly, is the Law of waters (St. G. No 67/1999) enforced in the beginning of 2000. In general, the Law and the fourteen new Regulations to it are transposing the philosophy of the WFD 2000/60/EC.

The consequences of the 1982-1994 droughts in Bulgaria are the model for a low level of water management in all aspects of the problem. The emergency water regime in Sofia and in many other settlements must be used to foresee and motivate the preventive measures by the creation and implementation of realistic RBMPs.

4. References

Bardarska, G., H.Dobrev, 2003. The impact of Drought on Surface water quality, in C.G.Knight Iv. Raev and M. P.Staneva (eds) *Drouth in Bulgaria. A Contemporary Analog for Climate Change,* BAS Publishing Company, Sofia, 82-94.

Directive 2000/60/EC of the European Parlament and of the council of 23 October 2000 establishing a frame work for Community action in the field of water policy, 22.12.2000 *Official Journal of the European Communities*, L 327/1-L 327-72.

Gopina,G., K.Vasilev, V.Kambourova, Il.Dimitrov, 2003. Health and Hygienic Aspects of Drouth, in C.G.Knight Iv. Raev and M. P.Staneva (eds) *Drouth in Bulgaria. A Contemporary Analog for Climate Change,* BAS Publishing Company, Sofia, 195-211.

Gopina,G., V.Kambourova, K.Vasilev, 2001. Report, *Survey of the Waste Water Management in the Basin of Rivers Struma, Mesta and Maritza on the territory of Bulgaria*, Programm DAC/OECD, University of Aegean in cooperation with Bulgarian National Center of Hygiene.

Gopina, G., K.Vasilev, 1998. Estimation of the Drinking Water Quality in Sofia by Conditions of "Water" Regime- during Period 1994-1995, *J. Vodno Delo*, 1/2, p 22-26.

Hristov,T., R.Nikolova, S.Yancheva, N.Nikolova, 2003 Water Resource Management during the Drouth, in C.G.Knight Iv. Raev and M.P.Staneva (eds) *Drouth in Bulgaria. A Contemporary Analog for Climate Change,* BAS Publishing Company, Sofia, 212-237.

Low for Waters, 1999. *State Gazette* No 67.

8. WHO, 1996. Guidelines for drinking-water quality, Geneva.

Figure 1. Drinking water dams in Bulgaria.

TABLE 1. Storage amount (million cubic meters) in dam “Iskar” during the dry period.

Year	1975	1976	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
30. VI	658	656	609	574	464	407	451	305	422	461	554	449	329	360	403	316	158
31. XII	602	633	459	412	288	332	286	207	307	342	403	348	184	323	284	148	66
Total volume						673	Mln	Cubic	meters								
Dead volume						90	Mln	Cubic	meters								
Water demand for Sofia						180	Mln	Cubic	meters								
Losses						57, 2	%										

TABLE 2. The status of the water supply in selected regional centers in Bulgaria, 1993-1995.

Administrative center	0	Losses, %	Total water used, mln m^3	Household water supply, mln m^3	% of population with water regime in the area
Stara Zagora	29, 958	57, 4	12, 777	4, 847	30, 9
Targovishte	12, 000	73, 4	3, 186	1, 154	50, 7
Vratsa	10, 682	48, 1	5, 540	3, 788	57, 7
Dobrich	13, 322	67, 5	4, 331	2, 384	82, 7
Lovech	9, 537	64, 9	3, 346	1, 447	83, 8

WATER QUALITY MANAGEMENT IN AGRICULTURE: THE CASE OF LOMBARDY - NORTH ITALY

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Abstract

The development of sustainable agricultural systems characterised by technologies and strategies of crop protection able to safeguard the groundwater resources and aquatic ecosystems has become one of the themes of the modern agriculture.

The objective of this paper is to delineate the procedures, the methods and the models used in Lombardy, North Italy in order to safeguard water quality in agricultural ecosystems. For nitrogen an accurate evaluation of aquifer vulnerability has been made considering soil and subsoil chemical and physical parameters. For pesticide a decision support system integrating leaching models and GIS techniques together with census agricultural data has been applied to the region in order to produce vulnerability and hazard map.

Keywords: aquifer vulnerability/ hazard maps/ GIS/ leaching model/ nitrogen/ pesticide/ sustainable agriculture

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 211–230.

1. Introduction

The development of sustainable agricultural systems characterised by technologies and strategies of crop protection able to safeguard the groundwater resources and aquatic ecosystems has become one of the themes of the modern agriculture.

The most recent environmental and agricultural policies, national and European, pursue these aspects and try to develop strategies integrating environmental problems in the management of the natural resources. The action lines of this approach are directed toward two main goals: on one side the identification and solution of environmental issues, on the other side the development and the improvement of monitoring actions. Whereas the monitoring represents the classical action directed to control the environment, the identification of groundwater vulnerable areas and the related risk scenarios are the most interesting and innovating procedures in the management of the environment. Considering this aspect, the most recent legislation gives a high importance to identification of areas where potential risk to environment and specifically for water quality can occur. Following this need for the decision-makers, the first objective is to identify the aquifer vulnerability of the region, in order to define and to carry out finalised action plans at regional and local level.

Considering in particular nitrogen and pesticides, all the legislation regarding this matter derive? by European rules, is receipted at national level. Following the European and national legislation regarding the plant protection products registration (Council Directive 91/414, 1991) and the water safeguard (D.lv2lllli 152/99 and 258/00 promulgated by the Italian Government, 1999 and 2000) experience has been gained in Europe to assess groundwater vulnerability to nitrogen and pesticides at spatial scale (e.g. national, regional) by using standard scenarios and geo-information in combination with pesticide leaching models and aquifer vulnerability methods. The objective of this paper is to delineate the procedures, the methods and the models used in Lombardy (North Italy) in order to safeguard water quality in agricultural ecosystems. (PianoPiano di Tutela e Uso delle Acque, 2004)

2. Environmental dataset of Lombardy – North Italy

The study area (1400000 ha) is mainly flat (Figure 1), characterized by Pleistocenic and

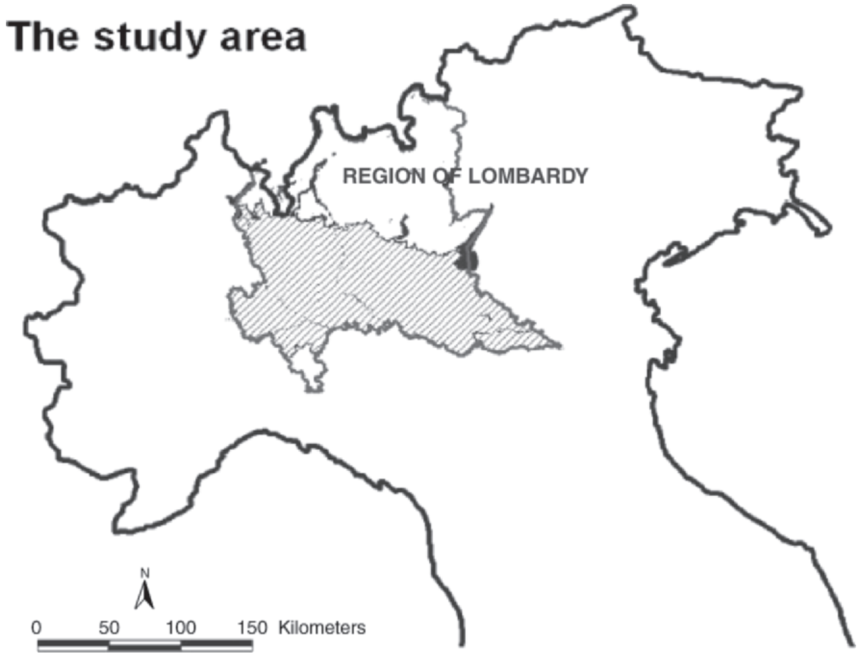

Figure 1. Localization of the study area.

Holocenic glacio-fluvial and alluvial deposits except for the glacial hills located north of the area. The major rivers of the region are the Ticino and Adda approximately South-North and the Po river (South boundary). In the area, soil texture ranges from coarse loamy to fine silty with organic carbon in top soil ranging between 1 and 2 %; higher amounts of sand and in some case gravel are present in Northern (high plain) and Western part of the region, whereas the South-Eastern part of the region is also characterized by fine and very fine soils. Along the main river valleys, soils are coarse textured, resulting in higher hydraulic conductivity. Groundwater is frequently shallow (also at 1 m depth) and generally ranging from 5 to 30 m depth. In Figure 2 main soil landscape of the region are showed.

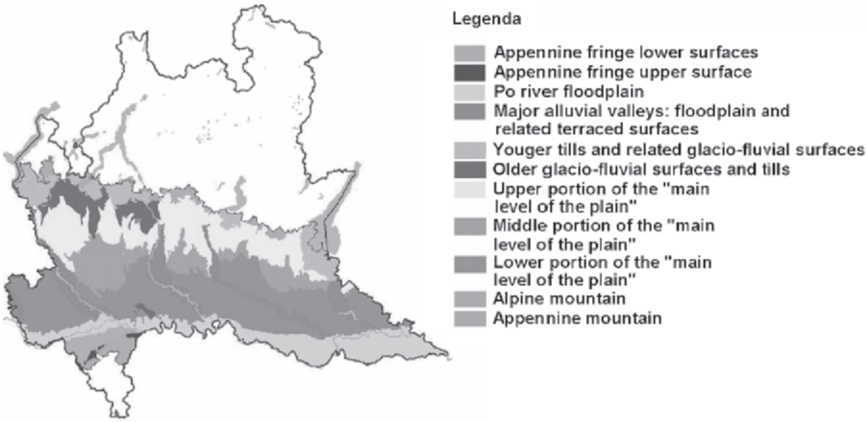

Figure 2. Soil landscape of the region.

The area is characterized by a mean annual temperature of 13 – 14°C, a mean temperature in summer of 23 – 24°C and 2 – 3°C in winter. Considering the Po plain the precipitations are concentrated during the autumn (October and November) and spring (April and May) and annual mean rainfall ranges from 1200 mm in the North to 600 -700 mm in south-eastern zones of the plain (Figure 3).

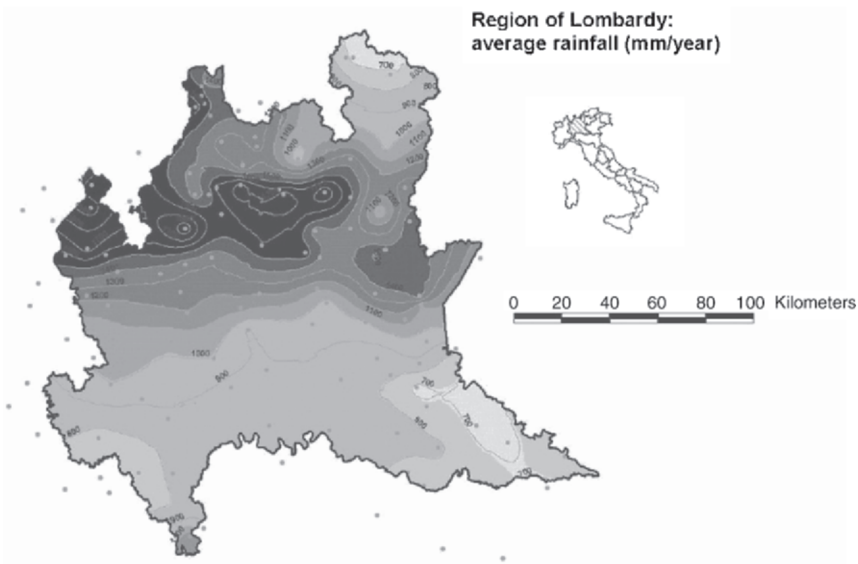

Figure 3. Rainfall distribution and meteorological station of the region of Lombardy.

All the area is intensively cultivated with cereals, maize, mainly used for feed, rice in southwest, barley and vineyard on the morainic hills, soybean and sugar beet in south and southeast of the region.

3. Vulnerability to nitrate

We can define the aquifer vulnerability as the possibility of penetration and propagation of a pollutant in the porous aquifer; so vulnerability mainly depends by the property of the defined porous medium like the capability to transmit contaminants, related to the thickness and litology of the underlying vadose zone. The good result of a vulnerability classification on a regional area depends by the density and quality of the dataset for every required parameter.

The approach adopted by the Regione Lombardia for the assessment of the groundwater vulnerability is based on a method considering the protective function of soil and the characteristics of the underlying aquifer.

3.1. SOIL PROTECTIVE FUNCTION

Since 1997 ERSAF developed a specific interpretative model, constantly upgraded and verified, to evaluate the soil protective function for the groundwater. This function describes the soil capacity to reduce water-soluble polluting substances percolation from the surface down to the subsoil and the groundwater.

The protective function is related to soil filtering and buffering capacity, due to mechanical, biological and microbiological activity that allows pollutants degradation. The model ranks soils in three protective capacity classes; high, moderate and low. A soil is assigned to a capacity class using the most limiting parameter (Figure 4).

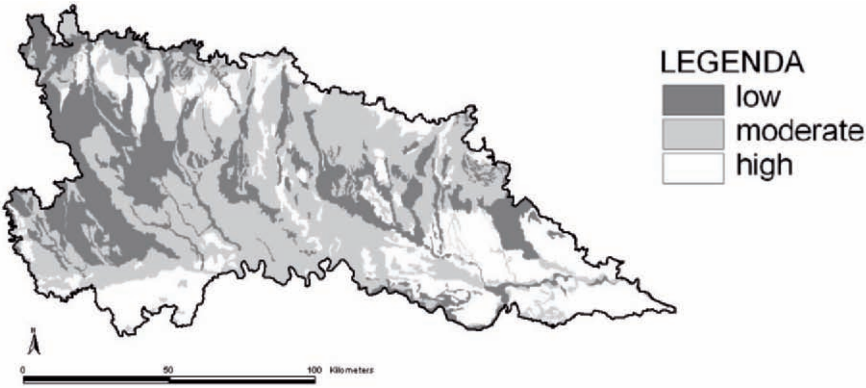

Figure 4. Soil protective function.

The model was applied on 1:250000 scale soil map, carried out by generalization of more detailed (1:50,000) soil information, that ERSAF prepared in the course of last 15 years for the Po plain area and surrounding hills.

3.2. HYDRO-GEOLOGICAL VULNERABILITY

The reference classification adopted to describe hydro geological vulnerability is derived by a method that gives an assessment of the vulnerability based on the hydro-geological characteristics of the vadose zone and the related aquifer. Beretta et al (2003) considered the two main parameters: the depth of the groundwater table and the thickness of the layers characterized by low hydraulic conductivity in the vadose zone. The so obtained vulnerability classification expressed by a qualitative judgment has been transformed in numerical by the attribution of weight to each interval, in order to perform geostatistical analysis (Table 1). Where groundwater table was less than 5 m, a more detailed approach was chosen introducing tree other classes as described in the table below (Table 2).

TABLE 1. Degree of vulnerability related to range of parameters.

Depth of groundwater table (m)	Thickness of low permeability layers (m)	Vulnerability classification	Score
<5	clay < 2 or silt <4	Extremely high	50
<5	clay > 2 or silt <4	Very high	40
5 – 15	clay 2 or silt <4	Very high	40
5 – 15	clay 2-5 silt <4 – 10	High	30
5 – 15	clay >5 silt >10	Moderate	20
>15	clay < 2 o silt < 4	High	30
>15	clay 2 - 5 o silt 4 – 10	Moderate	20
>15	clay > 5 o silt > 10	Low	10

TABLE 2. magnification for depth of groundwater table < 5 m.

Depth of groundwater table (m)	Thickness of low permeability layers (m)	Vulnerability classification	Score
<5	Clay 4	Moderate - High	25
<5	Clay 3 - 4	High	30
<5	Clay 2- 3	Very high. - High	35

The vulnerability assessment has been made using the wells stratigrafies, in order to derive texture, so calculating the permeability of the vadose zone, the number of considered wells for the Lombardy plain has been 2529. To complete and validate the vulnerability map derived by the interpolation of wells data, comparison with geology and geomorphology features was done.

The map obtained represents the hydrogeological vulnerability of Lombardy plain (Figure 5).

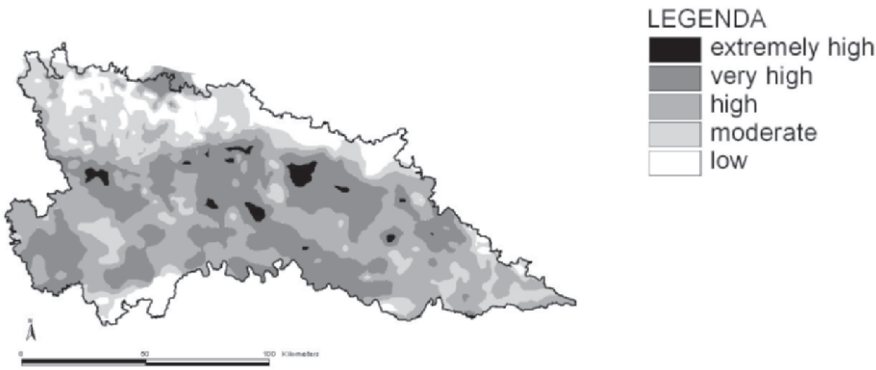

Figure 5. Hydro-geological vulnerability.

3.3. THE AQUIFER VULNERABILITY

The groundwater vulnerability was derived by intersecting the hydro-geological vulnerability with the soil protective function by means of Table 3 (Figure 6) (Beretta et al., 2003).

TABLE 3. Table intersection between hydro geological vulnerability and soil protective function.

Hydro-geological vulnerability	Soil protective function		
	Low	Moderate	High
Low	Low	Low	Low
Moderate	Moderate		
High	High	Moderate	Moderate
Very high	Very high	High	High
Extremely high	Extremely high	Extremely high	Extremely high

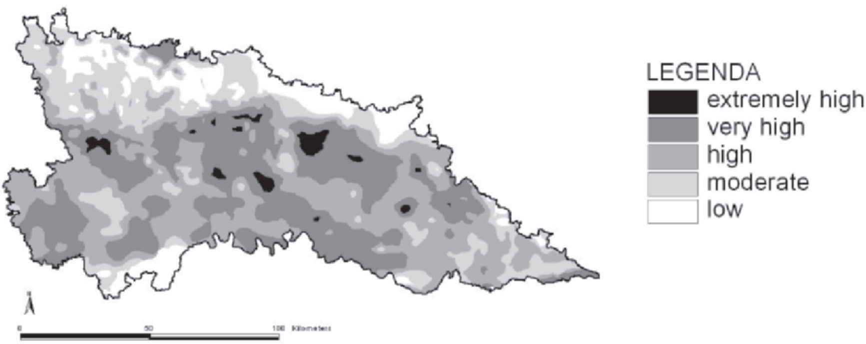

Figure 6. Final aquifer vulnerability.

3.4. THE NITROGEN LOAD

In order to determine the nitrogen load from the agriculture on the whole area two main nitrogen input, the organic and the chemical fertilisation should be considered. The first one is related to the number of livestock; the second one is related to the type and diffusion of crop and to the agricultural practices. In order to estimate the organic source of nitrogen a transformation from number and type of livestock has been made with one of existing several conversion tables, based on average weight and type of the animal. To do this, census data of year 2000 has been used considering the number of heads of livestock per each municipality. The legend of the map has been defined considering two important values of legislation: 340 kg/ha representing the maximum nitrogen load that is possible spreading on agricultural land in one year and 170 kg/ha that is the maximum limit for those areas previously defined as vulnerable (Figure 7).

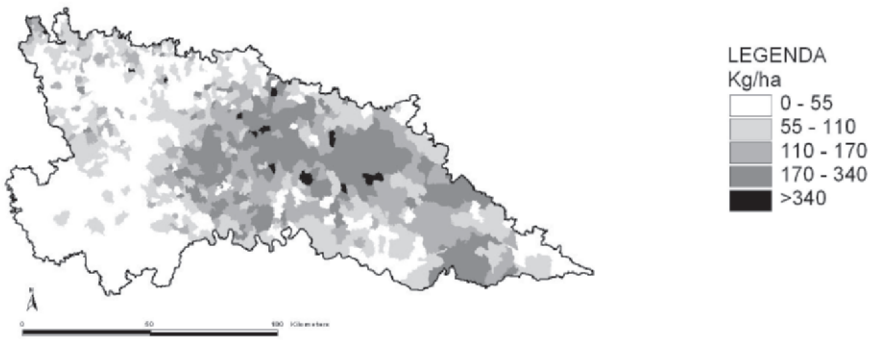

Figure 7. Load of nitrogen per each municipality.

3.5. THE HAZARD CALCULATION

The integration and combination of nitrogen load with groundwater represents a measure of the nitrogen hazard in the considered land; actually the areas with higher level of nitrogen hazard are those where high intrinsic aquifer vulnerability is combined with an effective possibility of contamination, due to presence of farm with high head of livestock.

To final combine the two layers, aquifer vulnerability has been represented per municipality (vulnerable, not vulnerable) so defining the dominant degree of vulnerability for each municipality; the two layers has been combined by means of the Table 4 considering the nitrogen limits described above.

TABLE 4. Combination between nitrogen load and vulnerability.

	Nitrogen Load	
Vulnerability	Low load of nitrogen <170 kg/ha	High load of nitrogen > 170 kg/ha
Municipality vulnerable	2	1
Municipality non vulnerable	3	2

So the municipalities have been defined as follow:

- High or moderate vulnerability and high nitrogen load (value 3);
- Low vulnerability and low nitrogen load (value 1);
- High and moderate vulnerability with low nitrogen load and high nitrogen load with low vulnerability (value 2).

For each of these classes a different action plan will be studied and applied.

4. Vulnerability to pesticides

Pesticide contamination may affect the quality of different environmental compartments such soil, water and air and, consequently, may pose a risk to humans, flora and fauna. Hence the need to assess the nature and degree of the risk and to take at the same time preventive measures aimed at minimising possible damages.

In order to reach an exhaustive assessment of pesticides impact on groundwater in very different environmental conditions, the integration between pesticide leaching models and GIS is a crucial point. The availability of powerful environmental databases containing site-specific information on soil, meteorology, crop and land use suggests that the direct application of a regional-scale model is to be preferred to standard scenarios, because it provides the user with frequency distributions and gives information about areas of safe usage.

Several examples of this approach have been developed in different countries in Europe. In The Netherlands a one-dimensional pesticide leaching model, PEARL - PEsticide Assessment Emission at Regional and Local Scale, is going to be used, coupled to a GIS in the GeoPEARL (Tiktak et al, 2000) system, to calculate the potential losses of pesticides into local surface waters and the regional groundwater. In England and Wales SEISMIC Spatial Environmental Information System for Modelling the Impact of Chemicals has been designed to provide the detailed soil and weather data necessary to modelling a diffuse-source chemical fate, using MACRO.

In Italy ERSAL, during the period 1998 – 2000, as a result of the EC LIFE project "Supplying Sustainable Agriculture Production" (LIFE98/ENV/000010) developed SuSAP (ERSAL 2000; Brenna et al, 2001), a system integrating pesticide leaching models and a Geographic Information Systems to estimate the fate of pesticide in the environment at different levels: regional, catchments and farm.

The commission of Lombardy which is expected to develop the plan for the accomplishment of the D.lvo 152/99, has already shown high interest in SuSAP for the specific aspect of pesticide impact to groundwater and it was used to build the Safeguard Water Plan of the Region.

4.1. THE PESTICIDES AND SUSAP

SuSAP is basically a computer program, integrating existing database (soil, climate, crop, pesticides) and the mathematical models PELMO 3.0 PEsticide Leaching MOdel (Klein et al., 1995) and PESTLA 3.4 - PESTicide Leaching and Accumulation (Van Den Berg et al., 1998) to assess the environmental risk of pesticides at three different levels as follows:

- Regional and catchments level - scale 1:250000 and 1:50000 - to produce soil vulnerability to pesticide leaching, integrating leaching models in a GIS environment;
- Farm level - scale 1:10000 - to define the best crop protection strategies on the basis of the pesticides impact on the environment, in relation with the plant protection products costs (Figure 8a, 8b).

On this paper we will focus on the regional level, showing the main SuSAP tools and an example of application of the system to the pedo-climatic datasets of the Lombardy Region.

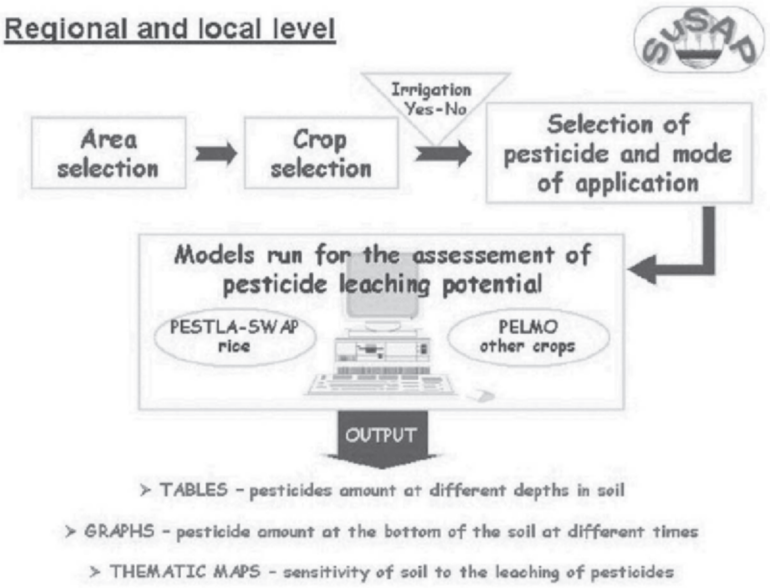

Figure 8a. SuSAP flow charts, describing the territorial level of the study.

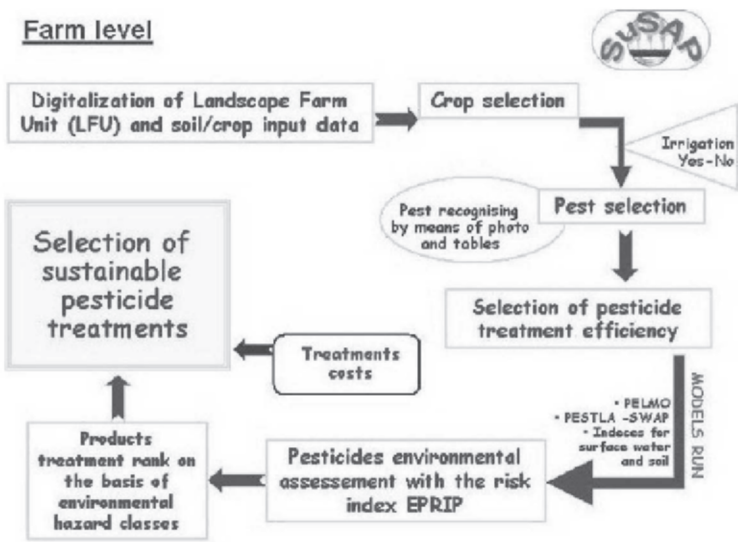

Figure 8b. SuSAP flow charts, describing the farm level of the study.

4.2. THE SUSAP DATABASE

The core of the system is the database, storing data and defining the complex relationships relating the different datasets.

Basic soil data have been previously surveyed at scale 1:250000 and at scale 1:50000 according to the different level of study. Several representative soil profiles have been characterised by field and laboratory analysis in order to collect specific hydrological parameters necessary for calibration modelling applications. The collected samples were compared with data calculated by a set of pedo-transfer functions (PTF); the best fitting PTF was used to derive field capacity, wilting point (Rawls et al, 1982) and bulk density (Manrique & Jones, 1991), necessary to the model runs.

Rainfall, temperature, wind, solar radiation, relative humidity, evapotranspiration of 125 meteorological stations covering the Lombardy region were collected and interpolated with geostatistical methods to obtain spatial patterns of rainfall and temperature.

The integrated analysis of soil and meteorological data allowed identifying 20 macro-areas, each one defined by a reference meteorological station (Figure 9).

Figure 9. Meteorological macro-areas.

More than 200 pesticides, including their chemical and physical properties, ecotoxicological data and the related plant protection products with information on the date, number, rate of application and the efficacy against pests has been stored.

The physiological and phenological characteristics of the main crops of the Po plain and images of weeds and pests complete the SuSAP database. Amounts, dates and type of irrigation have been calculated by means of CropSyst 2.02 model (Stöckle et al., 1999), applied to 10 soil scenarios with reference to a standardized maize crop.

4.3. THE MODELLING TOOLS AND THEIR INTEGRATION IN A GIS

The model PELMO 3.0 was integrated in SuSAP to estimate the pesticide leaching potential through the soil horizons based on an extended cascade model; processes include estimation of soil temperatures, pesticide degradation, sorption, volatilization, and potential evapotranspiration. The above model has been selected among those indicated and validated by the FOCUS (FOrum for the Coordination of pesticide fate models and their USe), jointly established since 1993 by the European Commission and the European Crop Protection Association to provide guidance to the Member States in EU pesticide registration process.

These models were integrated in SuSAP to simulate pesticide degradation and transport for each combination of soil map units and reference meteorological stations.

For integrating models in GIS, basically two methods can be distinguished (Tiktak 1999). In the first method a model (in this case PELMO 3.0) is applied to a unique combination of basic spatially distributed parameters. These unique combinations are assumed to be representative for one or more polygons or grid-cells within the area to be mapped (here referred to as so called mega-plots). In the second approach, a model is first run for a small number of crucial point locations within the area. On the basis of results from these simulations, regression functions between model inputs and model outputs are described (meta-modelling). These transfer functions are used to generate the maps. The first method is flexible and normally gives the most accurate prediction, but it is also rather time consuming. The meta-modelling approach is faster but less precise.

SuSAP is based on the first approach, defining 500 mega-plots in the considered area. Thus, thematic maps of potential contamination and hazard have been drawn according to the spatial variability of soil properties, weather conditions, crops and patterns of pesticide application.

Some of the most used herbicides applied on the considered crops have been identified; active ingredients properties and related plant protection products application data implemented in SuSAP are shown in Table 5 and Table 6.

TABLE 5. Active ingredients properties.

Active Ingredient	Molecular Weight (g/mol)	Vapour Pressure (Pa)	Water Solubility (mg/dm^3)	K_H (Pa m^3/mole)	Koc (dm^3/kg)	DT_{50} (day)
ALACHLOR	269.7	2.10	242	2.20E-03	170	15
CHLOROTOLURON	212.7	5.00E-04	74	1.44E-03	129	40
TERBUTHYLAZINE	229.7	1.50E-04	8.5	4.10E-04	162	60

TABLE 6. Active ingredients application data.

Active ingredient	Plant	Crop stages	Dose (kg/ha)	Date of application	Number of applications per year
ALACHLOR	Maize	Pre-emergency		April	
TERBUTHYLAZINE		emergency		May	
CHLOROTOLURON	Barley	Pre-emergency	2.18	28 October	1

4.4. SUSAP APPLICATION AND SOIL VULNERABILITY MAPS

For each of the three substances PELMO 3.0 has been launched and run for a period of 12 years, so describing a wide panel of different meteorological conditions, potentially occurring in the area. We have assumed that each selected pesticide is applied uniformly all over the area 100% covered by the selected crop, at the same date and application amount, starting from the third year simulation. For every of the resulting 12 years the cumulated amount of pesticide at 1 m depth in soil has been calculated, together with the recharge water; the values are so transformed in concentration (ìg/dm^3) performing the ratio between the pesticide amount and the water recharge amounts cumulated in each year. Irrigation periods and amounts have been calculated automatically for maize by means of CropSyst 2.02 and the water, added to precipitation files for each year. The 80th percentile of the output referred to each mega-plot (soil-meteorological combination) is extracted, ranked in five concentration classes and mapped using the Geographic Information System Arcview 3.2 (ESRI inc.), showing the vulnerability of soils to pesticide leaching (**Figures 10, 11, 12**). Three maps have been produced for the selected pesticides Alachlor, Terbuthylazine and Chlorotoluron.

Looking at the maps, strong differences could be observed from crop and a compound to another:

considering maize, Alachlor appears to be generally slightly leachable except on the south-western areas of the Lombardy. Terbuthylazine appears to leach moderately in wide parts of the plain, except in western and northern zones of the plain, where strong leaching amounts are predicted. Considering barley, a non-irrigated crop, Chlorotoluron seems to have behavior quite similar to Terbuthylazine with several areas characterized by severe leaching potential.

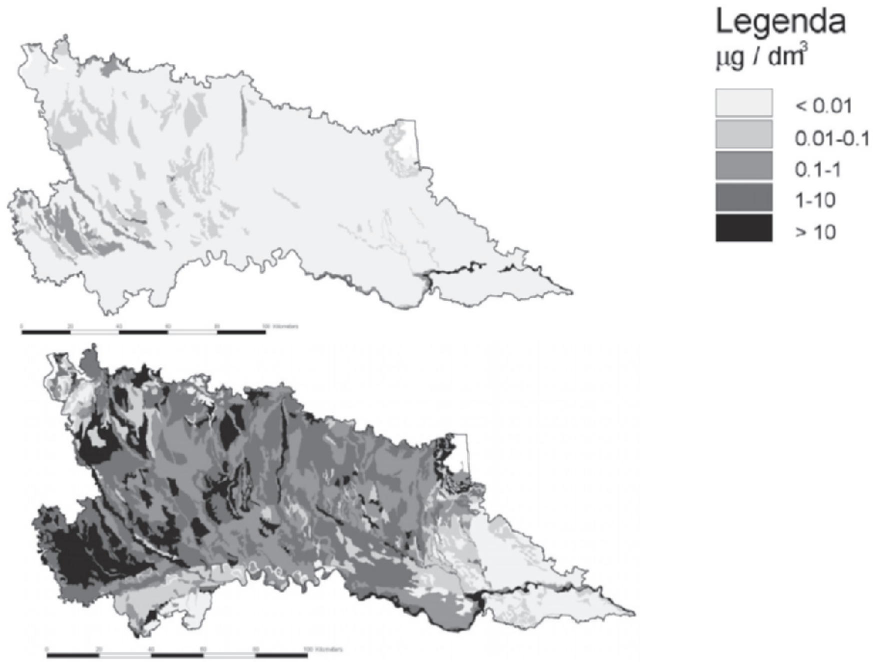

Figure 10. Soil vulnerability to Alachlor applied to maize. **Figure 11.** Soil vulnerability to Terbuthylazine applied to maize.

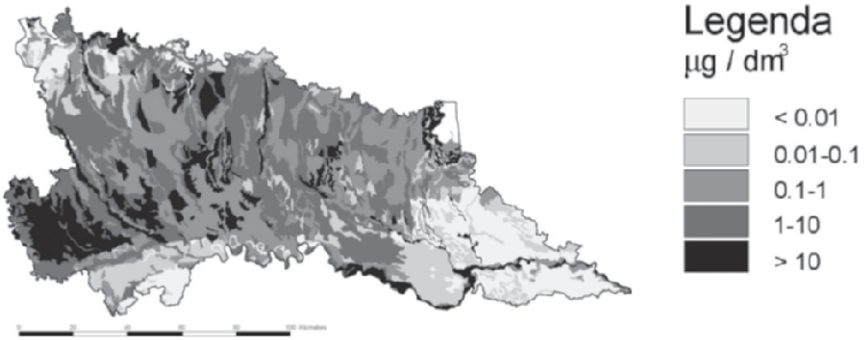

Figure 12. Soil vulnerability to Chlorotoluron applied to barley.

4.5. THE HAZARD MAPS

A further spatial analysis has been performed combining the layers soil vulnerability, agricultural land use and irrigation. The three layers have been converted in grid format with a square cell of 100 × 100 m.

The grid of soil vulnerability has been multiplied for the fraction of agricultural area of each municipality covered by the respective crop; a weight has been attributed to the cells corresponding to municipality where flush irrigation type is dominant. This spatial operation allowed obtaining the final maps, visualizing the hazard areas of Alachlor and Terbuthylazine, both applied on maize (Figures 13, 14) and Chlorotoluron applied on barley (Figure 15). We defined five hazard classes ranging from very high to very low hazard.

The mostly hazard areas for substances used on maize are mainly localized in the Western and Central part of the region; moderate and low hazard is shown for Chlorotoluron on barley.

Figure 13. Hazard map of Alachlor applied on maize.

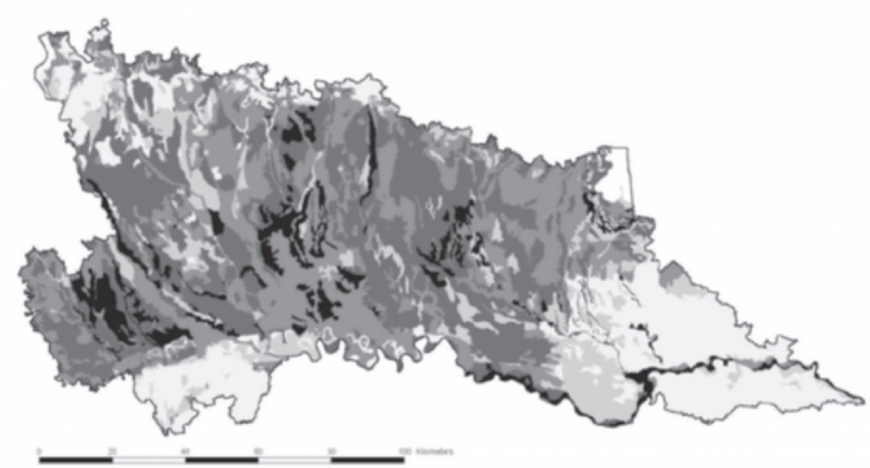

Figure 14. Hazard map of Terbuthylazine applied on maize.

Figure 15. Hazard map of Chlorotoluron applied on barley.

Looking at the vulnerability maps (Figures 10, 11, 12), the strong differences that could be observed from a compound to another should be caused by their physical and chemical behavior, according to plant protection products application rate and periods on the two different crops.

For the three herbicides, maps show also a high variability according to site-specific characteristics of soils and meteorological conditions.

5. Conclusions

As we introduced, the Italian legislation (Republica Italiana, 1999) requires proceeding beyond the identification of vulnerable areas and regulating the use of plant protection products, particularly at territorial level (e.g. regional, province, municipality, catchments areas).

Actually the use of deterministic models could help decision makers (Regional Government) to identify vulnerable areas where site-specific limitations to use of pesticides and manure have to be planned. Systems like SuSAP could give an important contribute to this task. Actually a Regional commission charged in Lombardy to identify the appropriate methodologies and instruments to accomplish to the European and national directives applied SuSAP for pesticide leaching evaluation together with the vulnerability map of aquifer to identify critical areas in Lombardy.

6. References

Beretta G.P, Masetti M., Pilati M. 2003 *Sintesi sulla modalità di determinazione della vulnerabilità della falda libera*, Università degli Studi di Milano – Dipartimento di Scienze della Terra.

Brenna S., Riparbelli C., Capri E., Trevisan M., Auteri D., Gusmeroli S. 2001. SuSAP: *a decision support system for a sustainable use of pesticides in agriculture. 2nd International* Symposium Modeling Cropping System. Firenze.

Council Directive 91/414/EEC, 1991. Official Journal of the EC. L230, vol. 34, 1-32.

ERSAL - Regione Lombardia. 2000. SuSAP, Manuale Metodologico. LIFE98/ENV /IT/00010.

Klein M. & Jene B. 1995. PELMO 3.0 Staatliche Lehr und Forschungsanstalt für Landwirtschaft, Weinbau und Gartenbau Fachbereich Ökologie - Neustadt Germany.

Manrique L.A., Jones C.A. 1991. Bulk density of soils in relation to soil physical and chemical properties. Soil Sci. Soc. Am. J. 55:476-481.

Piano di Tutela e Uso delle Acque 2004. Regione Lombardia. Direzione Generale Servizi di Pubblica Utilità. Unità Organizzativa Risorse Idriche.

Rawls W.J., Brakensiek D.L., Saxton K.E. 1982. *Estimation of soil water properties*. Trans. ASAE, 25, 1316 – 1320.

Repubblica Italiana. 1999., and 2000 *Tutela delle acque dall'inquinamento*, D.lvo n. 152, and 258/100 Roma.

Stöckle C. & Nelson R., 1999 *CropSyst 2.02*. Department of Biological Systems Washington State University USA.

Tiktak A. 1999. *Modelling non point source pollutants in soil*. PhD Thesis University of Amsterdam, The Netherlands.

Tiktak A., van den Berg F., Boesten J.J.T.I., van Kraalingen D., Leistra M. van der Linden 2000, A.M.A. *Manual of FOCUS PEARL 1.1.1*. RIVM report 711401 008, Alterra report 28.

Van Den Berg and J.J.T.I. Boesten. 1998. *PESticide Leaching and Accumulation model PESTLA version 3.4* – Technical Document 43 SC-DLO Wageningen The Netherlands.

PRINCIPLES OF CHEMICAL WATER SAFETY FOR REPRODUCTIVE HEALTH PROTECTION

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Abstract

This work has been attempted to show actual and potential danger of contamination of drinking water by bacteria and chemicals that may occur due to the act of terrorists or due to environmental pollution by toxic chemicals. Whatever it is, the consequences of such an emergency will have devastating effect on the health and life of the general population and its most vulnerable groups, women, children aging people, to say nothing of reproductive health which will also be at great risk.

The main instrument for proving quality-controlled drinking water is strict observance of relevant hygienic standards and their reliability for the water going from centralized systems.

Law of the Russian Federation On Sanitary Epidemiological Welfare of Russian Population safeguards the quality of drinking water in Russia supplied through centralized water systems and guarantees its chemical purity. The work gives key toxicants that may act as impurities in the drinking water and MAC values for them adopted by the Russian hygienic standards.

Key words: drinking water/ terrorism/ health/ reproduction impairment/ MAC values.

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 231–239.

1. Introduction

Recent acts of terrorism have been directed against peaceful general population. For this purpose explosives and poisoning substances have been used, access has been open to biological and chemical weapons.

In realization of terrorist acts various methods and instruments can be used depending on their availability to the criminals who are going to perform them.

It should be noted that there exists both the real danger of using biological weapon and its actual potential threat. Thus, using of biological or chemical weapons leads to specific outcomes. According to Dmitrieva (2004) if a biological weapon has been used it will result in: 1. Latent period from the onset of its exposure to the primary signs of health impairment that will eventually grow into the epidemic; 2. Uniformity in the development of the greater part of bacterial and virus- based pathologies till specific pathological manifestations of targeted body systems\ and organs.

Still, a great number of practitioners have not gained experience in recognizing dangerous infections. To this end the most vulnerable groups will be pregnant and nursing women, children and aging people. Current decline of birth rate and high mortality indices of Russia have put the problem of reproductive health protection as one of the priorities determining national safety at a state level (Sivochalova et al., 1999). This problem is gaining more and more importance due to the reality of current terrorist threat and, hence, a challenge for terrorists to use water basins for their 'dirty' aims.

Law of the Russian Federation (1999) On Sanitary Epidemiological Welfare of Russian Population safeguards the quality of drinking water in Russia supplied through centralized water systems and guarantees its chemical purity.

The main instrument for proving quality-controlled drinking water is strict observance of relevant hygienic standards and their reliability for the water going from centralized systems. SANPIN national hygienic norms regulate the quality of drinking water. (SANPIN 2.1.4.1074-01).

Taking into account the might be terrorist chemical attack which, no doubt, will result in mass poisonings by extremely dangerous agents, the question is arisen as to what response of the exposed reproductive system could be.

2. Key impurities for drinking water hazardous for reproduction

This presentation, thus, has attempted to analyze some standards of only those substances that show adverse health effects of human reproduction processes and threaten human posterity health.

It is of note that the methodology of evaluating MAC (maximum allowable concentrations) for drinking water developed in Russia does not differ in its concept from the one recommended by the WHO. For instance, mandatory by the Russian standard is:

- identification of maximum inactive and minimum active concentrations of chemicals in chronic toxicological trials;
- species /sex sensitivity registration to a certain agent;
- registration of different reserve coefficients with regard to chemicals, which show specific action (including, the ones affecting pre-natal phase), thresholds specific effects of exposure to gonads, mutagen and carcinogenic effects, extent of placenta impairment.

However methodology of evaluating MAC for drinking water in Russia compared with the one applied abroad has certain differences, such as:

- divergences of terms (for example, in Russia the term ‘threshold’, or ‘sub-threshold’ concentration is used, whereas the WHO reference books give NOEL and Low EL abbreviations;
- rating of a standard value is done regardless its simultaneous body administration with other media, with food above all (pesticides excluded);
- different are the requirements for counting threshold dozes (Low EL for minimal effects) for daily accumulation of a chemical with drinking water (in Russia threshold dozes are done for three liters, the WHO recommendations are for two liters).

Nevertheless, despite some differences in methodological approaches of Russia compared with other countries standard values for many chemicals accepted here actually do not differ from the ones recommended by the WHO. Among them are: barium, fluorine, mercury, chrome, benzene, and polyacrilamide.

Along with this MAC values in water for such chemicals as 3,4 - benzenepyrene, formaldehyde, cadmium considerably exceed internationally accepted ones.

The same is true with some key-impurities of drinking water that have adverse reproduction effects. For instance, MAC values for lead, nickel, antimony, threegalometans, acrylamide, vinyl chloride, styrene, epychlorhydride, and arsenic appeared to be higher in domestic regulations than in the EU and the WHO ones

It seems alerting that for some chemicals recognized by the WHO as drinking water impurities, Russian standards have not been developed (SanPiN 2.1.4.1074-01).

It is essential to analyze health hazards of the chemicals MAC values of which are higher than the ones recommended by the EU and the WHO.

Table 1 shows 13 key impurities of drinking water of the respective class of chemicals that affect human reproductive system. Despite observance of MAC values in drinking water (according to 2.1.4. 1074-01 SANPIN regulations) for acrylamide, vinilchloride, arsenic and 1,2 dibrome-three-chlorpropane, the respective admissible individual life risk is 5 to 10 times exceeded ($1 - 10^5$). High risk is due to excess administering of these chemicals through other media, which has not been regarded in MAC establishing for drinking water.

It has been found by the trial that for antimony, epychlohydride, hexochlorbutane, and dichlorpropane for which ADD values have been calculated regarding all routes and media of their administration, their MAC values two times exceed those of ADD ones; for nickel, styrene, lead, chloroform, 4 chloridecarbon they make up 30% from ADD values. If to agree to the fact that the share of drinking water in the total load of respective chemicals makes up no more than 10% from the overall administration, and the rest 90% fall to food and other factors, it appears total load for these chemicals is much higher than ADD value.

These considerations laid the basis of revised standards for the above chemicals in 2002. As a result of this revision MAC values for styrene, arsenic, nickel have been 5 times reduced, respectively, 3 times for lead, 100 times for acrylamide and epychlorhydride, 20 times for dichlorpropane, 10 times for vinylchloride and antimony, and twice as less for chloroform.

It should be specified that one more group of chemicals can be found in drinking water, however, they have not been rated yet. This refers to chloramines almost 24 mg/liter of which can be found in drinking water as a result of chlorination when the water contains ammonium nitrogen. Taking into account that ADD for chloramines is 0,094 mg/kg, dose equivalent of 24 mg/liter corresponds to 0,8 mg/liter, i.e. almost 9 times exceeds MAC value.

Table 2 shows chemicals hazardous to reproduction for which MAC values have not been established in Russia.

TABLE 1. Key impurities for drinking water hazardous for reproduction.

Chemicals	MAC value mg/l (SanPin 2.1.4.1074-01)	Dose-equivalent mg/kg	ADD Allowable Daily Dose mg / kg	Individual carcinogenic. risk	Why revised and included into GN 2.1.5.1093-02	How goes into drinking water?
Acrylamide	0,01	0,00033	-	$9{,}4{\cdot}10^{-4}$	Exceeds MAC for Carcinogenic Risk	Monomer in a flocculent
Borom	0,5	0,01	0,088	-	Administered with food Exceeds ADD	Underground waters
1,2 dibrom-3-chlorpropane	0,4	0,013	0,007	$3{,}5{\cdot}10^{-5}$	Exceeds MAC for Carcinogenic Risk	Water chlorination
1,2 dibromo-3-chlorpropane	0,01	0,0003	0,0002	-	ADD excess	- « -
Nickel	0,1	0,0033	0,005	-	Administered with food Exceeds ADD	Impurity in reagents
Styrene	0,1	0,0033	0,0076	-	Exceeds ADD	Goes from pipes and other water contact materials
Lead	0,03	0,0009	0,0035	-	Administered with food Exceeds ADD	Impurity in reagents
Chloroform	0,2	0,0066	0,015	-	- « -	Water chlorination
Chlorine methyl - oxyrane	0,01	0,0003	0,00014		Exceeds ADD	Monomer of resins used to purify water
Antimony	0,05	0,0015	0,00086	-	- « -	Goes from pipes and other water contact materials
Carbon tetrachloride	0,006	0,0002	0,0007	-	When administered from other media exceeds ADD	Water chlorination
Vinyl chloride	0,05	0,0015	-	$1{,}1{\cdot}10^{-4}$	Exceeds MAC for Carcinogenic Risk	Goes from PVC pipes
Arsenic	0,05	0,0015	0,002	$9{,}0{\cdot}10^{-4}$	- « -	Impurity in reagents

TABLE 2. Chemicals with no MAC values in Russian legal documents (2.1.4.1074-01 SANPIN) hazardous for reproduction.

The name of a chemical, how it goes into drinking water	ADD mg/kg	WHO value mg/l	Specific Effect
/2-ethyl-hexil /adipat, Migrates from ion substituted resin to 0,14 mg / l	0.28	0.08	
Diethylhexilphthalate migrates from ion substituted resin to 0,01 mg / l	0.0028	0.008	Carcinogen
Dichloracetonitrite Goes due to chlorination to 0,04 mg /l	0.015	0.01	Teratogenic effect
Dichloracetic acid, Due to chlorination to 0,08 mg / l	0.0076	0.05	Impairs testiswater as a result of chlorination when the water contains ammonium nitrogen. Taking into account that ADD for chloramines is 0,094 mg/kg, dose equivalent of 24 mg/liter corresponds to 0,8 mg/liter, i.e almost 9 times exceeds MAC value.
Pentachlorphenol Due to chlorination to 0,05 mg / l	0.003	0.009	Impairs fetus
Tetrachloracetic acid, Due to chlorination to 0,1 mg / l	0.017	0.1	Chromosomal aberrations found
Chloramines, Due to chlorination to 24 mg / l	0.094	3.0	Mutagen

Dose equivalent of chemicals most frequently registered in drinking water such as tetrachloreacetatealdehyde, pentachlorphenol, dichloriacetic acids, and dichloracetatenitrite also exceeds ADD values.

The fact that these chemicals can be encountered in drinking water, their extremely toxic nature (as in certain dozes they have adverse effects on reproductive), one more fact that several chemicals can be found in the water at a time (for example, when it is chlorinated) have been found important to be included into Russian list of MAC values (2.1.5.1093-02) in accordance with the WHO recommendations.

Observance of hygienic standards for drinking water is the basis for health prevention of general population and for the promotion of reproductive health as well. However acts of terrorism or any other emergencies may lead to impossibility to control the quality of drinking water.

Stability limit of human reproductive system exposed to dangerous factors depends on a phenotype, congenital factors, age, sex, somatic condition, quality of nutrition and drinking water, life standards, habitant, etc. (Izmerov et al., 2001).

Reproductive disorders (RD) make up 5% to 15% from the total burden of diseases including deaths and invalidity which is equal to 22% from all feminine pathologies in females aging from 15 to 44 years that is being in a reproductive age while in males it is 3% 7. (Abou Zahr C., Vaughan J.P. 2000).

3. Risk assessment and prevention of adverse effects on reproduction

In spite of the fact that reproduction should be equally protected in males and females, prevention of reproductive health in females needs introduction of particular measures, especially it concerns pregnancies as reproductive health risks are high at that time as well as they are high during carriage. Risks to develop pathologies of a fetus and a newborn should be added to it. (Izmerov et al., 2001; Health of women of Russia, 1998).

It is well known that quality of drinking water provides for normal human homeostasis. It has been found that if the pregnancy is normal 500 ml to 600 ml of amniotic waters, or one third of them are changed for an hour. Three hours are needed for complete amniotic exchange and during five days all the chemicals dissolved in them are withdrawn from the body. Thus, it may by assume that if a pregnant woman is affected by virus and/or bacterially polluted water, the fetus is exposed to high levels of acquiring pathology and lethal risks. For example, it is known that hydramnion in pregnancy in 10% to 16% of cases is of virus and/or bacterial origin (Milovanov 1999).

When virus or infection affects pregnancy, the parent, embryo and fetus are exposed to the agents and to the products of their intoxication formed in a parent organism due to impaired metabolic processes. Products obtained due to the decay of an infectious agent are not less dangerous to the female's health and the health of the posterity.

Hygienic standards for the chemicals capable of causing impairment of specific human functions should be strictly controlled. They are the most efficient prevention mechanism for health protection of the population in general and for reproductive health in particular in a state of peace. Not less than 1000 is sufficiency of a reserve co-efficient in-between general toxicity and specific effects.

However it is efficient if a standard is strictly controlled and if only one of the above toxic substances is registered in drinking water whereas in other media (such as food, ambient air, and the air of a working zone) it is not found.

In real conditions reserve co-efficient may undergo considerable reduction. For instance, it is known that if chlorine organic compounds are registered in drinking water, the air of a working zone and ambient air at a time, their action is spread in one direction and reserve co-efficient is getting reduced. This may have adverse health effects.

These circumstances require research for reducing exposure contamination parameters for drinking water as well as for MAC reduction of chemicals acting in one direction.

Thus, the most dangerous are terrorist acts that due to their unpredictability are similar in many respects to industrial emergencies. They are:

- salvo-like releases of polluted sewage into water basins,
- outflow of chemical agents into the soil,
- environmental pollution by oil products,
- accidents of water purifying systems and in the course of sewage transportation,
- accidents at centralized water purification and supply systems.

4. Conclusion

Measures to minimize health risks due to emergencies in accordance with hygienic legislation of Russia currently in force have been determined in Sanitary norms and regulations aimed at protection of surface and underground waters. Extra purification and disinfection blocks, minimal drinking water reserves, hyper chlorination and other things are mandatory when water supply programmes are to be adopted. Decision-making is done with regard to the magnitude of danger which pollution brings about as well to risks to encounter extra toxic agents. For instance, if oil products are spilt into water basins, negative health effects including reproduction may be developed by chlorine organic substances, which are formed when chlorine is deactivated.

A priority task in this case is to evaluate health risks due to pollution of drinking water due to chemicals formed when disinfection is done. One should compare these risks and make decisions, which could minimize contamination of drinking water by chemicals capable of showing carcinogenic, mutagenic, toxic reproductive, and teratogenic effects.

5. References

Dmirtieva T.B. 2004.Threat of terrorism, stressors and situation: new problems of theory and practice. Guidebook on rehabilitation of humans stressor loads Edited by RAMS Academician Valentine Pokrovskiy. M.: “Medicine”,.pp. 12-20.

Sivochalova O.V., Feytshans I.L., Denisov E.I., and Golovaneva G.V., 1999. The right of workers on reproductive health: priorities today and in the 21st century. Human rights in Russia: declarations, norms and life. Proceeding to the International Conference. M. pp. 214-217.

Law of the Russian Federation On Sanitary Epidemiological Welfare of Russian Population ¹ 52 dated March, 30, 1999
SANPIN 2.1.4.1074-01.
ÃÍ 2.1.5.1093-02

Izmerov N.F., Sivochalova O.V., Denisov E.I. 2001. Medical and social problems of reproductive protection and decision making in this field. Actual problems of reproductive health in conditions of anthropogenous pollution. Proceedings to the International Symposium. Kazan, pp. 5-13.

Abou Zahr C., Vaughan J.P. 2000. Assessing the burden of sexual and reproductive ill-health: questions regarding the use of disability-adjusted life years // Bulletin WHO. V.78.-N 5.-P.655-666.

Health of women of Russia. 1998. Analytical report (economic, social, ecological, legal and medical aspects). Presidential commission on questions of women, families and demography. M.: Joint-Stock Company Informatic, 96 p.

Milovanov A.P1999. Parent-placenta-fetus: pathological aspects of a system.Guidebook for SanPiN 2.1.4.1074-01 practitioners, Meditsina, pp. 338-345.

MAINTENANCE AND IMPROVEMENT OF DRINKING WATER SAFETY WITH ESPECIAL REGARD TO ITS ROLE IN FOOD SAFETY

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Abstract

The goal of the paper is increasing food safety through the improvement of the drinking water quality used in processing and distribution of food products. Provide water that is safe and adequate from the perspectives of technological requirements in every stage of food processing/distribution.

Keywords: water safety/ food and water/ situation analysis/

1. Evaluation of the prevailing conditions /situation analysis

In the evaluation we set the following objectives:

- Quality analysis of bottled drinking water, and water used in food processing and distribution
- A survey on the present state of water quality monitoring in the light of food safety considerations and consumer health protection.

When framing the policy during the EU accession negotiations Hungary did not apply for an exemption from the conditions of the 98/83/EK Directive on drinking water for public use. This indicates that the enforcement of the

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 241–248.

limit values, specified in the Directive, to the Hungarian law and compliance are obligatory for Hungary. In order to introduce the strict water quality parameters, Hungary needs indispensable technical developments.

The adoption of EU Directives in Hungarian regulation, and the government level Hungarian Drinking Water Program were substantiated by the "Impact Assessment and Program for the Introduction of the 98/83/EK Directive on Drinking Water Quality", which was prepared by the József Fodor National Public Health Center – National Institution of Environmental Health, the Hidrokomplex Ltd. and the ÖKO Company.

Besides the status evaluation, a survey dealing with the technologies improving and setting the Hungarian drinking water quality was carried out in the development phase of the Program. The elaborated program on drinking water improvment determines the tasks of the introduction of the directive, the affected population, and last but not least the health priorities. The document on the impact assessment, detailed time and cost schedule/plan of the adoption of the new EU drinking water quality directive impact assessment has also been completed.

The professional council discussed and accepted the joint submission on "The tasks related to the harmonization of the 98/83/EU Directive on public drinking water quality with the Hungarian law" complied for the Government by the Ministry of Environment, the Ministry of Health, and the Ministry of the Interior. Lastly the 201/2001(X. 25.) Government Decree dealing with the Hungarian new water quality requirements has been published.

The Government Decree comprises the exact plan about the implementation of the tasks. The following development tasks must be implemented proportionately by the end of 2006, and 2009:

- treatment and disinfection of water containing arsenic;
- treatment and disinfection of water containing ammonium, nitrire, and nitrate;
- treatment and disinfection of water containing boron, fluoride and iodide;
- and improvement of institutes and operating appliances (laboratory etc.). In this respect, it is especially important that the requirements are more stringent for food industry consumers. For instance, the temporary derogation for the use of water containing arsenic does not refer to the public-service water suppliers.

The estimated cost for the development tasks of a government programme, which presumably starts in 2003 and aims at the implementation of the quality requirements of public water service, is 111,3 billion Ft. The estimated cost for the development tasks of the projected complete programme to 2015 is about 200-220 billion Ft.

The state evaluation regarding public water service -based on a rank of 120 000 data- can be compiled relying on the water quality analysis for 1999-2001 prepared by the József Fodor Public Health Center – National Institute of Environmental Health and the National Health Service.

Unfortunately there is no country-wide scale database available for the execution of an evaluation about the water use of the food industry. A yearly national state evaluation report is submitted to the competent department of the Ministry of Agriculture and Rural Development until the end of June by the National Food Investigation Institute in collaboration with National Institute of Environmental Health. The participating units are arranged into different groups by weighting / regarding to adequate, objected and inadequate parameters.

2. Summary of the drinking water quality tasks

Objected water quality based on the limit values of the 201/2002 (X. 25.) Government Decree	Number of affected regions	Number of affected people
Objected on the basis of the chemical parameters	1,559	3 732 472
Objected on the basis of the microbiological parameters	134	232 879

The region groups, according to the health perspective priorities, of the planned governmental drinking water quality improvement programme are the following:

Group	Parameter	Number of regions	Population number
1.	Arsenic (>50 μg/l)	6	7488
2.	Arsenic (30-50 μg/l)	61	131529
3.	Boron (>1000 μg/l)	45	71135
4.	Fluoride (>1,5 mg/l)	8	7170
5.	Nitrite (>0,1 mg/l)	122	116757
6.	Nitrate	3	1707
1-6. Total		245	335786

Comment: it is a requirement for every region that a limit value should not be exceeded in the course of the programme.

2.1. TOXIC METALS AND ELEMENTS

The greatest concern of the programme from public health perspectives is occasional water arsenic concentrations that exceed the limit value. Complying with the new arsenic limit values (10 ìg/l) is the most difficult task, because many settlements are supplied with water that does not meet the requirements. Based on the available data, the majority belongs to the 10-30 ìg/l range. A minor proportion of the regions are affected by further serious chemical water quality problems, according to the WHO directives, such as nitrite, boron, fluoride, and nitrate contamination.

2.2. ORGANIC MICROPOLLUTANTS

It is not possible to get an overall picture on the ground of the available data. The sparse directed monitoring measures and research-development work resulted only scarce information about drinking water contaminants such as di- and trichloroethylene, pesticide residues, oil (hydrocarbons). The comprehensive examination of the provided water samples started in 2002, from 2003 the wells are involved. The response system presumably will get a proper insight from the obtained results.

2.3. OTHER WATER QUALITY PARAMETERS

The water quality objections affecting most regions and water consumers result from the exceedingly high concentrations of ammonium, iron, and manganese, which are considered indirectly less hazardous from public health perspectives and are mentioned as “indicator parameters” in the EU directive. Additional water quality objections are turbidity, unpleasant taste and odor. Their direct effect (f.e. accumulation of arsenic in iron sediment, colonisation of bacteria) might be dangerous. Water hardness and humin matter content also belongs to this category, because their concentrations exceed the limit values.

2.4. WATER DISINFECTION AND ORGANIC CHLORIDES

Drinking water disinfection is a basic public health requirement in the prevention of water borne diseases. Conventional water disinfection, chlorination of the drinking water practice has a greater chlorine demand in order to ensure a higher security level of the epidemiological services. In addition, the increased use of chlorine might lead to the formation of carcinogenic chlorides. Significant efforts were made to find the balance in order to reach the microbiological security with the use of the least possible amount of oxidants and disinfectants (f.e. chlorine) in the drinking water treatment process. This made it possible for Hungary to introduce a lower limit value for the group of organic halogen compounds (trihalogen-methanes THM) than the EU limit value. The situation is not so favourable for the case of organic halogens. In the course of the programme for the improvement of Hungarian drinking water quality, the main priority was the reduction of the total organic halogen concentration according to the water sanitation considerations.

2.5. BIOFILM CONTAMINATION OF THE WATER SERVICE SYSTEMS

The microbial biofilm contamination of water provided by the drinking water service systems (pipes, water basins) and marketed in bottles or tanks raise more and more problems. It is very difficult to remove or destroy the bacterial colonies, which are producing the biofilm, using the regular cleaning and disinfection methods. Superficial or flock-forming bacteria are reported to be more resistant to the effects that inhibit their life functions than suspended bacteria.

Some of the biofilm producers, superficial adherent and layer producers, flock-forming and plankton like bacteria pose a risk, or are potentially dangerous; others are known to be harmless, not pathogenic.The taxonomic and phylogenetic places of the latter group are less known, mainly because these bacteria cultures do not or hardly grow when using standard microbiological methods/media. Some of the biofilm producers (nitrifiers: ammonium and nitrite oxidizers, sulphare reducers etc.), which take part in the dangerous nitrite accumulation, emission of unpleasant odor in the water pipes, bottles and tanks, were determined applying modern biological and GC-fatty acid-esther analysis.

2.6. TASKS CONNECTED WITH THE QUALITY OF BOTTLED WATER

Consumption of bottled water is becoming more and more popular, because it is believed to be essential for healthy lifestyle. Safety of bottled water depends on the specific quality of the product, the protection of the water source/well, and bottling hygiene. According to international data, mainly the quality of "still" (non-carbonated) mineral water is objected occasionally. The excessive consumption of mineral rich (high fluorine, boron and iodine concentration) water might lead to health problems, if the consumers are not informed properly. We cannot provide comprehensive measure data recorded by the Hungarian authorities on the quality of bottled water. Because of the importance and the potential health aspects, the establishment of a national bottled water quality database and response system of the Hungarian bottling companies, importers of EU and third countries is proposed. The database would be partly based on the self-monitoring information of the bottling companies and the regular control data of the responsible authorities.

3. Priorities and problems arising from the state evaluation

- Harmonization of the Hungarian and the European Union regulation concerning drinking water is completed. However, some of the Hungarian drinking water samples do not comply with the requirements.
- Improvement in the quality of tap water- a National Drinking Water Quality Improvement Program was organized in order to complete the planned tasks of the 201/2001 Government Decree. The completion of the planned activities as scheduled, as well as ensuring the financial means and technical conditions, are major priorities.
- There is a postponement in the completion of the water quality monitoring of the public-service (detailed) state evaluation and the measures of the National Health Service. In a given region of the water service min. 20 % of the self-monitoring samples should be involved in the National Health Service Officer's authority/service? monitoring according to the regulations. However, effort in this matter failed.
- Water quality in food-processing units should already comply with the EU regulations, although it is not ensured in every unit.
- National monitoring data on the quality and safety parameters of bottled water (drinking water, mineral water, spring water) are not available for the public.

4. Proposals

- Within the frame of the government level National Drinking Water Quality Improvement Program to express and implement food safety priorities, the organization of a water quality improvement subroutine of the Hungarian food sector is required.
- According to the 201/2005 (X. 25) Government Decree regular reports should be provided about the water quality conditions of the food industry. Immediate response must be implemented whenever the quality of water might affect the safety or the suitability for export of the products.
- Auditing and water quality monitoring work must be strengthen in food industry units, cold-storage, bottling units, in order to promote the operation of a response system for an occasional contamination.
- We recommend the development of an extended self-monitoring program (collection and evaluation of data, examination of extra parameters in reasoned cases), which is already implemented in some of the export units, and the integration of the self-monitoring data of the units into the central database of the National Health Service. The evaluation of data is essential for the development of the prevention scheme.
- For the constant / continuous quality analysis of bottled water, the required sample size, the sampling method and the group of parameters needed for the monitoring must be determined in cooperation with the responsible authorities. The financial means of the authority/service? monitoring must be established, and an action plan should be developed to be prepared for adverse outcomes.
- The public should be provided with unbiased, proper and clear information about the pros and cons of the consumption of bottled drinking water and make the labelling of bottles understandable for everyone.

5. Priority tasks

- The full implementation of the drinking water quality control measures determined by the National Public Health Service's Decree is of pressing necessity.
- Water quality improvement needs prompt action when water of inadequate quality is used in food processing and cold-storage units. Exporters are to be examined in the first place, then downstream users.

- It is necessary to make the stakeholders (mainly food processing and distributing units) become acquainted with the new set of requirements, and follow the adequacy with outstanding attention.

PESTICIDES AND SURFACE WATER. THE ROLE OF MODELING AS A TOOL TO MANAGE CONTAMINATION

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Abstract

Surface water and groundwater compartments are of a particular interest for public health due to their use for drinking purposes. The extensive use of pesticides in agriculture can entail risks of contamination of these two specific compartments.

The objective of this paper is to describe how to manage risk for surface water in the pre-marketing phase: some of the recent advances made in the use of modelling within the regulatory framework of the Directive 91/414/EEC have been addressed, together with an application at national level in Italy.

Keywords: Surface water; pesticide; modelling; risk assessment.

1. Introduction

Protection of cultures is essential to maintain production yields at a level sufficient to ensure food needs of a continuously increasing world population. The extensive use of pesticides in agriculture can entail risks for human health, the environment and non-target organisms. Hence the need to assess

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 249–262.

the nature and degree of the risk and at the same time to take preventive measures aimed at minimising possible damages.

Registration of pesticides is regulated at European level by Directive 91/414 (EU, 1991). According to this Directive harmful effects on human or animal health and adverse effects on the environment should not occur following the use of a plant protection product. Uniform Principles used in the evaluation process have been set by Directive 94/43/EEC, which states the need for appropriate calculation models to assess the predicted concentration of active ingredients (PEC - Predicted Environmental Concentration) in the environment: surface water, groundwater, soil and air.

At present, no model has been validated at Community level but there are many models, which are already in use for the assessment of the environmental behaviour of chemicals. In order to "organise the use of models" within the EU countries and to help the user/regulator in using models a "Forum for the co-ordination of pesticide fate models and their use" (FOCUS) was established.

The FOCUS forum was established as a joint initiative of the Commission and industry; in their introductory report, the FOCUS Steering Committee mentions the need for guidance on the estimation of Predicted Environmental Concentrations (PECs) using mathematical models. To answer this need, three working groups were established and subsequently published guidance documents dealing with:

- Leaching Models and EU Registration (FOCUS, 1995);
- Soil Persistence Models and EU Registration (FOCUS, 1996)
- Surface Water Models and EU Registration of Plant Protection Products (FOCUS, 1997)

2. Pesticide impact upon water resources

Major routes of exposure of surface water and aquatic ecosystems close to pesticide-treated areas are spray drift and runoff. Sprayed substances can reach surface water through the air much far away from the application area. On the other hand, application of pesticides on the soil can contaminate watercourses close to the treated area by means of pesticide-contaminated soil that is carried along by rainy water *(run-off)*. The occurrence and the extent of run-off are dependent on the topography of the landscape (slope), the soil texture and the intensity of the rain event. The amount of pesticide that may be translocated into surface water is further dependent on the distance between the treated area and the receiving ecosystem, on the soil coverage as well as on the elapsed time between pesticide application and onset of rainfall. Moreover, the removal of surplus water from land, via within-field drains (*drainage*) can contaminate surface waters by pesticides leached out from the plough layer. Parameters influencing contamination of surface water are related to pesticide formulation (i.e. solvents used, particle size), mode of use (i.e. spray volume, droplet diameter, and height of application above ground surface), agricultural practices (i.e. ploughing) and meteorological conditions such as wind velocity, relative humidity, temperature and rainfall.

3. General approach to risk assessment

According to the Directive 91/414, risk assessments for pesticides are carried out according to a scheme as presented in Figure 1.

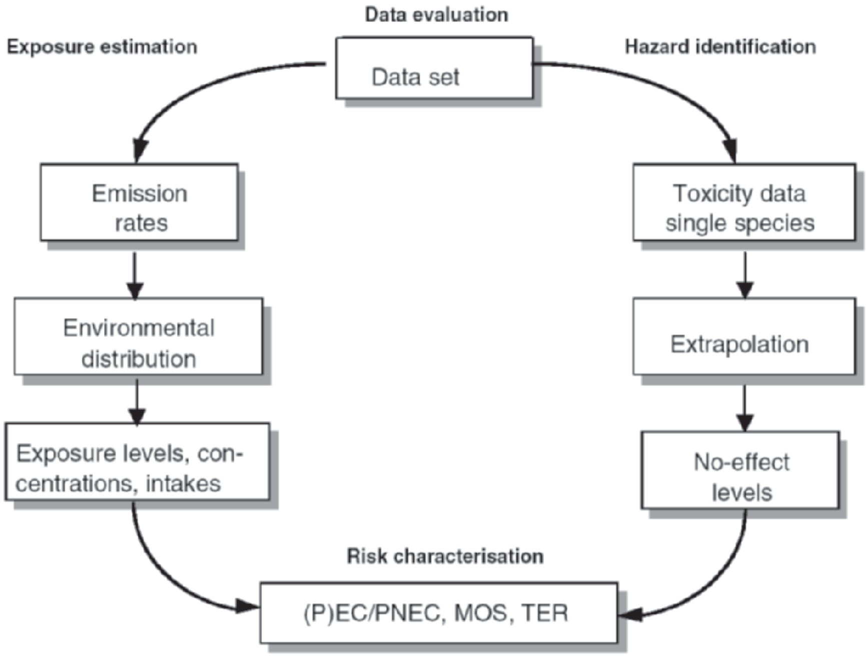

Figure 1. General Approach in Risk Assessment (from FOCUS, 2001).

Registrants are required to deliver a data set to the authorities. Part of these data is used to evaluate the fate and behaviour of a substance in the environment (Exposure Assessment). Other data are used to assess the potential Hazard posed by the substance by quantifying its effects on non-target organisms. The results of the exposure assessment and the hazard assessment are combined to produce an overall risk assessment. For the environment, risk assessment may be based on the ratio of the Predicted Environmental Concentration to the Predicted No-Effect Concentration (PEC/PNEC), or on the Toxicity Exposure Ratio (TER) or by applying a specified Margin of Safety (MOS) factor. Depending on the results of the initial risk assessment, more detailed data relating to environmental exposure or hazard may be required to clarify the environmental risk. Such data is generated from an increasingly comprehensive series of studies termed *higher tier studies*. At each tier a relevant comparison has to take place between the estimated exposure and the estimated hazard and there are thus separate tiers for both exposure and hazard estimation.

4. Use of modelling to evaluate PEC in surface water: results from the FOCUS workgroups

Simulation models are a very useful tool for assessing the potential pesticide contamination of surface water. In the absence of experimental data, models are the only quantitative option. Several models have been proposed for predicting pesticide concentration in surface water: major differences are in modelling approach, complexity of the equations used, and amount of data required. The complexity of the simulation modelling in multi-variable areas has led to the definition of standard scenarios. Scenario is a "representative", combination of crop, soil, climate and pesticide information to be used in modelling. "Representative" states for a realistic combination of information, which describes an existing geographical area in a standardised way. Standard scenarios are convenient for rendering complicated models easier to handle, due to the fact that fewer parameters are required and the variability of data is reduced, thus making the calculation more comparable.

The methods and models, discussed by the FOCUS Surface Water Group, apply only to the exposure estimation part of the risk assessment process.

The entry of pesticides into surface waters via routes other than spray drift, runoff and drainage are possible, for example via dry deposition, groundwater, discharge of waste water, accidents and incidents of various nature. Some of these were considered to be of minor importance or not Good Agricultural Practice. These routes were not considered to be part of the remit of the group.

4.1. SURFACE WATER

Lot of models are available for calculating surface water exposure. These have been reviewed by a FOCUS working group and described in a report published by the Commission (FOCUS, 1997). None of the models reviewed could be said to have been validated at the European level, as required in Directive 91/414/EEC, but the Working Group recommended a number as being suitable for use within Europe. The FOCUS Surface Water Group has limited its analysis to the scale of the field where plant protection products (PPP) are applied. The goal was to produce a limited number of 'realistic worst-case' scenario, and to take into account all relevant entry routes, target crops, surface water bodies, topography, soils and climate. Scenarios should reflect realistic combinations of runoff and drainage (different processes dominate in different areas) and, wherever possible, scenarios should be represented by a specific field site with monitoring data.

To evaluate PEC in surface water, the FOCUS group identified ten reference scenarios: based on the geographic distribution of agricultural soils, slopes and climatic conditions across Europe, a total of six unique drainage scenarios and four unique runoff scenarios were designed. The main characteristics of these scenarios are reported in Table 1.

A tiered approach, to evaluate the possible contamination of PPP entering surface waters is strongly recommended by the group: evaluation should start with a simple estimation of the PECs in surface waters. When toxicity-exposure-ratios (TER) are expected to be exceeded, more sophisticated approaches, which take into account realistic worst case assumptions have to be applied.

TABLE 1. Main characteristics of the ten FOCUS surface water European scenarios.

Name	Mean annual T (C)	Annual Rain-fall (mm)	Topsoil	OM (%)	Slope (%)	Water bodies
D1	6.1	556	Silty clay	2.0	0 – 0.5	Ditch, stream
D2	9.7	642	Clay	3.3	0.5 – 2	Ditch, stream
D3	9.9	747	Sand	2.3	0 – 0.5	Ditch
D4	8.2	659	Loam	1.4	0.5 – 2	Pond, Stream
D5	11.8	651	Loam	2.1	2 – 4	Pond, stream
D6	16.7	683	Clay loam	1.2	0 – 0.5	Ditch
R1	10.0	744	Silt loam	1.2	3	Pond, stream
R2	14.8	1402	Sandy loam	4.0	20*	Stream
R3	13.6	682	Clay loam	1.0	10*	Stream
R4	14.0	756	Sandy clay loam	0.6	5	Stream

The tiered approach suggested in the report of the FOCUS Working Group on Surface Water Modelling (FOCUS, 1997) is reported in Figure 2.

The first step estimates surface water exposure based on an “extreme worst case loading” scenario. If, at this first stage, the use is considered safe (that is, aquatic TER below the trigger) no further surface water risk assessment is required. If however, the result indicates that use is not safe, it is necessary to proceed with a Step 2.

Step 2 assumes surface water loading based on sequential application patterns, taking into account the degradation of the substance between successive applications. Moreover, some differences exist in runoff and interception by plants depending on the application area (North or South Europe), on the plant growth stage and on season. Again, if at this second stage the aquatic TER is below the trigger, no further risk assessment is required. When an ‘unsafe’ TER occurs, further work is expected with Step 3 calculation.

In Step 3, more sophisticated modelling estimations of exposure are undertaken using the set of 10 scenarios (Table 1) defined and characterised by the working group and representing ‘realistic worst-case’ situations for

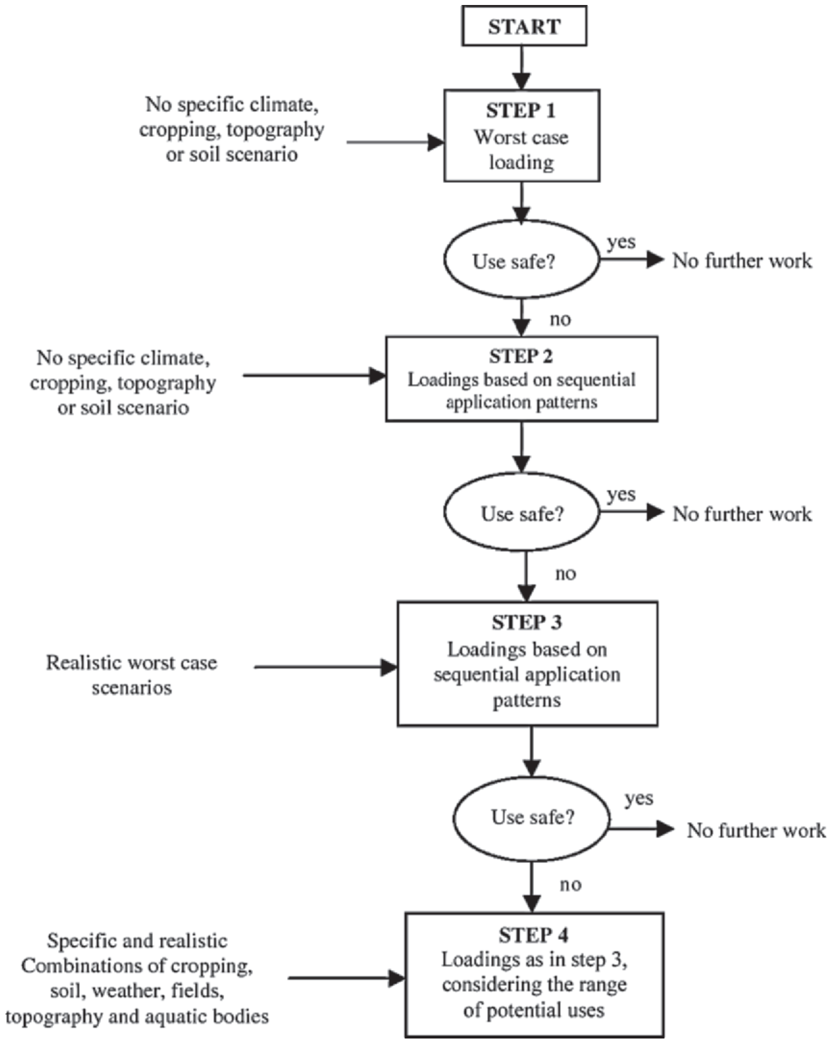

Figure 2. The Tiered Approach in exposure assessment of PPP, as suggested by FOCUS group (1997).

surface water within Europe. In order to limit the amount of work undertaken by the Surface Water Scenarios Working Group, the test calculations and the software tools, developed to perform and support Step 3 exposure assessments, use only one of the models recommended for calculating loadings from the different input routes and for surface water fate. The models chosen are: MACRO for drainage, PRZM for runoff and TOXSWA for evaluating aquatic fate (Figure 3). A specific shell, SWASH, was created to organise data necessary to the evaluation and to integrate the three models.

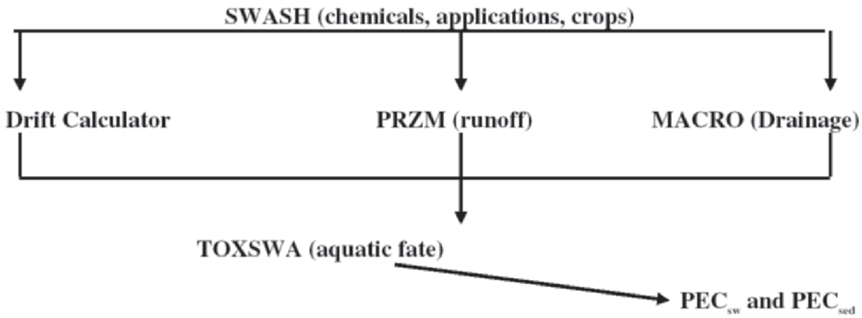

Figure 3. Scheme of the FOCUS Step 3 exposure estimation.

At this stage, the calculated PECs for each scenario are compared with relevant toxicity data and a decision made as to whether it is necessary to proceed to Step 4 exposure estimation. Risk assessments using Step 3 exposure estimation may incorporate higher-tier toxicity data generated from micro- or mesocosm studies. If the calculated TER, derived from the estimation of the PEC for a substance, may exceed the TER-trigger value for some and does not exceed the TER-trigger value for other relevant scenarios, then in principle the substance can be included on Annex I with respect to the assessment of its possible impact on surface water bodies. The scenarios represent major agricultural areas of the EU, and, consequently, also “safe” uses are significant in terms of representing large agricultural areas in the EU. However, when making decisions in these cases, the full range of results should be evaluated with the aim to specify critical conditions of use as clearly as possible to assist Member States in their national decision making on the basis of refined, regional assessments after Annex I inclusion of the active substance. The conceptual relationship between the Predicted Environmental Concentrations at Steps 1, 2 and 3 and the Actual range of exposure is described in Figure 4.

The final step of the FOCUS process is Step 4. In principle, Step 4 can be regarded as a higher-tier exposure assessment step. This may include a variety of refinement options of different degrees of complexity covering risk mitigation measures, refinement of fate input parameters, or regional and landscape-level approaches. A Step 4 analysis is considered necessary for those GAP applications that failed Step 3. It is conceivable that Step 4 approaches would be used both for Annex I listing and for national registration purposes. For example, for certain compounds it may be possible to identify a range of acceptable uses across the EU when appropriate mitigation measures (e.g., buffer zones) are applied. For certain specific uses, Step 4 approaches could also be useful for identifying safe uses at Member State level, for example if certain local or regional considerations mean that the lower-tier, EU level assessments were overly conservative.

5. Italian experience with the interpretation of FOCUS surface water scenarios from a regulatory point of view

In the frame of the registration process of a pesticide, appropriate procedures for identification of areas at possible risk of pesticide pollution are required. As far as decision-making policy is concerned, a great deal of information may be derived from the combination of provisional models and GIS.

The logic and approach followed by FOCUS group were taken into account in Italy, in a work in collaboration with the Ministry of Environment, to address FOCUS surface water scenarios for their suitability in representing

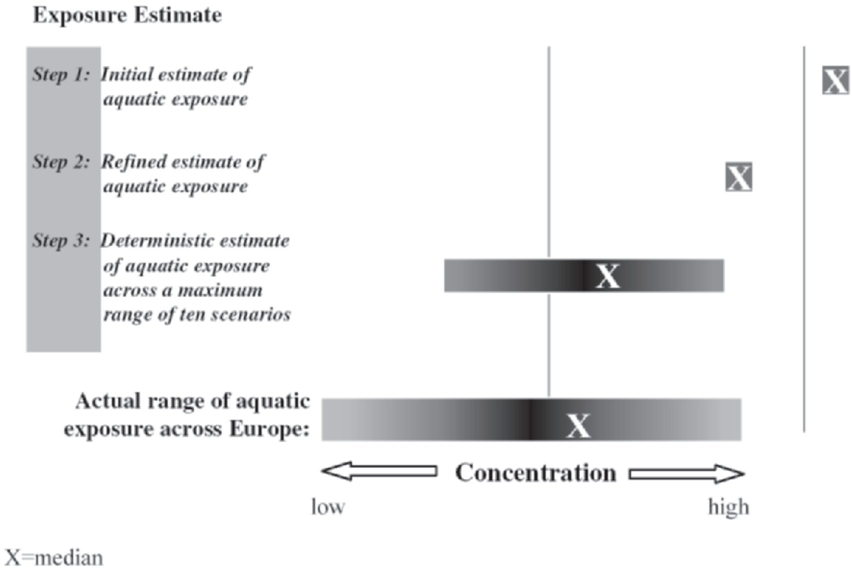

Figure 4. Conceptual relationship between the Predicted Environmental Concentrations at Steps 1, 2 and 3 and the actual range of exposure.

Italian conditions. To this purpose, different actions were performed: data were defined and searched at national level; data were collected, checked and organised; a statistical and spatial analysis was applied to compare Italian data with the ten $FOCUS_{sw}$ scenarios and to define the relevant scenarios for Italy.

Data on Italian soils and climate were collected and analysed by means of a Geographical Information System; a pedo-climatic geographical database covering the whole Italian territory was created.

The maps of rainfall and temperature and the ecopedological map were produced and intersected with a grid of 5×5 km cells. In this way, a raster spatial distribution of all the same pedo-climatic parameters, used by the

FOCUS group to characterise the European scenarios, was obtained for the Italian territory. A multivariate quantitative comparison of the characteristics of each cell with the ten scenarios was done performing a similarity analysis to address the suitability (degree of validity) of the European surface water scenarios for the Italian territory.

The Gower's General Similarity Coefficient (Gower, 1971) was calculated for all cultivated cells of Italy (about 9000 cells, 5 km ×5 km) with respect to the ten European surface water scenarios represented in Table 1.

Two different evaluations were performed: one did not take into account the definition of water bodies typology, the second one considered this definition. The results of these two different evaluations are shown in Figure 6, where the prevailing scenarios with respect to similarity analysis are reported. Each cell of the grid, represented in these maps, was associated to the scenario reporting the highest absolute value of the similarity coefficient.

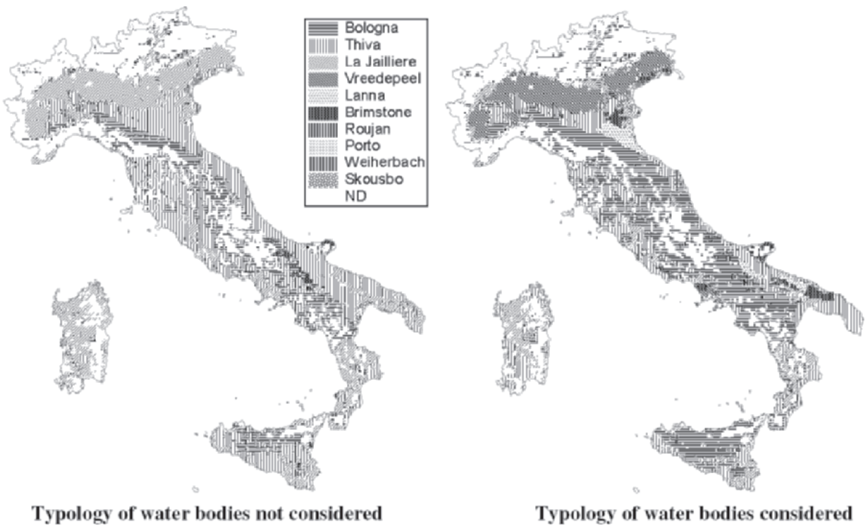

Figure 6. Prevailing scenarios with respect to similarity analysis.

From this first analysis, three major scenarios seem to be representative for Italy, for both the evaluations: La Jailliere (D5), Thiva (D6) and Bologna (R3), with different percentage of similarity, according to the type of evaluation (Table 2).

TABLE 2. Maximum similarity with respect to FOCUS scenarios. Comparison between the two evaluations.

Scenarios	Name	% (no water bodies)	% (with water bodies)
Lanna	D1	0.1%	4.4%
Brimstone	D2	1.6%	3.1%
Vreedepeel	D3	0.5%	13.1%
Skousbo	D4	1.4%	0.2%
La Jailliere	D5	35.1%	13.9%
Thiva	D6	42.2%	25.2%
Weiherbach	R1	1.3%	0.4%
Porto	R2	0.4%	0.4%
Bologna	R3	16.5%	37.4%
Roujan	R4	1.0%	1.9%

Going into a more quantitative analysis, similarity values were ranked in order to fix the level of correspondence between each single cell and the represented scenario. Observing the abundance of each class, about the 62% of the Italian cultivated territory is represented with a similarity higher or equal to 0.9, by principally three scenarios (D5 with 37.3% of cells, D6 with 48.0% and R3 with 10.3%), when the typologies of water bodies are not considered. This representativeness reaches 96.6% of the territory when the threshold of similarity is lowered to 0.8.

Situation changes when the typologies of water bodies are defined: representative scenarios vary according to the degree of similarity. When similarity threshold is lowered to 0.7, the 98.5%of the cultivated territory is represented by four scenarios (R3, D6, D5, D3). Increasing the threshold, a decrease in representativeness occurs: 43% of the territory is represented by FOCUS scenarios (mainly R3, 80.2% of cells) when similarity threshold is 0.8; 24% of the territory is represented by FOCUS scenarios (mainly R3, 89.6% of cells) when similarity threshold is 0.9.

It is evident, that the availability of good data is a prerequisite to obtain a proper evaluation. It has to be underlined that, in this evaluation, the suggestion of FOCUS surface water report was applied for defining typologies of water bodies.

In reality, a proper definition of typologies of water bodies, for a specific region, would require an in-depth investigation of the territory, integrating satellite images with soil data.

6. Conclusions

This paper has addressed some of the recent advances made in implementation and usage of modelling within the regulatory framework. Standard scenarios were developed and methodological approaches for the evaluation of PEC in surface water at European level have been developed by the FOCUS groups over the last few years.

An effort at national level has to be performed to address the national peculiar situations not covered by the FOCUS approach. To this purpose, development of appropriate databases of aquatic environment adjacent to agricultural land, soil types, topography, pedoclimatic characteristics, crops and pesticide information is necessary. Geographical database collecting all these data on land use, climate and all the environmental characteristics could be a powerful instrument supporting the work of risk assessors, at national and local level. In fact, at the simplest level, data regarding different spatial entities can be combined by overlay analysis to produce maps identifying areas at possible risk. At a more elaborated level, the combination of deterministic-mathematical model or screening indexes with GIS can produce more reliable thematic maps. This kind of exercise can be performed both in pre-marketing and in post-marketing phase of either pesticides or other chemicals.

7. References

FOCUS, 1995. *Leaching Models and EU Registration*. European Commission Document 4952/VI/95

FOCUS, 1996. *Soil Persistence Models and EU Registration*. European Commission Document 7617/VI/96

FOCUS, 1997. *Surface Water Models and EU Registration of Plant Protection Products*. European Commission Document 6476/VI/96

FOCUS, 2000. *FOCUS groundwater scenarios in the EU plant protection product review process*. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000

FOCUS, 2001. *FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC*. Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.1.

Gower, J.C., 1971. A general coefficient of similarity and some of its properties. *Biometrics*, 27, 857-872

LOW-COST ADSORBENTS FOR THE REMOVAL OF NITROPHENOLS FROM WASTE WATERS

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Abstract

The adsorption behaviour of three substituted nitrophenols, 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP), on different type natural materials, yellow/white bentonite, expanded perlite, perlite insulation filter, zeolite, and on the biosorbent *Rhizopus oryzae* was studied. The experimental results were analyzed on the basis of the effect of nitrophenol removal, *E*, calculated from the kinetic curves, as well as on the basis of the values of the equilibrium adsorption capacity, q_{max}. According to the equilibrium and kinetic data, the adsorption capacity of the studied materials follows the order:

yellow bentonite > Rhizopus oryzae > perlite insulation filter > white bentonite > zeolite,

while the uptake of the mono- and disubstituted nitrophenols increases in the order

2-NP < 2,4-DNP < 4-NP.

Key words: nitrophenols/natural minerals/Rhizopus oryzae/adsorption.

1. Introduction

Many industrial wastes contain organics that are refractory, which are difficult, or impossible to remove by conventional biological treatment

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 263–275.

processes (Crauford et al., 1990). Phenol and substituted phenols are common by-products of many industrial processes and they represent one of the most challenging classes of pollutants requiring removal from wastewater streams (Mohammad et al., 1996). Nitroaromatic compounds are widely used as pesticides, explosives, solvents, and intermediates in the synthesis of dyes and other chemicals. Many of these compounds and their transform products are of significant toxicological concern (Haderlein et al., 1996).

Mononitrophenols can be classified as compounds exhibiting moderate to high toxicity in the aquatic compartment. Based on the information gathered for 2-NP, 4-NP and 2,4-DNP, 2-NP will probably undergo slow photooxidation in an aerated biobasin. There is a possibility for photoreduction of the nitrogroup if 2-NP becomes absorbed by organic matter. 2-NP and 4-NP may be released to the environment in wastewater and as fugitive emissions during their production and use as chemical intermediates. 4-NP is also found in suspended particulate matter in the atmosphere, originating mostly from secondary photochemical reactions in the air.

Dinitrophenols are a class of manufactured chemicals that enter the environment in emissions or effluents from manufacturing plants, mines and foundries. 2,4-DNP, the most commercially important dinitrophenol, may form as a result of photochemical reaction between benzene and nitrogen monoxide in polluted air. If released to water, 2,4-DNP is expected to react with alkylperoxy radicals and it has the potential to photolyze. It is used in making dyes, wood preservatives, explosives, insect control substances and other chemicals, and as a photographic developer.

The Department of Health and Human Services (DHHS), the International Agency for Research on Cancer (IARC) and the Environmental Protection Agency (EPA) have not classified mono- and dinitrophenols for carcinogenicity (Agency for Toxic Substances, 1996).

Consequently, due to the harmful effects of these organic compounds, the wastewaters containing them must be treated before being discharged to receiving water bodies. The secondary biological processes are commonly used for domestic and industrial wastewater treatment, but their efficiency is not satisfactory at high pollutant concentration (Chern et al., 2002). Therefore the efforts are directed to the development of new treatment technologies such as chemical oxidation with ozone and hydrogen peroxide (Li et al., 1999), photocatalytic conversion in slurry reactors using TiO_2 or Al_2O_3 and gamma-ray irradiation (Salaices et al., 2004; Seino et al., 2003), etc.

In order to assess the fate of nitrophenols in wastewater and to control their mobility and reactivity during remediation processes, the sorption behaviour of these toxic contaminants must be understood and revealed.

Although carbon adsorbents are very versatile due to their high surface area, well-developed pore structure and surface properties (Nouri et al., 2002), there are economic objectives, namely high cost and need for regeneration after saturation, that restrict their applicability for wastewater treatment.

Literature reports many works concerning the optimization of adsorption by developing new adsorbent products and elucidating the mechanism of the process (El-Shahawi and Nassif 2003; Namasivayam and Kavitha 2003). Suitable alternatives are different clay minerals such as zeolites, bentonite (Koumanova et al., 2001, 2003), clinoptilolite (Sismanoglu and Pura 2001), kaolinite, illite, montmorillonite (Haderlein et al., 1996), etc.

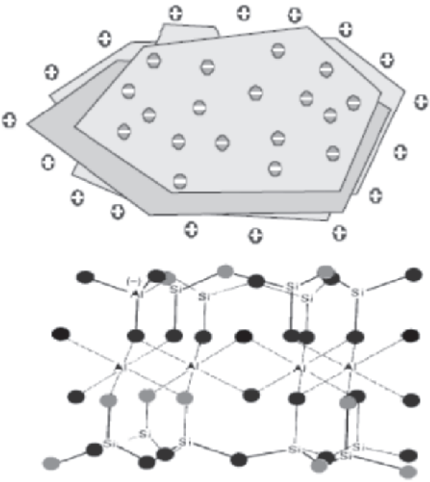

Figure 1. Bentonite structure.

Bentonite, a clay mineral, has the advantages of being both abundant and inexpensive. Its active ingredient, montmorillonite, possesses a 2:1 layer structure (Figure 1) resulting from the condensation of alternating silica tetrahedral (SiO_4) layers and aluminium octahedral layers [$Al(OH)_3$]. Isomorphous substitution of magnesium or iron (II) ions in the octahedral gibbsite-like layer or aluminium ions in the silica layer results in an over all excess of negative charge on the clay which is usually compensated with calcium or sodium ions in the interlayer spaces. The ability of bentonite to undergo cation exchange with these interlayer cations has been used to treat metal contaminated wastewaters or for adsorbing organic pollutants. The colour of bentonite ranges from white to light olive green, cream, yellow, earthy red, brown and sometimes sky blue when fresh but yellowing rapidly with exposure to air. Studies have also found that bentonite could be used as an efficient biological barrier against contamination of ground waters (Cox et al., 2001; Viraraghavan and Alfaro 1998).

Zeolites are naturally occurring minerals with high surface area that provides sites for cation exchange and adsorption. These sites promote the zeolite activity to remove suspended solids, heavy metals, ammonium and various organic compounds. The zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4 (Figure 2). The alumino-silicate structure is negatively charged and attracts the positive cations that reside within.

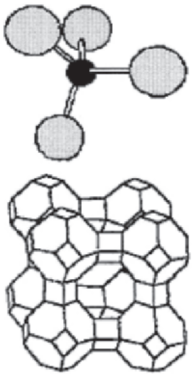

Figure 2. Zeolite structure.

Zeolites have large vacant spaces or cages in their structures that allow space for large cations such as sodium, potassium, barium and calcium and even relatively large organic molecules and cation groups such as water, ammonia, carbonate ions and nitrate ions. In some types of zeolites, the spaces are interconnected and form long wide channels of varying sizes depending on the mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. Zeolites are characterized by their ability to lose and absorb water without damage to their crystal structures (Ustinov and Do 2002; Razee and Masujima 2002; Baerlocher et al., 2001).

Perlite is a naturally occurring siliceous rock The distinguishing feature which sets perlite apart from other volcanic glasses is that when heated to a suitable point in its softening range, it expands from four to twenty times its original volume. This expansion is due to the presence of two to six percent combined water in the crude perlite rock. When quickly heated to above 870°C the combined water vaporizes and creates countless tiny bubbles which account for the light weight and other exceptional physical properties of expanded perlite. This expansion process also creates one of perlite's most distinguishing characteristics: its white color. While the crude rock may range from transparent light gray to glossy black, the color of expanded perlite ranges from snowy white to grayish white. Since perlite is a form of natural glass, it is classified as chemically inert and has a pH of approximately 7. There are many uses for perlite. These uses can be broken down into three general categories: construction applications, horticultural applications, and industrial applications.

Rhizopus oryzae are saprophylic microorganisms, which belong to the *Rhizopus fungi* group. Their cell walls consist of chitin and chitosan. The mechanism of biosorption is quite complicated. The capacity of dead cells might be higher, equal or even lower when compared to that of live cells. In most cases, however, the application of dead biomass is more effective. It was established a higher extent of humic acids removal from wastewater by dead fungi. The application of live biomass has some disadvantages: live cells systems are sensitive to the toxicity of the pollutants and to the working conditions (pH, temperature). Dead biomass is produced by physical (heating, autoclave treatment, vacuum drying), chemical (treatment with acids, alkali and other organic and inorganic substances) and mechanical (mechanical grinding) methods. It was established that the highest adsorption capacity of the biomass applied in this study was 263 mg g^{-1} for Reactive Red dye adsorption and 136.3 mg g^{-1} for Cu(II) removal. These values are relevant for the concentration range 50 – 1000 mg dm^{-3} for the dye and 25 – 275 mg dm^{-3} for the metal ions and 150 – 500 μm particle size range (Peeva-Antova, 2004).

2. Materials and methods

2.1. MATERIALS

2.1.1. Adsorbates

The sorbates used in the experiments are 2-nitrophenol (2-NP), 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP). All chemicals have e" 97% purity.

TABLE 1. Physical properties of 2-NP, 4-NP and 2,4-DNP.

Compound	Molecular mass, kg $kmol^{-1}$	Density, g cm^{-3}	Solubility, g/100g H_2O	Molecular volume nm^3 mol^{-1}	pKa	Effective molecular diameter, nm	λmax, nm
2-NP	139.11	1.495^{*}	0.2	0.191	7.23	0.813	272
4-NP	139.11	1.270^{**}	1.7	0.191	7.08	0.813	228
2,4-DNP	184.11	1.683^{***}	0.6	0.221	5.40	0.872	254

*at 14 ^{0}C; ** at 20 ^{0}C; ***at 24^{0}C

2.1.2. Adsorbents

The natural minerals, white/yellow bentonite, expanded perlite, perlite insulation filter and zeolite, used for the experiments were taken from deposits in the southern part of Bulgaria. The chemical composition and the specific surface area of the adsorbents are given in TABLE 2. The surface area of bentonite and perlite was determined on the basis of the Brunauer, Emmet and Teller (BET) method using a Sorptomatic 1900 (Fisons Instruments).

TABLE 2. Physicochemical characteristics of bentonite and perlite.

Composition, %	Bentonite	Perlite
SiO_2	59-75	70-80
Al_2O_3	12-16	10-15
Fe_2O_3	1-6	<1.5
CaO	1.8-5	<1.5
MgO	0.9-3	<1
K_2O, Na_2O	0.5-1	<10
TiO_2	0.1-0.8	-
C.L.	-	<5
Specific surface area, a, $m^2\ g^{-1}$	57.99	5.83
Mean particle diameter, d_p, μm	88	37

2.2. EQUILIBRIUM STUDIES

The equilibrium experiments were accomplished using model solutions of 2-NP, 4-NP and 2,4-DNP in distilled water. The investigations for the mononitrophenols were carried out at temperature 20±2 ^oC and pH 6.8±0.2 and for the dinitrophenol – at 27±2 ^oC and pH 7.5±0.2. Solutions were in the concentration range of 3-25 mg dm^{-3} for 2-NP, 5-25 mg dm^{-3} for 4-NP and 5-30 mg dm^{-3} for 2,4-DNP. Known masses of the corresponding adsorbent were added to 100 cm^3 of the model solutions in screw cap jars. The jars were shaken on a platform shaker. The solute from each jar was then filtered. The residual 2-NP/4-NP/2,4-DNP concentrations in the liquid phase (C_e) were determined spectrophotometrically with a Perkin Elmer 323 UV-VIS NIR spectrophotometer.

2.3. KINETIC STUDIES

The kinetic experiments were conducted in a standardized batch adsorber. 2-NP/4-NP/2,4-DNP solutions (1.7 dm^3) were placed into the reactor and stirred at 200-600 rpm with a two-bladed impeller with a Heidolph RZR 2100 motor. Samples were taken at definite time intervals by removing 5 cm^3 of the solution with a plastic syringe (10 cm^3). The samples were immediately filtered and analyzed.

pH measurements were made with pH-meter LHP 403T TACUSSEL. All experiments were replicated and the average results were used in data analysis.

3. Results and discussion

The experimental results were analyzed on the basis of the effect of the nature of the applied natural materials and the biosorbent on the extent of toxic organics removal from aqueous phase.

The adsorption behaviour of 4-NP on zeolite, white and yellow bentonite, perlite insulation filter and *Rhizopus oryzae* was studied. Figure 3 shows that the highest percent removal (86%) of the mononitrophenol from its model solutions was achieved by yellow bentonite.

However, the results with the biosorbent (79%) and perlite insulation filter (76%) are comparable. While the values of *E* for the other two materials, zeolite and white bentonite, are nearly 2-3 times lower. Thus, it could be concluded that greater relative part of active sites on the surface of yellow bentonite, perlite insulation filter and *Rhizopus oryzae* are available for

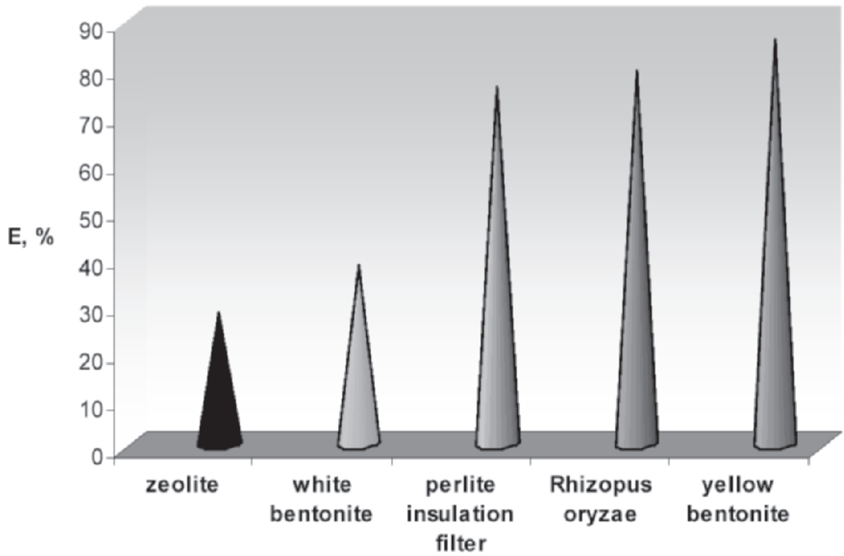

Figure 3. Effect of adsorbent nature on the adsorption of 4-NP from aqueous medium.

4-NP molecules. Actually the adsorption capacity of the studied materials follows the order: yellow bentonite > *Rhizopus oryzae* > perlite insulation filter > white bentonite > zeolite.

The comparative analysis of the results from the experiments of 2-NP (Figure 4) and 2,4-DNP (Figure 5) adsorption on yellow bentonite and expanded perlite evoked similar conclusions.

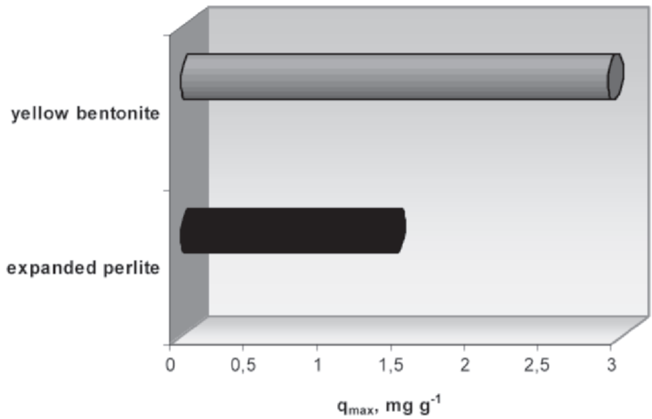

Figure 4. Effect of adsorbent nature on the adsorption of 2-NP from aqueous medium.

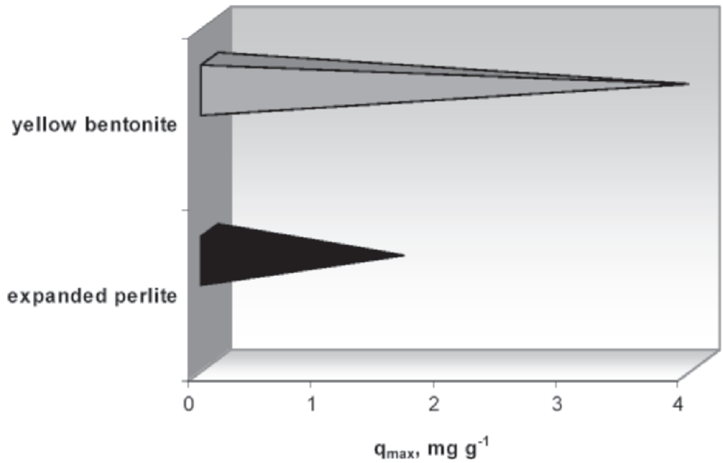

Figure 5. Effect of adsorbent nature on the adsorption of 2,4-DNP from aqueous medium.

Namely, the adsorption capacity of yellow bentonite determined during the adsorption experiments was 2.9 mg g^{-1} for 2-NP removal and 3.92 mg g^{-1} for 2,4-DNP removal, while the capacity of expanded perlite towards both nitrophenols were 2-2.5 times lower.

The effect of sorbate nature on the adsorption of the three substituted nitrophenols on yellow bentonite was also investigated (Figure 6, Figure 7).

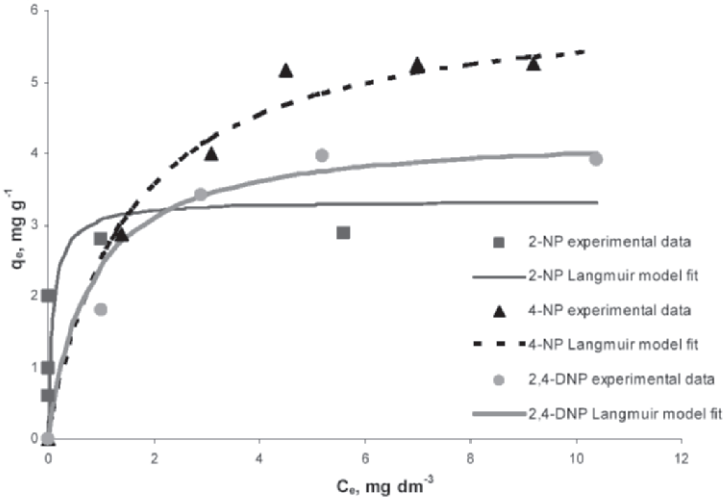

Figure 6. Comparison of the isotherms for 2-NP, 4-NP and 2,4-DNP adsorption on yellow bentonite – experimental data and Langmuir model fits.

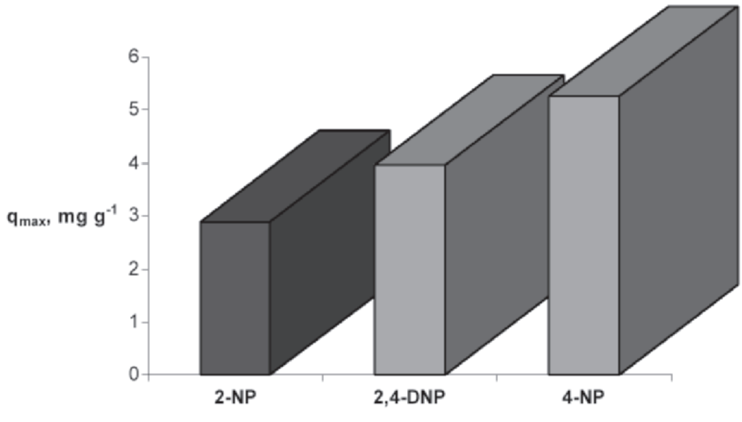

Figure 7. Effect of sorbate nature on the adsorption of 2-NP, 4-NP and 2,4-DNP on yellow bentonite.

It should be emphasized that they represent two different classes of substituted phenols. Due to differences in their molecular structures they exhibit specific physical and chemical properties that are responsible for the deviations in their sorption behavior. Probably the second NO_2-group in the

2,4-DNP molecule on *para*-place in the aromatic ring displays affinity for electron exchange activities with the metal ions from the montmorillonite. While the O-atom from the NO_2-group on *ortho*-place for 2-NP and 2,4-DNP is capable of forming a hydrogen bond with the H-atom from the OH-group. Thus, it could hardly participate in chemical reactions and is responsible for the lower solubility of 2-NP and 2,4-DNP in water compared to 4-NP, where the OH-group in *para*-position does not form a hydrogen bond with the NO_2-group.

The equilibrium adsorption capacity for 4-NP, 2,4-DNP and 2-NP, was 5.22 mg g^{-1}, 3.92 mg g^{-1} and 2.9 mg g^{-1}, respectively. Thus, during the parallel batch equilibrium experiments a greater relative part of 4-NP molecules saturated the surface monolayer of the bentonite particles.

Actually, according to the kinetic and equilibrium data the uptake of the mono- and disubstituted nitrophenols increases in the order 2-NP < 2,4-DNP < 4-NP. On the one hand, the reasons for the higher removal of 2,4-DNP when compared to 2-NP might be due to its high molecular dimensions (molecular mass, molecular volume and diameter) and increased acidity, i.e. low pKa values. On the other hand, 2,4-DNP uptake is lower than the 4-NP quantity adsorbed by the clay mineral. Probably the large 2,4-DNP molecules induce a molecular-sieve effect that appears in the molecule. From another point of view, strong adsorption of 2,4-DNP molecules might occur on sites near to the openings or inside certain pores, thus bridging the entrance. Consequently the strongly adsorbed 2,4-DNP molecules block some pores and it becomes increasingly difficult for a new molecule from the solute to find an available vacant site.

The only clear conclusion that could be drawn and applied to the three nitrophenols studied is that their uptake by the clay mineral is directly proportional to sorbates solubility in water.

4. Conclusions

According to the analyzes of the experimentally obtained data, it could be concluded that the natural mineral, yellow bentonite, and the biosorbent, *Rhizopus oryzae* , could be successfully applied as effective adsorbents for mono- and dinitrophenol removal from aqueous phase. The higher affinity of these alternative low-cost sorbents towards the nitrophenols is due as to peculiarities in their structures so to the physicochemical characteristics of the sorbates.

It was established that the equilibrium adsorption capacity was 5.22 mg g^{-1}, 3.92 mg g^{-1} and 2.9 mg g^{-1} for 4-NP, 2,4-DNP and 2-NP, respectively. Actually, it could be concluded that the sorption capacity of the studied toxic organic compounds is directly proportional to their solubility in water.

5. References

Agency for Toxic Substances, Nitrophenols, 1996.

Baerlocher, Ch.,. Meier, W.M,. Olson, D.H., 2001, Atlas of Zeolite Framework Types, 5th ed., Elsevier, Amsterdam.

Chern, J-M., Chien, Y-W., 2002, Adsorption of nitrophenols onto activated carbon: isotherms and breakthrough curves, Wat. Res. 36, 647-655.

Cox, M., Rus-Romero, J.R., Sheriff, T.S., 2001, The application of montmorillonite clays impregnated with organic extractants for the removal of metals from aqueous solution Part I. The preparation of clays impregnated with di-(2-ethylhexyl)phosphoric acid and their use for the removal of copper (II), Chem. Eng. J. 3871, 1-7.

Crauford, H.B., Cline, G., 1990 Water treatment plant design, American Society of Civil Engineers, American Water Works Association, McGraw Hill, New York, 457.

El-Shahawi, M.S., Nassif, H.A., 2003, Kinetics and retention characteristics of some nitrophenols onto polyurethane foams, Analytica Chimica Acta 487, 249ß259.

Haderlein, S.B., Weissmahr, K.W., Schwarzenbach, R.P., 1996, Specific adsorption of nitroaromatic explosives and pesticides to clay minerals, Environ. Sci. Technol. 30, 612-622.

Koumanova, B., Peeva-Antova, P., 2001, Adsorption of p-chlorophenol from aqueous solutions on bentonite and perlite, J.Haz.Mat. 90, 3, 229-234.

Koumanova, B., Kircheva, Z., 2003, Bentonite assisted bioprocess for 2-nitrophenol removal from wastewaters, J.Univ.Chem.Technol.Met., (Sofia), 1, 71-78.

Li, J.S., You, Y.H., Lien, E.T., 1999, Oxidation of 2,4-dinitrophenol by hydrogen peroxide in the presence of basic oxygen furnace slag, Arch. Environ. Contam. Technol. 37, 427-433.

Mohammad, R., Haghighi-Podeh, Bhattacharya, S.K., 1996 Fate and toxic effects of nitrophenols on anaerobic treatment systems, Wat. Sci. Technol. 34, 345-350.

Namasivayam, C., Kavitha, D., 2003, Adsorptive removal of 2-chlorophenol by low-cost coir pith carbon, J. Haz. Mat. 4017, 1-18.

Nouri, S., Haghsereht, F., Max Lu, G.Q., 2002, Comparison of the adsorption capacity of p-cresol and p-nitrophenol by activated carbon in single and double solute, Adsorption 8, 215-223.

Peeva-Antova, P., 2004, , Kinetics and equilibrium of the adsorption of chlorinated phenols from aqueous solutions, PhD Thesis, Sofia.

Razee, S., Masujima, T., 2002, Uptake monitoring of anilines and phenols using modified zeolites, Analytica Chimica Acta 646, 1-5.

Salaices, M., Serrano, B., deLasa, H.I., 2004, Photocatalytic conversion of phenolic compounds in slurry reactors, Chem. Eng. Sci. 59, 3-15.

Seino, S., Yamamoto, T.A., Hashimoto, K., Okuda, S., Chitose, N., Ueta, S., Okitsu, K., 2003, Gamma-ray irradiation effect on aqueous phenol solutions dispersing TiO_2 or Al_2O_3 nanoparticles, Rev. Adv. Mater. Sci. 4, 70-74.

Sismanoglu, T., Pura S., 2001, Adsorption of aqueous nitrophenols on clinoptilolite, Colloids and Surfaces A: Physicochemical and Engineering Aspects 180, 1-6.

Ustinov, E.A., Do, D.D., 2002, Mixed gas equilibrium adsorption on zeolites and energetic heterogeneity of adsorption volume, Langmuir 18, 3567-3577.

Viraraghavan, T., Alfaro, F. 1998, Adsorption of phenol from wastewaters by peat, fly ash and bentonite, J. Haz. Mat 57, 59-70.

ACTUALIZING WATER ETHICS IN THE REGIONAL CONTEXT OF THE ARAB WORLD

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Abstract

The main concern of the paper is to actualize water uses ethics among various stakeholders in the Arab region. The approach is cultural, that is propagating social learning and have "bottom-up" education and communication functions, as well as "top down" high level applied research aspects with industry and technology participation. The paper examines the key factors in the Arab water crisis, and assesses the progress made in implementing initiatives, programs of action based on the "Arab water vision" 2025, and *how* best water ethics could contribute to its realization? The central question is how we, as Arabs, can set in motion a process that actualizes our vision? And applying new tools and techniques based on participation of relevant stakeholders in decision making, knowledge and experience transfer among water institutions and organization, and through benchmarking and bench-learning of best practices.

Keywords: water ethics / social responsibility / Arab water crisis / water complexity issues / Arab vision and programs of action / knowledge transfer / code of conduct / best practices / networking / awareness building / social learning/

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 277–310.

1. Introduction

Water issues are among the most controversial, critical, and sensitive issues that face governments and nations. Water does not only concern the idea of the civic uses of clean water resources in conventional means relating to human usage but extends to cover a variety of usages that relate directly to national security. The use of water resources in generating electric power through hydroelectric power stations, the issue of land reclamation and food security, the issue of accessible replenishing clean water resources, and the issues relating to the environmental effects, desertification, climate change, and rich soil depletion all relate directly or indirectly to water availability and accessibility.

Water stress, and water scarcity is among the major problems that mankind is facing now and will increasingly face in the coming decades. The vulnerability of water resources is sharply augmenting due to many pressures emerging from increasing exploitation blurring side-effects such as pollution and environmental degradation, be probably sources of social and political instability, in many locations, and yield human disaster to an innumerable amount of people.

The World Water Council has highlighted world water challenges in the 21st Century, on same lines, emphasizing issues of endangering world peace and security, lack of awareness by decision makers and the public, decline of financial resources allocations and fragmentation of water management.

The region of the Arab countries[1] today is no exception. It is considered to be one of the main areas facing serious shortages of water. This is due to rapid population growth and climatic change, which could pose serious threats to the stability and prosperity of the region.

The paper examines the contribution of actualizing water uses ethics in alleviating Arab water crisis. The approach is based on a holistic and comprehensive system analysis. This is dependent on examining relationships among different components of the system of water resource management. Such an endeavor requires the choice of appropriate strategies for an integrated system. The systems metaphor also embraces the mental model scientists hold about crucial system properties, such as controllability and predictability. Any strategy must start from an analysis of the coupled "environment-technology-human" system and aim at an improved design of it (Pahl-Wostl, 2002).

[1] The Arab countries are the countries members of the Arab League, they are 21 countries.

Designing a strategy for actualizing water uses ethics in the Arab region needs to draw upon the work of UNESCO's COMEST[2] Sub-Commission on Water Ethics reports and recommendations. (COMEST 1999-2002). It is timely to give due consideration to these reports and initiate a process, by which Arab countries could benefit from such an important work. COMEST work brought about questions and issues that range from conceptualizing and building a framework for localizing regionally the "Global Freshwater Guidelines", to issues of capacity building; processes of social learning through better participation of different water research centers; education, water suppliers; water regulators; industrial and agricultural users; organizations concerned with information; exchange and dissemination (Lord Selborne, 2003).

In addition, actualizing water ethics in the Arab region needs to address the questions that matters and key characteristics of its water sector. In this regard the paper addresses four main parts as follow:

First: mind mapping of water crisis in its complexity, taking into consideration hard factors involved, i.e. water availability, withdrawal and usage, and soft factors of human dimension and ongoing institutional reform and change. This will define the key drivers for future course of action.

Second: assessment of responses made on the International and Arab regional Level to help avert the looming crisis and then assessment of progress made due these initiatives.

Third: proposed elements of a strategy for actualizing water ethics, and its contribution as leverage for averting water crisis. This will introduce action research as a method of work in policy making and strategy building. The strategy emphasizes learning from each other experiences for knowledge and experience transfer through:

- Using Benchmarking and Benchlearning as a Tool for Learning;
- Using Dialogue, Shared Vision and Action on the Ground exemplified in the Nile Basin Initiative;
- Highlighting Arab's Water Best Practices.

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[2] In 1998, the World Commission on the Ethics of Scientific Knowledge and Technology (COMEST) was established. A resolution, to that effect, passed at the 29th session of UNESCO's General Conference. Special attention has been given by COMEST to freshwater along other vital areas of energy and information technology, for which three working groups were established to investigate and research into their field, within specific mandate.

Fourth: The need for an Arab Network for Water Ethics;

- What kind of a network?
- The next step: establishing the network;
- Proposed activities of the Arab network;
- The Cairo Regional Center for Studies and Research of Water Uses Ethics.

Water Ethics, Law and Social Responsibility

In general, the term "ethics" is used to refer to the "science of morality". In philosophy, ethical behavior is that of which is "good". It is one of the three major branches of philosophy, alongside-de metaphysics and epistemology. But is ethics the same as law? Do ethics and law overlap? Literature available for different scholars concludes that ethics is related to but different from and above law; jugged by what you do and not by what you know (knowledge) and is the personalized way in which one makes value-*laden* decisions. However, ethics definition has a relative meaning and it differs from one culture to the other and one person to the other. For this reason, the paper advocates using the term "social responsibility", as it is based on the principle of accountability, as well as it could be measured on the basis of formulating indicators and standards of responsible social conduct. Hence, progress could be measured and ethics monitor could be established. (Mubarak, 1999).

In specific terms, Mrs.Vigdis Finnbogadottir, Chairperson of COMEST, explained that "ethics can be simply defined as an attempt to evaluate choices from essentially human perspective"(COMEST Proceedings, Oslo, Norway, April 1999). She has guided the work of the Sub-Commission on Water by putting several questions to investigate, inter alia,

- How to balance the right to water as a prerequisite for life with the right of ownership;
- How to agree on preventing contamination or selfish exploitation of a shared basic resource;
- Access to freshwater has increasingly been identified as a major potential threat to world peace in this century.

2. Mind mapping of arab water crisis

Reviewing recent literature, one finds resources that can assist mapping out the key factors that make the Arab water crisis, and explain its complexity. Renowned water sciences institutes and eminent scholars (Abu Zeid and Hamdy, 2004, El-Kady, 2003, ESCWA, 2003) in their recent studies concur on certain factors that shape the Arab water crisis. These factors in their interaction are illustrating the complexity of the crisis and its magnitude. Reflecting on these sources can draw the attention and bring together the big picture, as shown in Figure 1 (Annex 2) which reflects the complexity and interconnectedness among various factors that shape the crisis.

2.1. SEVEREST WATER SCARCITY IN THE REGION

The Arab region represents 10% of the world's surface; its population represents 5% of world population. However, it possesses only 0.5% of world renewable fresh water resources. This is due to the fact that the arid and semi-arid weather dominates 82.2% of the whole region. Rainfall precipitation estimated to be 2,228 billion cubic meters (bcm). The losses amount to 90.4% due to evaporation. The Arab region is home to 5 percent of the world's people, contain less than 1 percent of the world's annual renewable freshwater. The water demand in the region is growing fast. The population is more than doubled in the past 30 years to about 280 million, and could double again in the next 30 years. Water demand for domestic and industrial uses has exploded in recent decades. At the same time, tube-well technology and the development of agriculture have increased water use in rural areas.

2.2. WATER AVAILABILITY IS FALLING TO CRISIS LEVELS

About 45 million of the region's population (16 percent) is lacking safe water, and more than 80 million lacking safe sanitation. As population has grown against a background of finite freshwater resources, so water available to individuals has fallen dramatically (Figure 2, Annex 2). The most seriously affected Arab countries of water shortages are: UAE, Saudi Arabia, Libya, Qatar, Kuwait, Oman, Bahrain, and Jordan.

Table (1) (Annex 2) as annexed confirms this trend of serious water shortages for countries which are mostly located in arid and semiarid parts of the region.

2.3. FOOD SECURITY

In a recent paper, Diaz-Bonilla *et al*. (2000) have made analysis to classify the countries of the world into three different groups: food insecure, food neutral, and food secure. For most countries, their analysis was based on data for 1993-1997. Box 1 shows the classification of the Arab countries covered by their analysis. Their definition of food security is based on the following indicators: food production per capita (measuring the ability of a country to feed itself); the ratio between total export earnings and food imports (showing its ability to finance food imports); calories per capita and protein per capita (important explanatory variables for changes in malnutrition); and the non-agricultural population share (aimed at showing the extent of immunity from global changes in trade and agricultural policies) (Diaz-Bonilla *et al*., 2000, pp. 6-9). Trade-stress (high food imports relative to export earnings) tends to contribute to a lack of food security in the Arab region more than in other regions.

Box 1 Food security in Arab Countries, 1993-1997.

Food Security	Group Countries
Insecure (74)*	Sudan, Yemen
Neutral (51)*	Algeria, Egypt, Iran, Jordan, Kuwait, Lebanon, Libya, Morocco, Syria, Tunisia
Secure (37)*	UAE

Source: Diaz-Bonilla et al. (2000, pp. 55-57)
*The numbers in brackets show the total number of countries in the world that belong to the group.

In another paper by Lofgren and Richards. (2003) have shown that in the second half of the 1990s, available indicators suggest that food insecurity at the national and household levels was a serious problem in Iraq, Sudan, and Yemen, countries that also are likely to have the highest poverty rates in the region. At the household level, the performance of food security indicators was more positive up to the mid 1980s than in more recent years. For the national-level indicators, the picture is mixed. For the region as a whole, some of these indicators (per-capita food production and food import stress) show stronger gains since the mid 1980s whereas others (including per-capita calorie consumption) improved less strongly in more recent years. Finally, the influence of political instability and conflicts (internal and external) on food security is obvious. Continued strife makes the challenge of improving food security much greater for the cases of Iraq and Sudan.

2.4. WATER POLLUTION

Water shortages in Arab countries are compounded by pollution. Contamination by fertilizers and pesticides, dumping of municipal and industrial wastewater into rivers and lakes, solid waste deposits along river banks, and uncontrolled seepage from unsanitary landfills - all these factors are degrading freshwater resources and imposing health risks, especially for children, the primary victims of waterborne diseases.

2.5. POVERTY LEVEL

Mapping the true dimensions of income poverty in the Arab states is a complex task. The World Bank has published income poverty estimates for seven countries based on national poverty lines. The most recent figures indicate that poverty affects around 10 per cent of the population in Jordan and Tunisia, about 20 per cent in Algeria, Egypt and Morocco, 40 per cent in Yemen and 46 per cent in Mauritania (Figure 3, Annex 2).

2.6. PROLIFERATION OF DISPUTES OVER SHARED WATER RESOURCES

So, the development of the Arab water sector is confronting mounting challenges, not only because of water shortages in many countries, but also proliferation of disputes over shared water resources. Together with the stumbling peace process, disputes relating to accessibility and to replenishing clean water resources have caused uncertainty and instability in the region. Such dispute related to water issues spread as far as Anatolia incorporating Turkey, Syria, and Iraq in a severe dispute around the appropriation of the Euphrates water supply. Among Israel, Occupied Palestine, Syria and Jordan another dispute relating to Lake Tiberius and the Jordan River Basin together with the disputed water resources in the Aquifers that are supposed to be shared by Israel and the Palestinian territories in the West Bank and The Gaza Strip.

However, dispute over shared water in the River Nile is less in severity and intense among the ten riparian countries, whether upstream or downstream. The Nile Basin Initiative (NBI) launched in 1999 is progressing towards more collaborative actions among Nile riparian countries. More progress could be seen in establishing the Nile Basin Secretariat in Entebbe, Uganda and operationalizing “The Strategic Action Plan” with a basin-wide “Shared Vision Program and “A Subsidiary Action Program” to work with projects that have a real impact at the community level.[3]

[3] NBI (2001). Nile Basin Initiative Shared Vision Program.

3. Characteristics and complexity of the crisis

Water issues are thus regarded highly as complex in the Arab region and should be dealt with in their complexity. One important aspect to be looked upon is the interaction between what is global and what is regional regarding water issues, and how these two levels of handling affect the national security of states. The formulation and re-formulation of strategies and water policies have to be designed in a way to suit well the changing international positions regarding access of the country in concern to replenishing water resources. In addition, water issues deserve to be looked upon from a professional institutional point of view that would establish the solid bases for a better understanding of these issues.

Soil erosion, pollution and food insecurity; confirm the scale of the problem. Depletion of non-renewable ground water is rampant and remaining water resources are polluted. Salt water intrusion in many of the coastal aquifers is common. Conflicts in the region on shared international water are at its highest anywhere in the world. In addition to being water deficit, there is a rampant food deficit as well. The region is one of the largest food importers and forecast under whatever scenario indicates that the region will remain in a permanent food deficit for a long time in the future.

According to a recent study (El-Kady, 2003) key water issues were highlighted in the following fifteen categories (Box 1), this can be regarded as a summary of the previously described issues.

3.1.1.1. External Forces

- Traditional and cultural practices, especially in water use and crop production as well as land tenure.
- Demography: - rapid population growth, rapid urbanization, settlement patterns and population policy.
- Economic development patterns: - agriculture, industry and water-conscious development schemes.

Box 1 – Water Key issues in the Arab Countries

1. Water scarcity and population growth
2. Mismanagement of water especially in the agricultural sector
3. Problems of trans-boundary rivers
4. Limited of information on water resources
5. Water policy overlaps
6. Water quality degradation and water pollution
7. The growing gap between water supply and demand: the structural imbalance
8. Lack of broad spectrum vision in water management authorities
9. Limited awareness of water issues
10. Slow transfer of technology from applied research to practice
11. Shortage of capacity building and institutional development
12. Inadequate stakeholder participation and gender issues in water management
13. Political pressures imposed by anti-Arab parties in the region
14. Shortage of available funds for water development and conservation projects
15. Rejection of changing the unfavorable social habits and attitudes towards water uses due to poor public awareness programs

These challenges could be driven by external and internal forces as follow (El-Kady, 2003):

- International trade and globalization: - food availability, market prices, level of investment and trade agreements.
- Institutions and Human Resources: level of quality of life, awareness and participation, education level, lack of education for water issues, cultural restrictions imposed on women preventing their involvement in water management.
- Environmental degradation: - land, water, forest, air, planned development, destruction of fertile land for housing, depletion of natural resources.

- Conflicts, emergencies, natural disasters: - floods, droughts, wars, civil unrest and climatic changes.
- Restriction imposed on modern means of communication and information flow such as the use of Internet, E-mail, etc.

3.1.1.2. Internal Forces

- Inefficient use of water resources: - rapid depletion and irrational use of fossil groundwater, limited recycling and conservation practices, high cost of desalination, poor irrigation systems and practices.
- Technology and science: - lack of adequate attention for development and adaptation of suitable technologies and research on water.
- Rationalizing the demand: - ineffective framework for demand management, poor cost recovery (especially for irrigation use).
- Water sector strengths: - policies, strategies, political support, access to funding, modern management and skilled human resources.

3.2. KEY DRIVERS FOR FUTURE COURSE OF ACTION (WORLD BANK GROUP, 2003)

The leverage in addressing the foregoing challenges and affecting change could be through using key drivers; these are suggested by the World Bank, as follow:

Water and Finance:

- Financing Operation and Maintenance and progressively investments through user payments is essential for sustainability of water infrastructure investments
- High cost of next best options for supply augmentation (e.g., treated wastewater reuse, inter-basin water transfer, desalination of sea water) makes pricing policy reform essential
- Targeted programs for low income communities also requires to be formulated

Water Resources Planning and Management:

- Resource: supply augmentation to manage scarcity, variability, and quality.
- Demand: improving efficiency and cost recovery in complex and politically sensitive atmosphere.

- Allocation: among irrigated agriculture, urban, and environment uses. A complex challenge requiring addressing rights, trade, incentives, economic2s.

Water and Institutions:

- Policy, legal, institutional, and regulatory frameworks to manage resources at the lowest appropriate levels is required.
- Involving stakeholders in key decision making suggests the need for community participation in all stages of the project cycle
- Tapping into the enterprise of the private sector could help improve performance in the sector.

Driven by these challenges and consistent with the worldwide movement towards implementing integrated water resources management, several countries have embarked on reforming their water sector (e.g., Tunisia, Jordan, Yemen) and some others have made a good start. Many countries, in partnership with donors and financial institutions, are taking steps in water sector reforms. A shift in thinking and action in water management is slowly taking place in the region.

4. International and arab initiatives in response to the looming water crisis

In recent years, the Arab water and sanitation sector has been under a lot of review and debate. This reflects the strong commitment by the International community and the Arab leaders towards its development. This has been shown in efforts deployed to create the following Arab water initiatives:

- Regional initiatives, frameworks, strategies, and action plans for meeting the horrendous challenges of creating wealth and winning the battle over Arab's spreading water stress and poverty. These initiatives range from region-wide coordination under the consultation on Arab Water Vision 2030, the targets provided in the United Nations Millennium Development Goals (MDGs), to the Johannesburg, WSSD outcome, and river basin initiatives.

4.1. THE ARAB WATER VISION 2030

The prospect for an Arab Water Vision, in respect to concepts and main strategic components, implies a critical review of the previous endeavors towards sustainable water resources development, and identifying the constraints, which impeded their adequate implementation, in order to learn lessons and to be used as constructive guidelines. In view of the above, the Arab Water Vision includes the following approaches and trends (see Annex I).

1. 1. Vision for Optimizing Water Resources Supplies
2. 2. Vision for Rationalizing Water Resources Demands
3. 3. Vision for Water Conservation and Protection
4. 4. Vision for supporting institutional and legislative frameworks

4.2. THE UNITED NATIONS MILLENNIUM DEVELOPMENT GOALS (MDGS)

All Arab states agree that human development is a fundamental aspiration. In affirmation of this commitment, all countries in the region adopted the Millennium Declaration from which the eight Millennium Development Goals (MDGs) are derived. The MDGs include a selection of numerical and time-bound targets that encapsulate people's most basic aspirations for a better life. Between 1990 and 2015, countries agree to halve income poverty and hunger; achieve universal primary education; promote gender equality; reduce under-five mortality by two-thirds; cut maternal mortality by three-quarters; combat HIV/AIDS, malaria and tuberculosis; ensure environmental sustainability; and build a global partnership for development.

4.3. PROGRESS IN ACHIEVING MDGS

Over the last few decades, the Arab countries have made progress towards many of the MDGs. Literacy rates for the 15-24 years old steadily increased from 35 per cent in 1970 around to 77 per cent in 2001. Life expectancy soared from 51 to 68 years between 1970 and 2001. New infrastructure extended access to safe water to 83 per cent of the population, while sanitation networks spread to 87 per cent of the urban population (United Nations Development Program Report 2003).

However, progress began faltering in the 1990s.The proportion of children in primary school stalled around 80 percent, while the ratio of girls to boys in primary and secondary education inched slowly upward. Maternal mortality figures remained high at 500 per 100 000 live births.

Today, the Arab states face significant development challenges. About 10 million children still do not go to school. Even though women's access to education has tripled since 1970, gender disparities persist. Over half of women remain illiterate; women occupy less than five percent of the seats in Arab legislatures.

Progress has been uneven across the region and within each country. Regional aggregation is not often telling of how individual countries are performing, or how socio-economic groups are benefiting from ‘average’ progress. Several countries are successfully addressing education, health and housing needs. Others, however, continue to be afflicted by poverty, ignorance, disease and hunger; all areas that call for immediate attention if they are to reach the MDG targets by 2015 (United Nations Development Program Report 2003).

4.4. THE JOHANNESBURG, WSSD OUTCOME ON WATER

(i) A target on Sanitation to match that of Drinking Water (Halve people with no access by 2015)
(ii) A target on developing IWRM plans by 2005
(iii) Replenishment of Global Environmental Facility, $3 billion to 2006
(iv) Water, Energy, Health, Agriculture, and Biodiversity’s Framework for Action on water & sanitation

4.5. INITIATIVES ON THE REGIONAL LEVEL

There are regional initiatives to harmonize policies and coordinate development approaches and partnerships. However, these will need to address joint planning of river basins, sharing water data, and establishing effective networks for the exchange of information on water development and management.

Building on the GWP[4], the MENA Partnership delineates actions that countries and their international partners could take over the next five years, with goals to be attained by 2000.

The long-term goals of the MENA Water Partnership are to:

- Improve the efficiency and allocation of water use, thus reducing the overall per-capita extraction of raw water to sustainable levels.
- Make the water sector self-financing.

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[4] At the Stockholm Water Symposium in August 1995, the World Bank announced the creation of a Global Water Partnership (GWP) that would bring together key participants in integrated water resources management, to pool their efforts for more effective country-level programs.

- Ensure consistent water supply to the largest possible number of consumers.

4.6. EFFORTS TO IMPROVE THE WATER SITUATION ARE UNCOORDINATED

For years, great efforts have been made to keep pace with the burgeoning demand for more water in the Arab region. Massive investments have brought water supplies and safe sanitation to millions of people and have similarly enabled agriculture to remain a major contributor to the economy of the region. Nevertheless, water demand increasingly outstrips supply throughout the region. This worsening imbalance between supply and demand has brought many countries to the brink of crisis.

However, local, national and international initiatives are underway to overcome the water crises. Frequently, however, the benefits are small. The reasons: national institutions do not work together; plans and programs are often duplicative and sometimes contradictory; donor involvement is fragmented and unfocused; and water is generally heavily subsidized, providing no incentives for conservation.

5. Elements of a strategy for actualizing water ethics in the arab region

5.1. INTRODUCTION

Water ethics actualization is part of reforms taking place in the Arab region, on demand side to change human behavior of water uses and users. And in order to change behavior, we need to change structures (education curriculum) and the systemic structures in the society, e.g. laws, principles, rules. In this way, it is possible to allow for making progress on a wider basis and creating interests, as we need:

- to change behavior for team learning among stakeholders,
- to enhance the very rich values inherited in the Arab society, using cultural approaches to embody them into our behavior, and
- to monitor progress on the basis of developing the set of principles and rules of right water ethics conduct.

- “A Proposed Code of Water Ethics” could be developed for the Arab region.

In addition, it comes to mind “to ask the questions that matter” on each level or domain:

(1) *On the language level*: What do we mean by the term water ethics? Water ethics could be expressed in terms of:

- Set of principles of right conduct; a theory or system of moral values.
- The study of the general nature of morals and the specific moral choices made by a person; moral philosophy.
- The rules or standards governing the conduct of members of a group or profession. So, the progress made in this area is to be measured against principles of right conduct and behavior of users, researchers, engineers and experts or consultants engaged in the water sector.

(2) *On how do* these apply to users of public / private sectors, researchers and experts?. What are the major ethical issues regarding conduct and behavior of each group?

(3) *On why* is this concern for Egypt, and the Arab region at this point of our time?

(4) *On what we want to do next?*

In this regard, here are some suggested ideas and reflection on elements that could support the initiation of an Arab Strategy for Water Uses Ethics, which takes care of Arab’s main challenges in developing the water and sanitation sector (see Figure 4, Annex 2):

5.2. EMPHASIZING THE RIGHT TO WATER AND WATER FOR THE POOREST PRINCIPLE

The right to water is enshrined in the Universal Declaration of Human Right. Article 25 provides that “Everyone has the right to a standard of living adequate for the health and well-being of himself and his family...”

The right to a certain standard of living clearly encompasses the right to live in an uncontaminated environment with clear air and access to clean water.

The 1989 Convention on the “Rights of the Child” states in Article 24 that:

States Parties recognize the right of the child to the enjoyment of the highest attainable standard of health and to facilities for the treatment of illness and rehabilitation of health. States Parties shall strive to ensure that no child is deprived of his or her right of access to such health care services. States Parties shall take appropriate measures:

- To diminish infant and child mortality;
- To ensure the provision of Necessary medical assistance and health care to all children with emphasis on the development of primary health care;
- To combat disease and malnutrition including within the framework of primary health care, through, inter alia, the application of readily available technology and through the provision of adequate nutritious foods and clean drinking water taking into consideration the dangers and risks of environmental pollution.

This statement makes emphasis on the responsibility of the State that no child is deprived access to clean water. The words of "all children" suggest that States are required to also work towards the provision of water to children in other countries. It also gives an absolute priority to basic domestic uses of water, of which drinking is the most essential, above all others and indicates the related responsibility to avert the risks associated with pollution.

5.3. THE NEED FOR LAUNCHING "WATER FOR THE POOR" CONFERENCE FOR THE ARAB REGION

The experience of the 'Water for the Poor' Conference in Stavanger, Norway, 4-5 November 2003, represents a model to follow for organization and conducting business that allowed dialogue with wide possible participation and engagement among representatives of decision makers and doers. The Conference aimed at serving as a step towards international coordination and target oriented measures for fulfilling the water related MDGs and WSSD goals. The outcome of the conference represented a valuable input to the work of the Committee on Sustainable Development in New York, in finalizing its report, 2003.

The Conference took stock of the National Poverty Reduction Strategies in a number of countries in Arab, African and Asian regions. It examined the status of Water and Sanitation (W&S) supply and demands, as well as current measures for improving services to the poorest. Topical working sessions focused on the W&S agenda of these countries as follow:

- Policymaking and governance (national / local);
- Mobilizing the means for supply, how providers and users may organize and be funded;
- Emergency relief management, bridging between relief and longtime aid towards sustainability.

The conference concentrated on the hardest-hit areas, especially with reference to:

- Practices and lessons learned in relief- and -development work from areas of drought and unrest in Africa and Asia;
- Bridging between short-term emergency, and longer-term sustainable solutions;
- Overcoming constraints;
- Illustrated by strategies and actions that has worked.

Dialogue between Decision-makers and Doers has taken the shape of:

- A conference of dialogue for learning and committing to action;
- Cooperating to increase access to water & sanitation to improve human health and reduce infant and child mortality, prioritizing water & sanitation in national sustainable development strategies and poverty reduction strategies.

5.4. USING DIALOGUE, SHARED VISION AND ACTION ON THE GROUND EXEMPLIFIED BY THE NILE BASIN INITIATIVE

Integrated Water Resources Management requires also a comprehensive systems view. This refers to inter-connectiveness among environmental, ecological, and social concerns together with the traditional hydraulic, economic and political concerns. Dr. Mahmoud Abu-Zeid emphasized on many occasions during the ongoing dialogue in the 2002 Nile Conferences that: "the idea behind the interdisciplinary system approach is a reminder of what is forgotten and to clear the ambiguity of what is not understood" (Abu-Zeid, 1999).

It is the view of the author of this paper, that the Nile 2002 Conferences have taken a systemic approach, that each conference is connected to the other in a series of themes focused enough to bring about specific outcome in a process of consensus building (Hefny and Amer 2002): The way the themes were defined, throughout the process brings together a design of a process that is goal oriented. It is characterized by complementarity to each other, in a spectrum ranging from:

"Getting Started" in Aswan (Egypt) in 1993 to

"The Vision Ahead" in Khartoum (Sudan) in 1994, then

"Taking Off" in Arusha (Tanzania) in 1995, then

"An Action Plan", which was presented in Kampala (Uganda) in 1996, then

"Basis for Cooperation" in Addis Ababa (Ethiopia) in 1997, and

"Benefits for All" in Kigali (Rwanda) in 1998.

The culmination of this process was in Cairo (Egypt) in 1999, when the Conference agreed on "A Shared Vision for the year 2025".

2002 Conference in Nairobi, Kenya's theme emphasized local community Action on the ground.

Apart from this complementarity, it seems that each theme played a function in a sequence. It is based on the assumption that each function corresponds to a distinct phase in the riparian policy making process: either for collaborative action or for water resources management and sustainable development

5.5. LEARNING FROM EACH OTHER EXPERIENCES FOR KNOWLEDGE TRANSFER

5.5.1. Bench-marking and Bench-learning of Arab's Water Best Practices

In this regard, we need to depict on the Arab detailed stories of experiences of scientists, engineers, researchers, household users, farmers and industrialists who have, in this difficult circumstances, demonstrated wisdom that enabled them to save and rationalize their conduct in the water sector. Their actions and success stories are used as a tool for learning and could provide guidance for others who want to do the right thing in circumstances that are similarly difficult. Many of these experience stories of moral leadership and stewardship could be illustrated with presentation of their practices. A Proposed Reward for "Best Practices" to be recognized on the Water Day in March of Every Year, and to be documented and disseminated on a wider scale in the region. This activity could be initiated through 'the Arab Water Partnership' in collaboration with the RENEW node in Egypt.

5.6.2. Country Level Experiences

Egypt: the role of Water Users' Associations in reforming irrigation Case (Metawie 2003)

The case describes the institutional and management changes involved in introducing participatory irrigation management in Egypt, in the context of wider policy changes. The government of Egypt is now committed to a long-term irrigation improvement program, which will continue for the next 15 years. For this reason the Irrigation Improvement Program (IIP) was launched. The program involves a combination of technical changes and infrastructure investment, together with institutional and organizational changes in the way irrigation water is managed. Of key importance, Water Users' Associations playing a major role in decision-making and the operation and maintenance of the pumps and mesqas by themselves, with minimal assistance from the Irrigation Advisory Service (IAS) staff.

Lessons learned

- The new programme has been built of the experience if earlier irrigation programmes; there is a body of knowledge that has been tested and piloted which provides underlying strength to the new reforms.
- In order to increase the efficiency as well as the performance of the system, users' participation in the management is a must since their decisions and ideas have a great impact on the operators and the modernization process of the systems would assure the sustainability of the system.
- Increased crop production and achievement of real water savings in the system is dependent on the awareness and understanding of both users, and operators and managers of the system.
- Increasing the capacity of users, operators and managers require intensive training. Now in Egypt the new generation has accepted the concept of users' participation in the management and the MWRI has legalized the formation of water users' association.

Main tools used:

- Reform of existing legislation;
- Participatory capacity and empowerment;
- Improved efficiency of use;
- training of professionals.

5.5.3. Morocco: Toward Integrated Water Management

(Mahdi and Tazi 2003)

Morocco faces a growing challenge in managing its water resources. Demands from expanding irrigated areas and a growing urban population are running up against the rapid depletion and pollution of accessible water resources. Sanitation infrastructure and drinking water supply have not kept pace with demand. Only 15 percent of the rural population has access to potable water. Contaminated water is the major cause of disease in rural areas. Municipal, agricultural and industrial effluents, as well as unsanitary solid waste deposits, contribute to pollution of surface and groundwater.

Past government strategies emphasized the development of additional water resources, an approach reaching technical and economic limits. The government has now committed itself to an integrated water resources management approach, based on a long-term national strategy, including a national water law that defines water quality standards, water conservation and cost recovery policies. Under this approach, Morocco plans to develop autonomous river basin agencies that will be responsible for regulating and monitoring the use and safe disposal of water, as well as for planning and funding related investments.

5.5.3.1.1. Lessons Learned

The case shows the importance of setting up clear regulations and water codes and building on existing institutions.

5.5.4. The Need for a Change in the Hydraulic Mission and its Approach

In the hydraulic mission, Integrated Water Resources Management is considered an evolving and recent paradigm, since early 1990's. It requires a new holistic approach and unprecedented political cooperation. Indeed, there is a shift in paradigm, that water is not a narrow hydrological phenomenon rather it is a multi-dimensional resource with its nested political economy factors. The virtues of technical and economic efficiency and environmental consideration are well recognized in the reports of World Water Forums.

The forums of La Hague (March 2000), World Water Council 2000, Global Water Partnership 2000 and World Water Commission 2000, initiated a dialogue among civil society, stakeholders, but the emphasis and advocacy was on that water is an economic resource rather than a social economic resource. Water pricing instruments and privatization were contested from the first moment at The Hague Forum. Integrated Water Resources Management is to be linked to Dublin principles and Agenda 21. The key concepts of IWRM imply: (a) an inter-sectoral approach (b) representation of relevant stakeholders (c) sustainable development, which is sound socio-economic development that safeguards the resource base for future generation (d) emphasis on demand-driven and demand-oriented approaches (e) decision making on the lowest level. The question here is that this new hydraulic mission and its approach need to be part of the Arab Strategy for the future.

5.5.5. The Need for a Strategy Implementation Monitor

Figure 5 illustrates that Challenges and Visions could be bridged over the span of time until 2030, if we would consider having a monitor that could guide the process and evaluate its progress. There is a tension and stress between Challenges and Visions as long as the vision is not realized and both are far apart. However, tension is dwindled if we initiate policies and take actions. In this way we will be able to take the vision rather than challenges as our main direction to measure progress. A matrix to that effect could be used (Figure 5) Strategy Implementation Monitor). Tension is more released, if we make progress towards actualizing the vision.

5.5.6. The Establishment the Arab Water Council

The Arab Water Council (AWC) was formally inaugurated on April 14, 2004 in Cairo, Egypt following many years of planning, discussions and consultations. The AWC is a civil society, not-for-profit, regional organization dedicated to water issues in the Arab States.

The mission of Arab Water Council is: The Arab Water Council endeavors to: promote better understanding and management of the water resources in the Arab States in a multi-disciplinary, non-political, professional and scientific manner; to disseminate knowledge; to enhance sharing of experience and information for the rational and comprehensive water resources development of the region for the benefits of its inhabitants.

The main objectives of the Arab Water Council are to (The Second Conference on Arab Water Security April, 2004):

- Influence decision-making process, policy formulation, and strategic orientation for better water management in the region.
- Represent the regional views at international and global for a ? dealing with issues of political, institutional, legal, and financial nature, transfer of knowledge, conceptual development of policies, strategies and plans of actions related to water resources and its uses.
- Advocate the rational and comprehensive water management to ensure efficient, effective, and equitable utilization of available water resources and technologies for the benefits of the inhabitants of the region.
- Advise the public, private and voluntary sectors on undertakings, development, planning, design, operation and maintenance of water systems at regional, national and local levels.
- Assure the appropriate participation of the stakeholders in decision-making processes and equitable sharing of the benefits of water development.

6. The need for an Arab network for water ethics

6.1. WHAT KIND OF A NETWORK?

In the knowledge and experience economy, we need to allow for creating a space and time, in what is becoming known now as a "Knowledge Park". Its aim is to develop an interacting triangular partnership (as shown below), for creating knowledge-based 'idea' that could be translated into 'a project', which could be subject to 'finance': This means that it is indeed a network shaped along a triangular partnership among researchers, engineers/experts and the private sector (see Diagram 1).

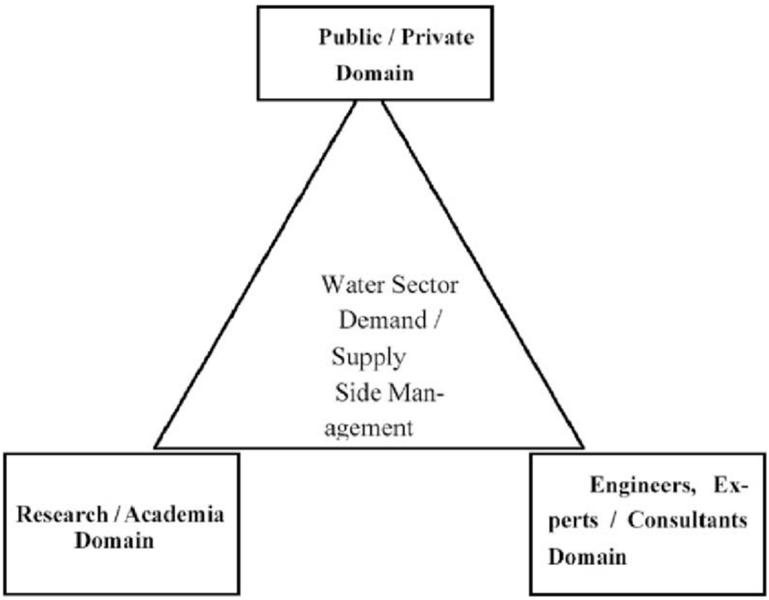

Diagram (1) Creating a Knowledge Based Idea and Project.

Thus in our view the establishment of an Arab network for water Ethics should take the shape of this triangular relationship among applied research of the academia domain, engineers-experts-consultant domain and public-private domain.

6.2. THE NEXT STEP: ACTIVATING THE RENEW NODE OF ARAB REGION FOR WATER ETHICS

It is proposed to launch the establishment of An Arab Network for Water Ethics, using the Node that is existing in Cairo, Egypt as the focal point to serve Arab's interest in actualizing water ethics. In this case, it is possible to benefit from the work already started within the Cairo Node: "Regional Center of Studies and Research of Water Uses Ethics", as well as drawing upon the Work of UNESCO's Sub Committee on Water and its recommendations.

The Aswan Conference[5], Egypt (November, 2000) has deliberated on possible ethical guidelines for the Use of freshwater". Guiding principles were suggested on: consuming water, protecting water and distributing water. The question now is how best such ethical guidelines could be initiated and applied on the national and regional Arab level.

In October, 2002 an International Conference was held in "Bibliotheca Alexandrina" on Ethical and Social Responsibilities in Science and Technology. A special Committee addressed, among other issues, ethics on freshwater and emphasized the importance of initiating and localizing the guiding principles for water as an ethical issue. The report and its recommendation considered to be an extended opportunity to localize such global initiative on the Arab regional level.

In addition, Arab region could benefit from the wider circle of the "Global Research and Ethical Network Embracing Water" (RENEW) that has been created. And node points of RENEW started to take shape in some geographic regions (Middle East and North Africa, South East Asia and Nordic Countries). The program for such a node would embrace all aspects of water, and have "Bottom-Up" education / communication functions, as well as "Top-Down" high level research aspects, with industry participation. RENEW also includes best examples of ethical practices in all aspects of freshwater use. These activities could be of special interest to the node point for Africa region and its future programme of work.

6.3. PROPOSED ACTIVITIES FOR THE ARAB NODE

Upon the establishment of the Arab Network for Water Ethics, it is envisaged that the sphere/scope of activities could include: (1) the water sector, where strategies and policies represent the guidelines; (2) the national

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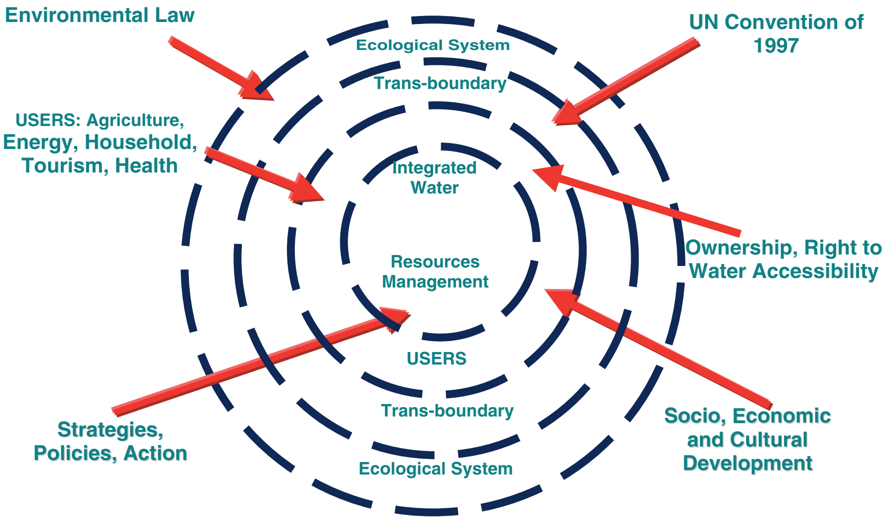
[5] The Conference was held under the patronage of H. E. Mrs. Susan Mubarak, the first lady of Egypt, and member of the Global COMSET, in November 1999.

economy level, where sustainability and team working among departments and cross disciplines is needed; (3) Cross-boarders activities among riparian countries of same river basin; (4) International level, where environmental law has an important role in guiding the activities. The diagram belo2w shows this circle of activities.



6.4. THE CAIRO REGIONAL CENTER FOR STUDIES AND RESEARCH OF WATER USES ETHICS

In this Node (RENEW-Egypt, www.mwri.gov.eg/egyptrenew) its wide-ranging expertise in water management, its water research and educational institutions, and in cooperation with a consortium of other research and educational centers, industry, water utilities, non-governmental organizations, and inter-governmental bodies in other countries will serve as a much needed and long overdue forum to:

- Publicize and disseminate information on the Ethics of freshwater use as embodied in the work of the COMEST Sub-Commission on the Ethics of Freshwater.
- Highlight the role of social and cultural variables in the resolution of water-related conflicts in the region and promote the ethics of trans-boundary rivers collaboration and cooperation
- Engage all stakeholders in exploring issues related to the ethics of freshwater use, to develop guidelines for just practices of water technology, water science and water management

- Promote an awareness of the social, cultural and ethical issues involved in technical, political and demonstrative aspects of water management.
- Undertake and encourage innovative research in issues related to water-related problems in Arab and Africa regions.
- Develop a specialized social science research and educational program in water-related topics.
- Develop an educational program with a focus on the application of ethics and ethical guidelines to water-related issues.
- Develop a regional training course on the ethics of managing water resources for various levels from policy makers to technicians.
- Develop an institutional framework for exchanging scholars, experts and trainers.
- Organize workshops, seminars, field trips and on-site training in specialized water topics to insure equitable access to the most-up-to-date water research data.
- The ethical, social, cultural and ecological issues of the following water-related issues will be on the agenda of this program: Long term variability and predictions as a result of current policies, trajectories and climate change. Intra-regional variability in water resources, water policies; Social / ecological dynamics; Trans-boundary optimal integration of knowledge, labor, natural resources, economic activities, hardware and finances; Linkages with international institutions, foundations and agencies; Partnership with trans-regional economic enterprises; Equity.
- To create a partnership among research, educational, governmental, non-governmental organizations, the public and industry to build a viable water society in the region.

7. Conclusions

The above analysis has proven that soft factors of human nature and social learning need more attention for change and development of the water sector in the Arab world. It is absolutely necessary to have a cultural approach to actualize water ethics. The paper proposed that the first step would be to establish an Arab Network for Water Ethics. Upon the establishment of the Network, a special workshop could be convened to create the strategy, vision and plan activities for the “Arab Network”. As a result it is proposed that a necessary mechanism of a Steering Committee could be created within the Cairo Regional Center for Water Ethics to take care of the implementation process.

Notes: Vigdis Finnbogadottir, Chairperson of COMEST, she is the ex-president of The Republic of Iceland. COMSET is composed of 18 prominent personalities, including Mrs. Suan Mubarak. The first lady of Egypt. COMEST started its work in April 1999 in the First Conference in Oslo, Norway.

8. References

Abu-Zeid, M. 1999. Statement made to the Nile Basin Conference, Cairo, Egypt.

Abu Zeid. M, and Hamdy, A, 2004, "Water Crisis and Food Security in the Arab World: Where We Are and Where Do We Go?, The Mediterranean Agronomic Institute of Bar, Italy,

COMEST, UNESCO 1999-2002. Reports of Ethics of Freshwater Use Subcommittee.

Diaz-Bonilla, E., M. Thomas, S. Robinson, and A. Cattaneo, 2000. Food Security and Trade Negotiations in the World Trade Organization: A Cluster Analysis of Country Groups, Discussion Paper 59, Trade and Macroeconomics Division. IFPRI: Washington, DC

El-Kady, M., 2003 "Water in the Arab World" , The National Water Research Center of Cairo, Egypt introduced this theme at the 3rd World Water Forum, Koyoto, Japan.

ESCW (Economic and Social Commission for Western Asia) 2003, "Updating The Assessment of Water Resources in ESCWA Member Countries", United Nations Publication, New York.

Hefny, M. and Amer, S., 2002, "Egypt and the Nile Basin", Paper presenting at the EAWAG Workshop on Sustainable Development and International Cooperation in the Eastern Nile Basin.

Loöfgren, H. and Richards, A.. 2003. Food security, poverty, and economic policy in the Middle East and North Africa (Discussion Paper) Washington, D.C.: International Food Policy Research Institute (IFPRI) 41 pages.

Lord Selborne 2003 The Ethics of Freshwater Use: A Survey. Report of COMEST, UNESCO, Paris.

Mahdi, M. and Tazi L. 2003, "Morroco: Community Management of Water Resources in Imlil Valley near Marrakech", http://gwpforum.netmasters05.netmasters.nl/en/listofcasesFrame_en.html

Metawie, Abd Elfattah 2003 "Egypt: the Role of Water Users' Associations in Reforming Irrigation" A case presented to the Global Water Partnership. http://gwpforum.netmasters05.netmasters.nl/en/listofcasesFrame_en.html

Mubarak, S. 1999. "Towards An Ethical Approach in Water Uses." Aswan Conference, UNESCO, Sub Commission on Water Ethics (Regional Approach to Water Ethics).

Pahl-Wostl C, 2002 "Towards sustainability in the water sector – The importance of human actors and processes of social learning, Water Policy article, Aquatic Sciences, Vol. 64, page 395, EAWAG, Dubendorf, Switzerland.

IWA (The International Water Academy) 2003. Final Report "Water for the Poor", Conference in Stavanger, Norway, 4-5 December 2003.

United Nations Development Program's Report 2003, "The Millennium Development Goals in Arab Countries", New York.

World Bank Group 2003. Water Resource Management in Mena. Sector Brief

WSSD, 2002 (World Summit on Sustainable Development) in Johannesburg .

Internet Addresses:
www.svf.uib.no/sfu/renew/australia.htm
www.svf.uib.no/sfu/renew/nordic.htm
www.mwri.gov.eg/egyptrenew

Annex 1 Arab Water Vision 2030

The prospect for an Arab Water Vision, in respect to concepts and main strategic components, implies a critical review of the previous endeavors towards sustainable water resources development, and identifying the constraints, which impeded their adequate implementation, in order to learn lessons and to be used as constructive guidelines. In view of the above, the Arab Water Vision includes the following approaches and trends.

1. Vision for Optimizing Water Resources Supplies:
   a. Necessity for reaching adequate agreements between riparian countries.

b. Need for exploring all natural water resources, specifically in respect to deep groundwater reservoirs, geomorphic drainage basins.

c. Possibility for inter-basin transfer.

d. Possibility for artificial recharge of groundwater reservoirs.

e. Suitability of climatic conditions for rainfed irrigation.

f. Assessment of water import projects including icebergs transfer, and

g. Promoting the use of non-conventional water resources; reuse of agricultural drainage water; treatment and reuse of sanitary wastewater; desalination processes; use of brackish and sea water in agriculture; and possibilities for rain seeding.

2. Vision for Rationalizing Water Resources Demands:

a. Relevance of absolute or relative water and food security concept and its relation to food self-satisfaction.

b. Reform and modification of irrigation practices.

c. Identification of Agricultural appraisal.

d. Views on water allocation to industry.

e. Views on water allocated to domestic usages.

3. Vision for Water Conservation and Protection:

a. Impacts of globalization, privatization and open market trends.

b. Concepts and impacts of water pricing.

c. Adequate allocation of water resources.

d. Measures for water resources protection; and,

e. Impact of global climate changes.

4. Vision for supporting institutional and legislative frameworks:

a. Need for a common regional policy.

b. Necessity for the provision of sufficient financial resources.

c. Need for governance and institutional reforms.

d. Adequate performance and functions for capacity building.

e. Promotion of public awareness, and

f. Revision and modifying of legislative rules, laws and regulations.

Meanwhile, it should be stressed that the regional water vision should focus on innovative approaches leading ultimately to a better situation of the water sector in the region with an economically sound and environmentally safe vision. In this regard, the continuous advancement in science and technology will constitute the driving power and tool for achieving the targeted water vision.

Annex 2 Figures & Tables

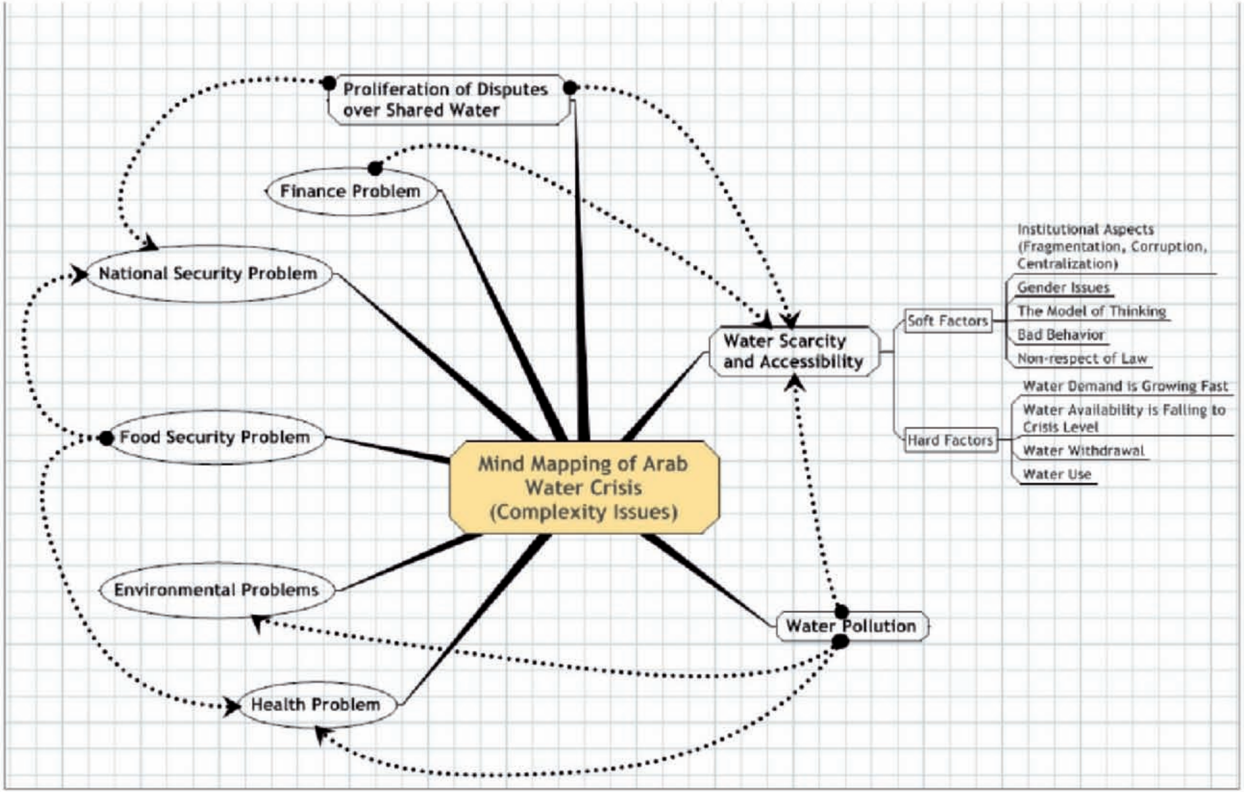


Figure 1. Mind Mapping of Arab Water Crisis.

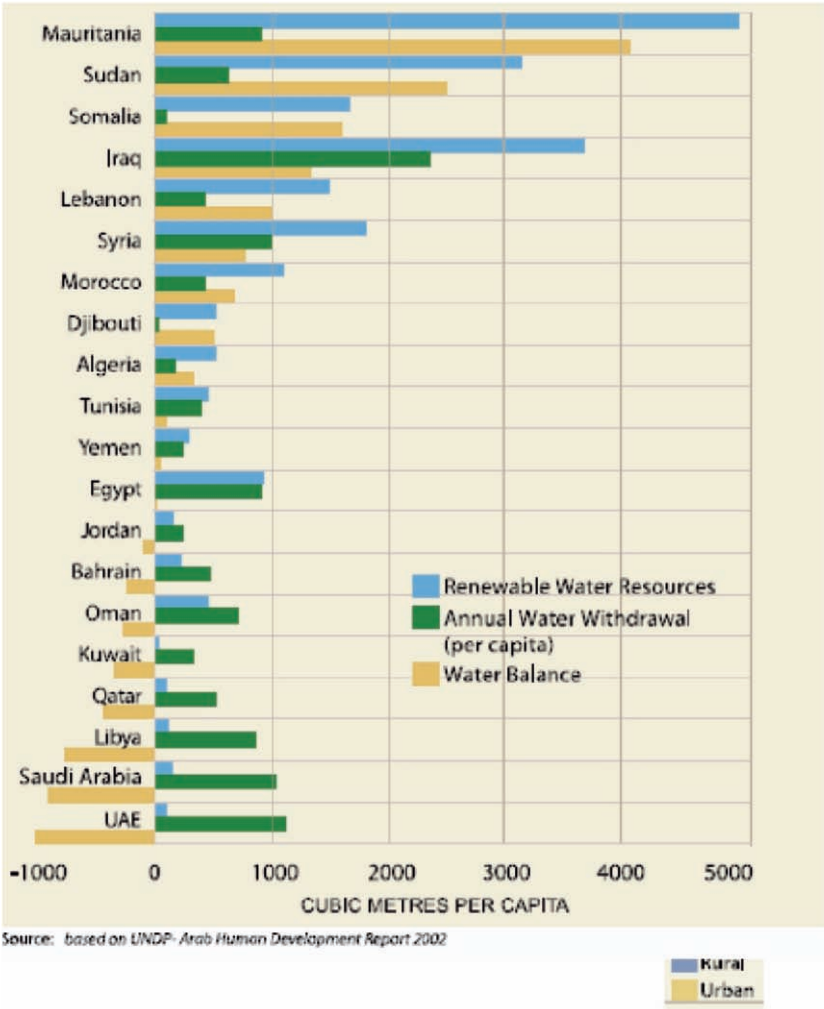
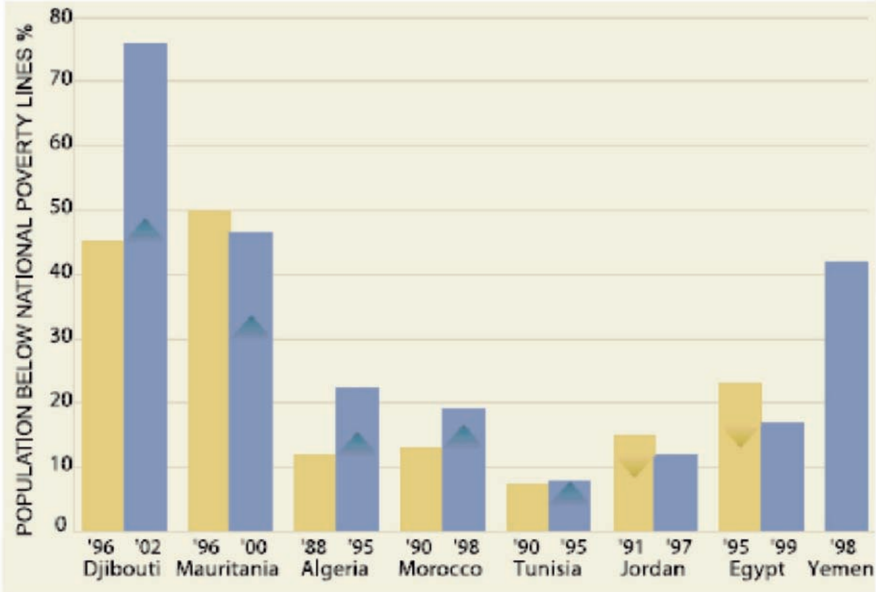


Figure 2. Water Status in the Arab States.



Source: *based on World Bank 2003 (earlier figures for Yemen not available)*

Figure 3. Poverty is on the Rise in Some Arab Countries.

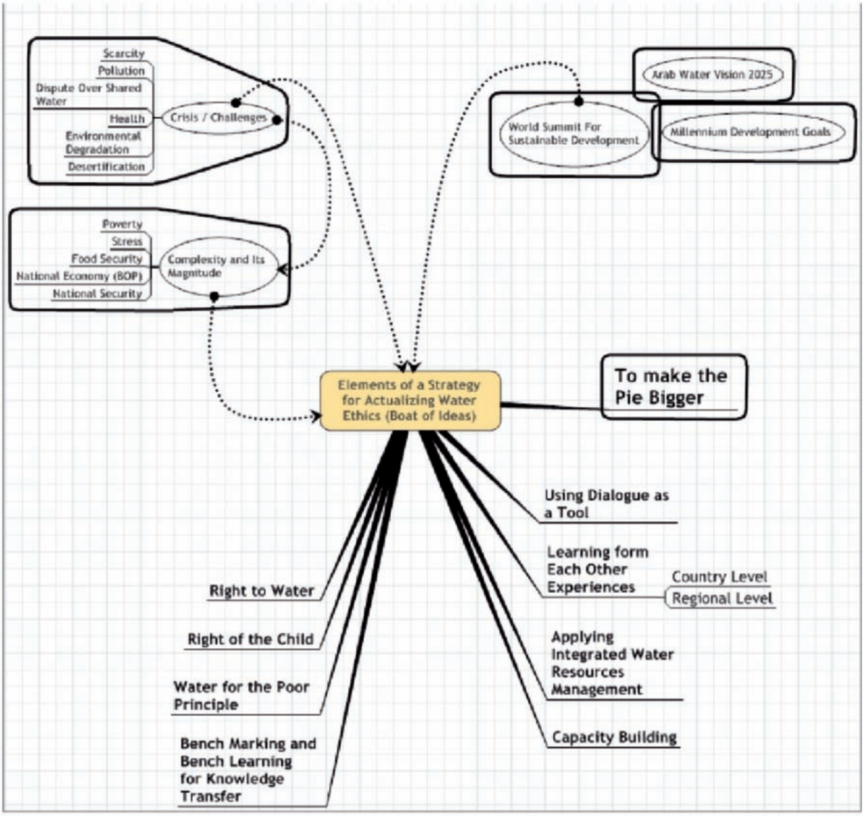


Figure 4. Elements of a Strategy for Actualizing Water Ethics.

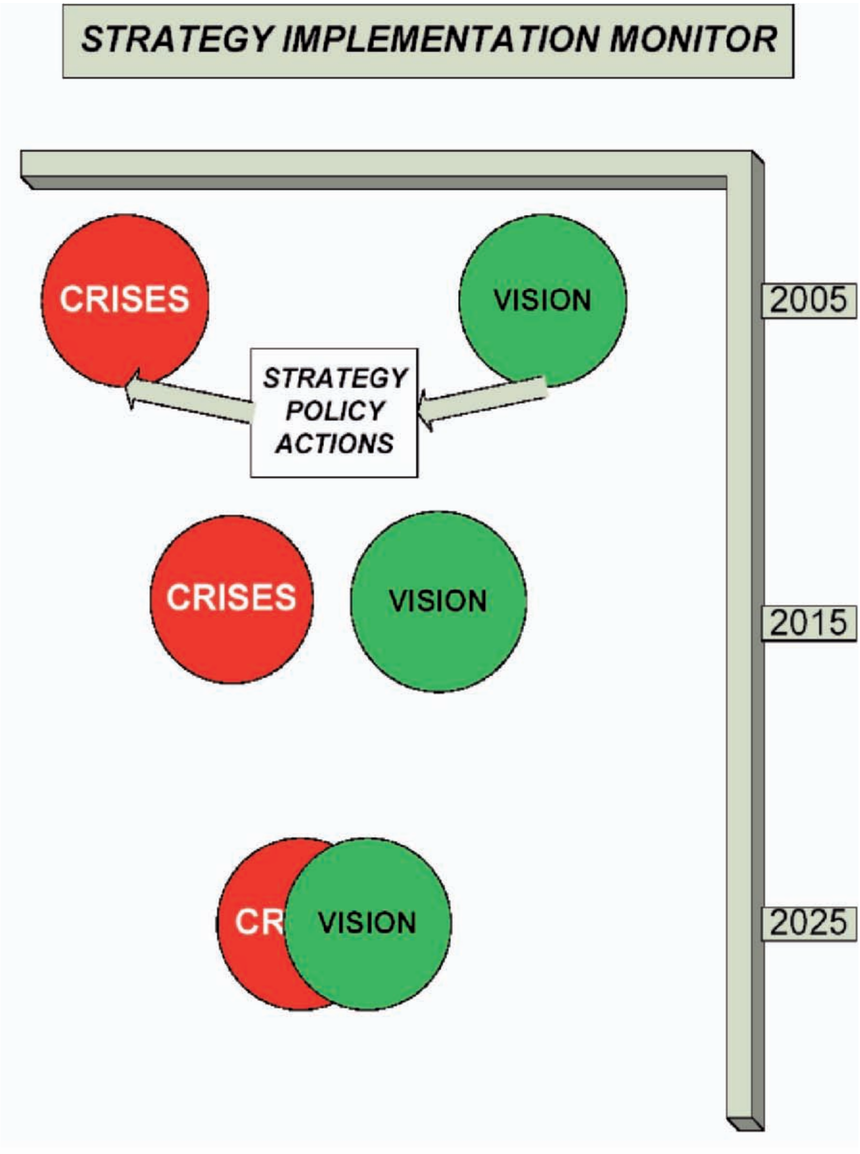


Figure 5. Strategy Implementation Monitor.

Table (1): Water Availability and Usage in Arab Countries

Country	Annual Re-newable Resources BCM	Annual With-drawals		Per-capita Renewable Availability in 1995 (CM)	Water Usage (%)		
		BCM	as a % of Annual Re-newable Resources		Domestic	Industry	Agricul-ture
Algeria	18.4	3.0	16	655	22	4	74
Egypt	58.0	56.3	97	1005	7	5	88
Bahrain	n.a	0.2	-	-	60	36	4
Iran	118.3	46.5	39	1826	4	9	87
Iraq	104.0	43.9	42	4952	3	5	92
Jordan	0.8	1.0	125	213	20	5	75
Kuwait	-	-	-	-	64	32	4
Lebanon	4.8	0.8	17	1200	11	4	85
Libya	0.7	2.8	400	130	15	10	75
Morocco	30.0	11.0	37	1083	6	3	91
Oman	2.0	1.3	65	1053	3	3	94
Qatar	0.02	0.15	750	-	36	26	38
Saudi Arabia	2.2	3.6	164	118	45	8	47
Syria	5.5	3.3	60	385	7	10	83
Tunisia	4.4	3.0	68	489	13	7	80
UAE	0.3	0.4	133	167	11	9	80
Yemen	3.0	3.9	130	176	5	2	93
West Bank & Gaza	0.2	0.2	100	105	12	13	75

Sources: World Resources 1992-93; Pacific Institute for Studies in Development, Environment and Security; Stockholm Environment Institute; and World Bank estimates, 1990-1995.

ETHICAL ASPECTS OF WATER POLLUTION AND MANAGEMENT

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Abstract

Water, the common symbol of humanity, valued and respected in all religions and cultures, has also become a symbol for social equity. Common ethical principles in water use and water management should be accepted as applicable in all geographies, in all stages of economic development and for all time. We need to recognize that in implementing these principles there can and will be different strategies and methods, which will be appropriate for different situations. However, the ethical principles, which inform such policies, will be consistent throughout the world.

Key words: ethical principles/ water management/ ecology/ health/ international co-operation.

1. Introduction

"The Earth is one but the world is not. We all depend on one biosphere for sustaining our lives. Yet each community, each country, strives for survival and prosperity with little regard for its impact on others". These words, taken from the Report of the World Commission on Environment and Development (1987), are as true today as they were eighteen years ago. Their context was the concept of sustainable development, a radical departure from previous

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notions and brought to the forefront the idea of development that meets the needs of the present without compromising the ability of future generations to meet their own needs. Thus, the traditional economic, material and technological parameters of development now had to be seen in a new light - one of sharing, caring, saving and conserving - in other words, in an ethical framework without which all efforts would be piecemeal, fragmented and ephemeral.

Water, the common symbol of humanity, valued and respected in all religions and cultures, has also become a symbol for social equity (General Conference of UNESCO, 1997). Common ethical principles in water use and water management should be accepted as applicable in all geographies, in all stages of economic development and for all time. We need to recognize that in implementing these principles there can and will be different strategies and methods, which will be appropriate for different situations. However, the ethical principles, which inform such policies, will be consistent throughout the world. While we should beware of technical fixes as the way to resolve our problems, there is a need to develop and harness new technologies for conserving, harvesting, transporting, recycling and safeguarding our water resources. We must ensure that once these innovative systems and practices have been successfully developed, they are widely disseminated and the participating process is able to assess their relevance for other areas.

Most responses to water problems require finding a balance among uses and among traditional and technological solutions and will differ according to the region. However, among the participants influencing regional management are powerful international corporations whose agendas must be adjusted to serve rather than dominate regional needs. Data is essential: more data, better use of data and public access to water data are all ethical imperatives. This is particularly true in order to anticipate and mitigate floods and drought, which kill more people and incur more costs then any other cataclysms, and to prevent these natural hazards from turning into humanitarian disasters.

While conflict over water can lead to violence, the history of water management records much more? .often the establishment of practical communitarian ethics. This subsumes both the private and public aspects of water management, making necessary a new sense of water ethics at the personal and social level. Most of the earth has been built and rebuilt and today the fundamental need of water managers is for an ethic of ecological design and not only preservation.

Clearly, there are conflicting factors, which make it difficult to set out universal ethical principles in water use. There will always be tensions rising from legitimate demands for development, for conservation and preservation of the environment, for company shareholder profit in a world dominated by the market, and from corruption and ignorance of decision makers, nationalism... the list is long. Specific local conditions also come into play, for example, geography: in arid countries with limited available water, agricultural clearing and the over-utilization of land assisted by damming and irrigation often result in salinization. In tropical countries with poor topsoil in rain forests, clearing for timber production results in runoff of the soil and flooding and pollution of the ocean, with reduction in fishing resources and dependence on foreign aid for food. In high rainfall lowland, the clearing of waterlogged regions to produce agricultural land results in aerated soils, reduction of bauxite and release of aluminium ions that are after a short period toxic to crops, eventually rendering the land useless. As hydrological engineering projects proceed on a massive scale, nascent industries can intensify water pollution. Irrigation produces one third of our food from about one sixth of our land, however, as population and food needs grow, the amount of irrigated land per-capita decreases and irrigation infrastructure degrades, leaving communities vulnerable to food insecurity. As one writer puts it: “All these issues boil down to a single question: who, if anyone, owns the water? ...In trying to apply our concept of ownership to a resource whose very nature runs contrary to the idea, we have a recipe for conflict” (Ball, 1999).

Nevertheless, the interplay between these conflicts sheds light on where we can begin to identify some ethical issues that are indisputable. First, the ethics we require should be built on a sense of shared purpose and in harmony with nature. Second, ethics must be based on a balance between traditional human values regarding conservation and the use of new technological advances. Rarely have either worked alone and it is time to stop pitting one against the other. Third, ethics, even in our advanced technological age, should seek to find a new harmony between the sacred and utilitarian in water, between the rational and the emotional. Water resources managers need to understand the wisdom encoded in traditional religious and secular symbols and rituals surrounding water.

Today, our technology tells us that there is enough water - if we co-operate. One of the most important elements for co-operation is something that experts in negotiation call “superordinate values”, meaning those that are beyond immediate utilitarian benefits and to which competing parties can subscribe.

2. Ecology

Natural ecosystems, such as forests and wetlands, play a valuable role in managing the hydrological cycle. Vegetation encourages infiltration of water into the soil, aiding the recharge of underground aquifers, lowering flood risk and anchoring the soil, thus reducing erosion. Forests also take up water and release it into the atmosphere.

Ecosystem conservation can be a cost-effective solution to water management. Many ecosystems support a wide range of species and a large number of individuals. Water availability is often a key controlling factor in maintaining biodiversity. The important question is at what level to maintain the Earth's ecosystems. The concept of sustainability suggests that the answer is so that they yield the greatest benefit to present generations, whilst maintaining the potential to meet the needs and aspirations of future generations. The problem is to decide how much water should be utilized directly for people for domestic use, agriculture and industry and how much water should be used indirectly to maintain ecosystems that furnish environmental "goods" and elemental services. It is essential, therefore, that the costs and benefits to society of allocating water to maintain ecosystems and those involved to support direct use be quantified.

3. Health and sanitation

Clean water is life; contaminated water is disease and often death. Human health depends on providing safe, adequate, accessible and reliable drinking water. Throughout history people have equated clean water with health even before the relationship was fully understood towards the end of the nineteenth century; indeed, several ancient religious codes included rules for hygienic practices that remain appropriate today. Human populations were also acquainted with the notion of using water only once and then discarding it; if the water supply became tainted; it was always possible to turn to a nearby clean source.

With the tremendous increase in world population, the provision of safe and clean water and the maintenance of sanitation systems have become more difficult to achieve. The shift in population from rural to urban areas has also put pressure on already inadequate structures. In 1955, 68% of the global population lived in rural areas and 32% in urban areas. By 1995 this had changed to 55% rural and 45% urban and it is foreseen that by 2025, the balance will be 41 % rural and 59% urban. In almost the entire developing world the rate of water supply and investment falls behind urban growth. Within cities, mortality rates are higher in low-income settlements due to poor housing, high population density and lack of basic services.

A recent UN report states that more than 5 million people die annually from diseases caused by unsafe drinking water and lack of sanitation and water for hygiene. According to the World Health Organization, billions of people are at risk due to water-borne diseases. In 1 997, 33% of all deaths were due to infectious and parasitic diseases. Diarrhoeal diseases caused 2.5 million deaths, typhoid fever caused 600,000 deaths and dengue and dengue hemorrhagic fever caused 1 30,000 deaths. By 2025 there will be 5 million deaths among children under five years of age and 97% of these will occur in developing countries, most of them due to infectious diseases combined with malnutrition.

In sum, the issue of water and health must focus on a number of basic conditions: supplying water in adequate quantity and quality; conserving water by promoting policies to 'reduce, reuse and recycle'; establishing 'highest priority use' to buttress the concept of the right to clean water; making public participation work; ensuring equity in access to water supply and sanitation services; placing health and well-being at the forefront in setting out efficiency indicators for water projects, and searching for alternative water treatment approaches which are affordable in developing countries and which reflect cultural practices.

4. Natural hazards and disasters

Hazards may be man made or natural; all hazards neither are not disasters nor all disasters the result of natural hazards. The link between them is the degree of vulnerability, which is generally defined as the capacity to anticipate, cope with, resist and recover from the impact of the natural hazard. The variation of vulnerability between countries and between socio-economic groups in the same country is a major factor in any consideration of ethical questions arising from disasters, for some population groups are far more defenseless than others: the poor, women, children and youth, the elderly and some minorities are the most disadvantaged. Women in particular are more exposed to immediate disaster impact, more affected by household disruption and more likely to have no access to resources during recovery than men. Because they play a key role in the area of water, their vulnerability is a vital element in dealing with disasters. It is only by taking steps to relieve this situation before disaster strikes that long-term solutions may be found.

Disaster prevention, mitigation and preparedness are better than disaster response which is not sufficient, as it yields only temporary results at a very high cost.

The problems associated with droughts and floods are integrated, that is, they emerge as a result of a system of behavior around the river basin. However, institutions to deal with them, even in the developed world, are fragmented and solutions tend to be ad hoc, partial and reactive. A more seamless web between the agencies responsible for anticipating and sensing disasters and those charged with response, planning and relief needs to evolve, and nowhere is this more clear than in the collecting, processing and use of hydro-meteorological data. But it cannot be overlooked that although adequate information is of the utmost importance, it is not the whole story - professionals have a responsibility not only to provide and share data but to recognize the equal importance of ethical principles in using such information to benefit those who are at greatest risk so that natural hazards do not automatically trigger humanitarian disasters.

5. Water management

Water management is fundamentally a question of environmental justice based on three essential concepts: equity, fairness and access between and across generations. Its ethical dimension may be perceived in the way answers are found to the following questions: who participates in the decision-making process; what are the decisions they act on; are they involved in formulating options or are they expected only to react to proposals that are already well-developed; how and what type of opportunity costs are considered; what is the basis of ascribing the value of various decisions that may have to be played one against the other; what kind of information is open to the public; to what extent are impacts taken into account and how are they characterized; how do professionals interact with non-professionals and how is technical and professional information used.

The linkage between development strategies and conflicting issues of water allocation, supply and pricing must be seen in the context of macro-economic national and regional approaches. The current debates over private versus public roles in water management are too narrowly focused and frequently ignore important historical realities. Privatization is often seen as a way to increase efficiency and to bring more and safer water to more people. However, it also raises questions of open information channels and transparency. Profit-making organizations are not necessarily as prone to share critical information on water flow or quality as their public counterparts, particularly where there is a weak regulatory environment. Moreover, privatization of the vendible aspects of water can result in single-purpose planning and management, which contradicts the ethic of integrated water resources management. Some water services such as flood control cannot be privatized; others, such as navigation, may be only to a degree. Thus, attempts to privatize may encourage the fragmentation which integration seeks to overcome.

There is a difference between a public good and a common property under public trust. The evolution of water law and institutions historically has been inspired far more by the latter then by issues of private or pubic ownership. Indeed, the debate in Europe is moving from private versus public to one that focuses on public regulation on the one hand and, on the other, a form of common-property based governance whereby water is held in trust by the state, but managed at more adapted subsidiary levels. This is often called "municipalism" and it moves from the concept of ownership rights to that of user rights. Even in this context, state intervention is vital to ensure equity among users and to introduce needs outside the municipality such as those demanded by the river basin or watershed. International water law is also moving in this direction by increasingly referring to transboundary and international waters as common waters and thus subject to ethical and legal norms beyond those generated by the nation-state.

Recognizing water as an economic good, now expressed in many declarations and in the policies of major lenders and donors, has generated heated political debate, much fear and revealed fundamentally differing cultural values associated with water. Some claim that fostering the notion of water as a commodity moves public perception away from the reality of water as a common good and from a sense of shared duty and responsibility. In other words, there are profound ethical implications in perceiving ourselves as water citizen as opposed to water consumers. Seeing water as a common good focuses on the former while the question of private or public ownership rights emphasizes the latter.

It is clear that the democratic management of such a particular common property as water requires a complex institutional arrangement. Simple and straightforward solutions designed for the sake of pure economic efficiency, such as privatization of water rights and their transferability may well end up as unsustainable. If water management is moving towards a balance between the traditional role of the state and the re-emerging communitarian ethic, we must broaden our knowledge of what each of them can bring to achieving the goal of equitable policies and management.

6. International co-operation

Almost everyone lives downstream. An estimated 40% of the world's population depends for drinking water, irrigation, or hydropower on the 214 major river systems shared by two or more countries; five or more countries share twelve of these waterways. In some countries, almost the entire flow of surface water originates beyond their own borders — 98% in Turkmenistan, 97% in Egypt, 95% in Hungary, 95% in Mauritania, and 89% in the Netherlands, for example. Disputes between upstream and downstream riparian over water use and quality simmer in virtually all parts of the world. These involve reduced water flow and siltation because of dams, water diversion for irrigation, industrial and agrochemical pollution, salinization of streams due to unsound irrigation practices, and floods aggravated by deforestation and soil erosion.

Most scholars agree that outright conflict has the greatest potential to emerge when the downstream (most vulnerable) nation is militarily stronger than the upstream (water-controlling) nation and feels that its interests are threatened. When downstream countries are relatively less powerful than water-controlling upstream countries, conflict may be less likely, but social and economic insecurity - which in turn can lead to political instability - may be great. However, not all water resources disputes inevitably lead to violent conflict; on the contrary, it may be said that most lead to negotiations, discussions, and non-belligerent resolutions. In some parts of the world, river commissions with representatives of riparian countries provide a forum in which disputes can be addressed adequately. Elsewhere, however, adversarial relations among riparian states make for a much greater challenge and it is not certain that existing international water law will be able to handle the strains.

Measures that historically have been used to promote water-sharing equity include rights-based measures, largely addressed by the international legal community; needs-based measures, particularly using population, arable land, or historic use parameters; and measures based on economic definitions or efficiency. None of these alone, however, can incorporate all of the physical, political and economic characteristics that are unique to each of the world's international waterways. A process for co-operative watershed management is vital and international lenders and donors must create the incentives for such an approach and encourage the development of social organization around river basins.

Numerous agreements have been hammered out in the attempt to define what constitutes fair sharing of a particular waterway. The Food and

Agriculture Organization (FAO) has identified more than 3,600 treaties related to non-navigational water use between the years 805 and 1984. Since 1945 approximately 300 treaties dealing with water management or allocations in international basins have been negotiated. None of the various and extensive databases on causes of war have indicated water as the primary factor. Even in the highly charged Middle East, the first paper signed by three major parties during multilateral peace negotiations concerned water. Indeed, water agreements have actually prevented major conflicts, such as on the subcontinent between Pakistan and India.

Nevertheless, it is clear that the increased competition for water both within and between countries as supplies increasingly fall short of needs could pose a major threat to human security. Of the three principal forces which conspire to create scarcity and its potential to incite conflict - the depletion or degradation of the resource, population growth and unequal distribution or access - it appears that unequal distribution often plays the most important role.

This means that the question of "equity" is at the heart of water conflict management and that the solution to water scarcity lies not necessarily in building water markets but in consolidating the rules for sharing found in customary international law, which develops through a process of claim and counterclaim, with the nations making the claims appealing to legal rules to establish their rights. Customary law does something that the market cannot: it recognizes the unique nature of water. Instead of trying to determine who "owns" what proportion of a river, it lays down a set of rules for sharing, among them equitable and reasonable use, obligations not to cause appreciable harm, commitment to co-operate, regular exchange of data and information and recognition of relations between users.

The international community took a major leap forward in 1997 by approving the United Nations Convention on the Non-Navigational Uses of International Watercourses by a vote of 104 to three. It will unquestionably be the leading law governing internationally shared fresh waters once it is ratified by 35 nations - a process that could take many years. The convention provides a set of standards in codifying the rule of equitable utilization based on a long list of diverse factors - from geographic and ecological considerations to the economic value of existing and potential uses of the waterway. The aim is to help arbitrators and judges determine "equitable" sharing, which does not necessarily mean equal shares.

Water is forcing us to rethink our notions of security, dependency, and reciprocal obligations. Although water sharing plans and infrastructure networks are viewed by some as increasing vulnerability and reducing security, there is an alternative way to look at interdependence: it can be seen as a means of providing safeguards by boosting our flexibility and capacity to respond to exigencies of nature such as droughts and floods and of fostering a climate of mutual respect and rapprochement.

Water can be an overarching value capable of coalescing conflicting interests and facilitating consensus building within and among societies. The symbolic content of water as cleansing, healing, rebirth and restoration can provide a powerful tool for co-operation and for promoting acts of reconciliation so necessary to conflict resolution in other areas of society. In a sense, negotiations over water use in themselves may be seen as a secular and ecumenical ritual of harmony and creativity (Selborne, 2000).

7. References

Ball, P., 1999 *H2O: A Biography of Water,* London, Weidenfeld & Nicolson.

Our Common Future, Report of the World Commission on Environment and Development, Oxford University Press, 1987, p.27.

Resolution 29C/13.2 of the 29th session of the General Conference of UNESCO, October-November 1997.

Selborne, L., 2000 *The Ethics of Freshwater Use: A Survey*, COMEST- UNESCO, Vincennes.

ENSURING ADEQUATE REACTION IN CASE OF EXTREME WATER POLLUTION THROUGH TRAINING AND EDUCATION

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Abstract

Extreme water pollution is a severe environmental accident, endangering the local or even regional safety of human community and of the entire environment as well. Adequate awareness and preparedness to respond to such emergency situations must be reached in all strata of population. Developing a national training and education strategy is the responsibility of all level authorities. Training and education endeavors must offer basic knowledge about epidemiology, prevention and control measures to be taken efficiently and promptly. Training must be addresses to all individuals having direct responsibility for protecting the environment, who may affect the environment in the performance of their job, or who have overall responsibility for environmental performance. Education or training has to ensure such individuals could meet their environmental responsibilities.

Key words: Water/ pollution /training/ awareness/preparedness

"To teach is to create a space in which obedience to truth is practiced"
Abba Felix, Desert Father

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 321–329.

1. Introduction

Briefly mentioning few words about the water pollution itself could help in better understanding the specific methodological comments and requirements of training and education that will follow.

Water pollution is defined as contamination of streams, lakes, underground water, bays or oceans by substances harmful to living things (Water pollution) Water pollution could be caused by any chemical, biological or physical changes in water quality that makes water unusable for human or ecological use. It might happen incidentally, at different scales, up to the level of ecological disasters (of natural or terrorist origin).

2. What should be known?

Several factors must be in place and connected for persons to be harmed by something in the environment (Water pollution; What should we know? Okun, 1992):

- A **source of harm** must exist, which has chemical, biological, and/or physical properties that make it persistent and/or transportable (miscible, volatile, water soluble) in the environment.
- An **environmental medium** is necessary for transport of polluting agent(s): air, surface water or groundwater, soil, or combinations of the three.
- A **receptor population** must be within the exposure pathway for harm to human health. Potential population exposures are important if the contaminant is persistent and land/property use changes over time.
- **Route of exposure.** Humans can be exposed to water contaminants via three routes: inhalation, ingestion, and dermal absorption. Inhalation may occur through aerosols. Ingestion may occur through drinking contaminated water or milk, eating contaminated plants, animals, or soil. Dermal absorption requires direct contact with a contaminant that is capable of penetrating the skin, water included.
- The final ingredient for exposure is **dose**. There must be an adequate amount of the polluting agent to result in human harm.

Natural disasters create many public health concerns: insuring safe water supplies, restoring water, safe food, solid waste, liquid waste / sewage, vector control, safety / injury prevention, hazardous materials disposal and post disaster assessments. **A terrorist attack** concept includes that biological, chemical and/or radiological agents might be spread via environmental delivery system, through air, food or water, towards public or individual. **Emergency preparedness** would include training and certification, planning, defining roles, partnerships, and funding support (Buchanan, 2004).

2. Informatin and communication

Information is essentially needed when/if wishing to create and apply skills, and to understand how to appropriately respond to public health concerns, environmental extreme situations included. **Communication** is the only way making sure the right information is timely transmitted to the right people. National authorities are in charge of identifying and implementing the requested initiatives, procedures and programs in order to offer specific information to specific audience involved in supporting these three objectives (What should we know? 2002).

3. Training and education

Training and education are – together – one of the eight major communication areas, being a part of what is considered as information needs of the responder community. Responder training and education programs contribute to strengthen the preparedness of public officials and responders for future environmental accidents by providing needed knowledge and skills in this respect. This is one of the bridges to be built above the gap between individuals and agencies during such an environmental accident like extreme water polluting events, facilitating the creation of social networks among officials and responders (What should we know?, 2002).

Training and educating responders and officials who may be called upon to respond to environmental accidents is the key issue of a good pre-accident internal communication strategy. It is largely accepted that the skills achieved through training programs could not be entirely replicated during an environmental accident. It is also well known that practical experiences gained through training and education would be useful by improving the response community (What should we know?, 2002). Training and education are critical information flows, playing a crucial supportive role if its content and deliverance could improve internal and external capabilities as well. Participation in training and education programs help establish the above-mentioned social networks.

Training and education programs provide special opportunities for networking and relationship building, bringing together members of the responder community who may not normally have the opportunity to interact. Training and education help to facilitate communication in public information, and communication between certain types of responders, officials, policymakers, and managers. Better communication systems of the public safety and health and medical communities will facilitate internal communication. National training efforts facilitate the implementation and the use of essential standardized operating procedures and terminology among frontline responders, improving their abilities of communicating with one another during an environmental accident response.

Training and education requirements differ between army, public safety, public health and medical, response mangers and policy makers. Common core elements must be included in the training programs provided to each of the four responder communities mentioned above (Environmental guidelines for military sector, 1996):

- the content of applicable emergency operations plans and collective responsibilities under those plans;
- common terminology for equipment and procedures, in order to facilitate communication between responders from various organizations;
- methods for coordinating and communicating with other responder agencies to meet the collective responsibility of maintaining the safety of the public; and
- the means to recognize a chemical, biological, radiological, and nuclear (CBRN) accident and maintain a safe working environment under toxic/improper conditions.

Training and education must meet a number of criteria:

- the integration of hands-on training; a degree of repetition;
- the incorporation of a method of students' evaluation and/or proficiency testing;
- the ability to reach a wide audience;
- cost efficiency;
- time efficiency.

All level authorities are similarly responsible for developing a national training and education strategy, for both domestic preparedness and homeland security. Such a national training and education strategy should (Environmental guidelines for military sector, 1996):

- Assign roles and responsibilities for training and education providers in the frame of a national training program, developing standards and best practices for training and educational curricula, materials, and training techniques.

- Assign governmental responsibility of financially supporting local or regional authorities that would keep the main responsibility for implementing in the field/community training programs for national, regional or/and local response agencies located within their jurisdictions.
- Continuously assess the training requirements of the broadly defined responder community. A formal structure must be developed to certify and provide accreditation for members of the responder community that have achieved certain skill types and levels.
- Coordinate and integrate training and educational programs currently in existence throughout the country, including training programs offered by NGOs.
- Develop mechanisms for disseminating information about the training opportunities available to responders. National databases – continuously updated with the new course offerings and opportunities – to catalogue and advertise current training programs and resources available to the responder communities would be extremely useful; such databases, of different providers, must be made available to responders and their respective organizations.
- Revise and update the training programs to include response techniques for a wider spectrum of environmental accidents: e.g. recognizing the early symptoms of a variety of chemical and biological agents and treating such patients/symptoms.
- Improve and make more accessible the tools the policymakers, officials and response managers need to appropriately direct a response.
- Focus on accident managers and senior government leaders in all levels of government.
- Promote familiarity with current methods and resources for dealing with such accidents, crisis decision-making, and communication skills, and the roles and responsibilities of different responders, levels, and departments.

To teach/learn is to create a Space/Community in which obedience to truth is practiced. A Community of Practice means: general competencies, open data systems, celebrate benchmarks across disciplines, build knowledge about medical education, build knowledge about improving patient care, and enhance public accountability.

The first step in the development of an effective education and training program is to identify all individuals who have direct responsibility for protecting the environment, who may affect the environment in the performance of their job, or who have overall responsibility for environmental performance. The next step is to identify the type and level of education or training that is required to ensure that these individuals can meet their environmental responsibilities. A plan must be developed that identifies the positions, the type of training or education required, and where the training or education is available. Environmental professionals may require separate technical courses. However, it would be cost prohibitive to provide a special environmental course for every individual. Within the army, the best approach for the majority of the military and civilian personnel is to insert the environmental instruction, when possible, in existing training activities. All recruits entering into the military should be given general environmental awareness training as part of their basic training. Technical specialty training should include instruction on environmental concerns directly applicable to the execution of that specialty (Environmental guidelines for military sector, 1996; Water pollution).

Medicine, education and management are cooperative arts rather than productive arts. Therefore the quality is dependent on the quality of the relationships. If talking about research in Public Health, the model of research to be developed would incorporate greater expertise & emphasis in Epidemiology & Public Health, then it would fight for broader understanding of various diseases in society.

Development of a health system begins with solid core of primary care, reinforced by the Primary Health Care concept, and emergency medicine; such a system looks at the needs of the frailest in society. Actually, the existing healthcare systems are organized around acute catastrophic illnesses, the patients are treated until they are well, and it works episodically, fragmented. Most of the time, the health system responsible persons complain about health financing, and health financing is based on "causality" or "catastrophic" approach of health insurance, and on fundamental unpredictability of diseases & injuries; the expensive existing health systems stay based on "acute care" model, taking care almost exclusively of 'today' and not taking care too much of 'tomorrow' or even at all of 'the day after tomorrow'. Or, the future is not about predicting, is about designing, and then making it happen!

Future vision statement must stay "Readiness to respond to unexpected!" and the Vision: Just the "Right Stuff": Just the right Content, to just the right Person, at just the right Time, on just the right Device, in just the right Context, and in just the right Way.

An efficient educational plan might start by completing an inventory of all known environmental research and development needs, identifying processes and applications that use the largest quantities of hazardous materials, generate the largest volumes of hazardous wastes, or produce the largest releases of contaminants in air and water emissions.

There is a need to determine if there are any existing technologies available that might satisfy the need and if any research is being performed that might satisfy the needs.

The laboratories should develop project proposals to respond to environmental needs. These projects should then be prioritized based upon the following factors:

- size of problem
- criticality of solution to mission performance
- existing risk to human health
- potential return on research and development investment
- timeliness of effort to meet needs
- confidence in possible success of effort (Environmental guidelines for military sector, 1996):

4. Prevention includes a number of approaches

As primary preventive strategy, **education** includes educating individuals, groups, and communities, to be educated on environmental concepts and ways to prevent environmental problems. **Schools** provide – by definition – excellent settings for education on environmental issues. Current environmental and health education programs include:

- Providing educational materials
- Incorporating a K-12 environmental curriculum with teacher training by school districts
- Experiential environmental camps for children and youth
- Reward and recognition of environmental projects developed and implemented by youth.

Water was, is and it will stay forever a vital environmental element. Our life depends on its quality. In the same time water is one of the main vectors for causal agents of so many infectious and non-infectious communicable and non-communicable diseases. To the end, the global environmental changes and also the catastrophic water pollution disasters illustrate difficulties facing civil and military public health practitioners all around the world. Reinvigoration of public health practice would include (Beaglehole and Bonita 2003; Okun, 1992)

- leading role of public health practitioners to immediate health crises;

- leading role of public health practitioners in protecting and improving population health;
- public health practitioners will promote intersectoral actions for health improvement and reduction of health inequities;
- public health research, training and practice will be a high priority in all health services.

Public health training should be provided through a combination of rigorous academic and supervised practical experience (Environmental guidelines for military sector, 1996):

1). There are training needs in institutional strengthening, in legislation, in laboratories, in monitoring and sanitary inspection. Training will develop sets of skills which are essential to staff working in the public health and hygiene sector in the area of drinking water and bathing water, particularly:

- Investigative skills,
- Analytical skills,
- Interpretive skills,
- Communication skills,
- Educative skills, and
- Organizational skills.

One of the very important and significant successes of a training program is the one allowing the participants to reach and understand the meaning and importance of the five "Be's" (Buchanan, 2004):

Be involved in response planning activities;

Be knowledgeable of governmental plans/authorities;

Be aware of local assets;

Be knowledgeable and understand governmental assets;

Be aware of your limitations.

Education should not be considered an end in itself. It supports all other aspects of the environmental program. The effectiveness of the education program will be reflected indirectly in the success of the pollution prevention, conservation and cleanup efforts. Every effort must be made to share technologies among nations and to focus research and development programs on those problems. The success of the research and development program will be reflected indirectly in the success of pollution prevention, cleanup and conservation efforts (Environmental guidelines for military sector, 1996):

During the last decade, UN Development Programme (UNDP) implemented different disaster management and preparedness projects in CEE and CIS countries, many of them focused on water pollution disasters, all projects answering to concrete national situations/needs.

5. References

Beaglehole, R., BonitaRuth, 2003 Strengthening public health for the new era, in R.Beaglehole (ed) *Global Public Health: a new era*, OUP, Oxford New York, p. 253-268.

Buchanan, S., 2004 *Building Capacity for Environmental Emergencies* 133rd APHA Annual Meeting, oral presentation, Washington DC, 11/06/2004.

Environmental guidelines for the military sector. A joint Sweden-United States Project. March, 1996. http://www.nato.int/ccms/general/guidemil/guide.html.long

Okun, D.A., 1992 Water Quality management, in J.M.Last and R.B.Wallace (eds) Maxcy – *Rosenau –Last Public Health & Preventive Medicine*, Appleton & Lange, Norwalk. p. 619-648.

Water pollution. http://www.exampleessays.com/viewpaper/100627.html

What should we know? Whom do we tell? Leveraging communication and information to counter terrorism and its consequences. Project Report, December 2002. Chemical and Biological Arms Control Institute CBACI.

ROUND TABLE DISCUSSION

POSSIBLE BIOLOGICAL THREATS FOR EUROPE

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Abstract

Microbiological agents can appear in the drinking water network by accidental events like breaking the pipe and the drinking water can be contaminated with sewage or contaminated soil, or neglected procedure and handling of water treatment plant and pipe system. On the other hand bioterrorism should be considered when different biological agents like viruses, bacteria, rickettsia, fungi, toxins, chimeras and prions can be used as biological weapons. If producing biological weapons is supported by governments like in the period of cold war this term of production can be regulated and controlled by international contracts, agreements. But nowadays the main threat is bioterrorism when agreements are ineffective. The primary goal of terrorism is to erode the security of a nation, to disrupt the continuity of society, and to destroy the nation's social capital – its morale, cohesion, and values. In case only the international collaboration can decrease the efficiency of bioterrorism.

Keywords: Waterborne outbreaks/ bioterrorism/ biologic agents/ bioassays

1. Introduction

Most of the outbreaks caused by drinking water are connected with untreated surface water, untreated ground water, treatment deficiency (e.g., temporary interruption of disinfection, inadequate disinfection, and

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 333–336.

inadequate or no filtration), distribution system deficiency (e.g., cross connection, contamination of water mains during construction or repair, and contamination of a storage facility). In the period 1986 to 1996, a total of 778 outbreaks were reported in 19 European countries. Sweden alone reported 53 outbreaks and England and Wales 20 (Lack 1999). The causative agent was not identified in 90% cases in Sweden, in the period of 1980-1999. The identified microbial agents were *Salmonella, Shigella*, *Campylobacter*, toxin producing *E. coli*, *Giardia, Entamoeba, Cryptosporidium, Calicivirus*. In England and Wales 41 waterborne outbreaks with 8617 cases were reported in the period of 1971 to 2000 using public supplies and 23 with 1549 cases were reported in the same period using private supplies (Stanwell-Smith et al., 2003). In Hungary in the period of 1988-1992 there were 8 outbreaks with 1764 cases. In three of eight outbreaks the causative agent was not identified in 821 cases. In 1985 an outbreak of *Campylobacter jejuni* was registered. Some wild birds nested in the water tower and they died off into the water causing an outbreak in the village of Poroszlo (Csanády, 1995a, 1995b). In another paper where data are summarised in the period of 1986 to 1997: 12 outbreaks transmitted by public drinking water supply in 12 years with 3344 known cases.

Pathogens: *Salmonella* spp involved in 4 outbreaks

Shigella sonne: i involved in 2 outbreaks

Campylobacter jejuni: involved in 1 outbreak

pathogen not recovered in 5 outbreaks

Source water: confined groundwater in 7, unconfined groundwater in 2, mixed type in 2 and surface water in 1 case (Kádár, 2000).

On the other hand extensive biologic-weapon programs in Iraq and the former Soviet Union are financed (Khan 2001). The bioterrorism is a global problem nowadays so the prevention should also be global.

2. Methods

As first step to identify the biologic agent in the outbreaks and in the water with conventional methods (e.g., culturing methods). These methods can be used for accidental outbreaks and defending the bioterrorism as well. The most frequent used strains in bioterrorism are the easily producible microorganisms such as *Anthrax*, *Vibrio cholerae*, *Salmonella* strains, *Shigella*, EHEC and EPEC (toxin producing *E. coli*), *Campylobacter*, *Aeromonas*, *Calicivirus, Cryptosporidium* etc. It is essential to have quick and effective identification methods for the organisms above. There are two sites, Copenhagen and Budapest in Europe where all the typing serums can be found for all *E. coli* strains. It means about 600 kinds of serums.

The next step is using molecular epidemiology (e.g., sequence analyses, 16S RNA PCR etc.) to determine the real connection between the outbreak and the water supply.

3. Conclusions

- It is necessary to find out the causative agents in the outbreaks with greater effectiveness and quick methods to make defensive measurements on human health in accidental and bioterroristic attacks.
- It is necessary to carry out conventional culturing methods to identify the strains.
- It is necessary to use animal experiments to detect toxins produced by bacteria (E. coli, cyanobacteria). It can be proved by these methods if something is toxin producer or not.
- It is necessary to use biosensors or continuous bioassays for detecting hazards in larger water supplies.
- It is necessary to carry out molecular biological examinations to prove the causative agents.
- It is necessary to establish surveillance systems on national, international and global level to link the data of water supplies and outbreaks.

4. Acknowledgements

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5. References

Csanády M., Straub I., 1995a. Health Damages due to Water Pollution in Hungary In E.G Reichard. G.A. Zapponi (eds.) Assessing and Managing Health Risks from Drinking Water Contamination.IAHS Publications No. 233, Wallingford (UK) pp. 147-152.

Csanády M., 1995b Víz okozta járványok és ivóvízszennyezési esetek tanulságai. *Környezetgazd. Int., Budapest, p. 67.*

Kadar M., 2000. Microbiological safety of water supplies. In: Security of public water supplies. Nato Science Series „/66. R.A. (ed.Deininger et al.) Budapest. pp. 185-195.

Khan A.S., Ashford D., 2001. Ready or not – Preparedness for bioterrorism. New England J. Medicine 345. 287-289.

Lack T., 1999. Water and health in Europe: an overview, B.M.J., 318, 1678,

Stanwell-Smith R., Andersson Y., Levy D.A., 2003. National Surveillance Systems. In: Drinking water and infectious disease. Establishing the links. eds. Hunter P.R., Waite M., Ronchi E.,CRC Press, IWA publishing Boca Raton, London, New York, Washington, D.C. pp. 25-40.

WATER SECURITY AND THE THREATS FROM BIOLOGICAL AGENTS OF CONCERN

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Abstract

Water safety has always been of the highest priority however communities and the water industry are now engaging in how to develop a specific program for water security. In particular, research is needed on new analytical methods which can address water contaminants of concern and an improved understanding of the risks. There are a number of disease causing microorganisms which have characteristics that would facilitate their use as agents for terrorist type of activities or as biological weapons. The prevention and control of these potential biological agents of concern (BAC) requires an understanding of the ways bacteria, viruses and parasites are spread. The scientific mathematical calculations support an amount in grams depending on where the contamination takes place.
Keywords: water security/ biological agent threats/ control of BAC

1. Introduction

In the United States the horrific events of September 11th , 2001 and the following emergence of anthrax cases have brought the issue of security to the forefront of everyone's agenda. Water safety has always been of the

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 337–342.

highest priority however communities and the water industry are now engaging in how to develop a specific program for water security. Khan et al. (2001) have reported that "deliberate food and water contamination remains the easiest way to distribute biological or chemical agents for the purpose of terrorism." In 2002, a plan in the US began to be formulated, directed by the US Administration (*The National Strategy for Homeland Security 2002*) and (The Public Health Security and Bioterrorism Act 2002). Under these directives, the US Environmental Protection Agency (EPA) is responsible for national efforts to address water security. Action plans included vulnerability assessments, approaches needed for technical support, communications and research needs. In particular, research is needed (listed in Table 1, Herrmann et al., 2004) on new analytical methods which can address water contaminants of concern and an improved understanding of the risks.

TABLE 1. Research Needs for Water Security as Identified in US Action Plans (Herrmann et al., 2004).

Infrastructure	Protect drinking water systems (reservoirs, storage tanks, distribution systems) from physical and cyber threats. Protect wastewater treatment and collection systems.
Water Quality	Identify contaminants of concern. Improve analytical methods for monitoring systems. Contain, treat, decontaminate and dispose of impacted waters safely.
Risk Assessment and Communications	Identify likely threat scenarios. Evaluate the impact on public health (communities)and ability to inform the public. Develop contingency plans.

2. Biological agents of concern for water

There are a number of disease causing microorganisms which have characteristics that would facilitate their use as agents for terrorist type of activities or as biological weapons [ability to be produced in large amounts, purified, stored and delivered to large populations] and a number of biological agents of concern (BAC) have been weaponized particularly for aerosol dispersion as inhalation can often cause more severe outcomes. Historically, there are records of poisoning of the water supply as early as the 6th Century

B.C., use of plague in 1348 by the Mongols in the city of Caffa and use of Small pox in the French & Indian War. In our more recent history, in 1984 the Rajneeshee Cult contaminated salad bars with *S. typhimurium* (where 750+ individuals became ill) in an attempt to influence an election outcome in Oregon (Torok et al., 1997) and finally the experience of the Anthrax letters contamination event of 2001 is still quite fresh in our minds (Jernigan et al. 2001). In fact, anthrax has been reportedly used more often as a real threat or implicated in a hoax than any other BAC.

A number of publications have listed the microorganisms that could be potentially used as biological weapons. Burrows and Renner (1999) have listed 18 organisms and 9 biotoxins of which 44% and 89 % are listed as threats to water, respectively and another 28% and 11 %, respectively as probable threats to water. The characteristics of BAC associated with water security risks involve both issues of dose-response, exposure and healh outcome. Table 2 describes some of these characteristics.

The prevention and control of these potential BAC requires an understanding of the ways bacteria, viruses and parasites are spread. Knowledge of the transmission systems [including environmental transport and survival] of many BAC is incomplete; thus we need to greatly enhance our data and models for the ability to effectively predict and anticipate the extent of an epidemic following a bioterrorist event, and control the outcome and exposures where possible. The new challenges for homeland security require improved levels of specificity regarding the infectious agent and assessment of exposure. This will require the application of a quantitative microbial risk framework.

3. Quantitative microbial risk assessment (QMRA). Frameworks and research needs

QMRA is a statistical approach that can be used for defining the risk of microorganisms spread through water. However, the exposure assessment presents the greatest uncertainty. Based on dose-response data, small concentrations of many of the possible BAC could contaminate large volumes of water causing sporadic cases and wide-spread fear and concern if intentional contamination becomes known and reported. The scientific

TABLE 2. Examples of Risk Descriptors Associated with Water Transmission for Biological Agents of Concern.

Descriptor	Types of BAC	Notes
Low infectivity associated with dose-response.	Viruses (eg rotavirus, HAV, Noroviruses); Parasites (Giardia, Cryptosporidium) Bacteria (Shigella, E.coli 0157 H7; Campylobacter)	Low concentrations capable of initiating infection.
Exposure Issues: Resistant to treatment (disinfection)	Viruses resistant to Chloramines, UV. Parasites resistant to the various types of Chlorine disinfection. Spores (eg. Anthrax) and toxins.	Often little is known about the concentrations and contact times needed to adequately inactivate the BAC.
Health impacts	Anthrax; SARS; Norovirus; Cryptosporidium, E.coli 0157H7.	Mortality. Easily transmitted secondarily. Sensitive populations in the community at high risk (eg. Children).

mathematical calculations support an amount in grams depending on where the contamination takes place. Anthrax inhalation dose-response data analyzed by Haas (2002) has revealed that levels at low as 10 spores/L could be associated with risks of 1/10,000 for a single exposure with the end-point being death. Other microorganisms will cause greater likelihood of illness (1/10 to 1/1000 risks) at even lower levels of contamination (1 gram of feces per 1million gallons of water) (Table 3). While there will be less potential for death with many of these others microorganisms, the severity and mortality will be of greater significance in the sensitive members of the community including the elderly, very young, immunocompromised, those with underlying disease (eg. cancer) (Gerba et al., 1996). The contamination of water means that this subgroup in the community could be exposed.

TABLE 3. Risk Associated with the Contamination of 1 Million Gallons of Water with 1 Gram of Feces* Based on Dose-Response Data (Haas et al., 1999).

Microorganism	Risk
Rotavirus	1/10
Cryptosporidium	1/1000
Giardia	5/1000
Shigella	2/1000

* Assuming 10^6 organisms/g of feces (Gerba, 2000), 1 liter of water consumption, no inactivation.

Initially it was suggested that the water supply, due to dilution and treatment would not be at risk of biological terror attacks. Rose (2002) has previously described why the assumptions used to support this premise were not justified. BAC and water security associated with intentional contamination do need to be examined using a risk-based approach. While research programs are being currently established by the US federal government, there are three broad areas that should be included as major foci for furthering research agendas for biological water security. These include:

Host-pathogen interactions: Better understanding of the dose-response, genetic diversity, virulence, and mechanisms of pathogenicity for BAC are needed. Animals could be a source of these BAC, thus diseases and infections in the animal world need to be better identified and cataloged.

Environmental Exposure Assessment: Developing data and modeling the pathways for exposure should be particularly focused on the movement of contaminants in the distribution system and potentially from the distribution system to the indoor environment. EPA and other groups have developed programs (eg. EPANET, a water distribution modeling package) which can analyze an entire water distribution system, or selected portions, under steady state of extended period simulations, with water quality analysis. These need to be tied to evaluation of new methods for detection and require that specificity, sensitivity and safety goals for each method be established.

Community modeling and risk assessment: Population models are capable of integrating various aspects of the population including immune status and outcomes in addition to primary and secondary modes of transmission for understanding the disease dynamics. Interventions, such as vaccination and quarantines can be examined via these types of models.

4. References

Burrows, W.D., S.E. Renner. 1999 Biological Warfare Agents as Threats to Potable Water. Environ Hlth Perspec. 107(12): 975-984.

Gerba, C.P. 2000 Assessment of Enteric Pathogen Shedding by Bathers during Recreational Activity and its Impact on Water Quality. Quant. Micrbiol. 2(1)55-68.

Gerba CP, Rose JB, and Haas CN. 1996 Sensitive Populations: Who is at the Greatest Risk? Internat. J. of Food Microbiol. 30: 113-123.

Haas, CH., Rose, JB., and Gerba, CP. (eds) 1999 *Quantitiative Microbial Risk Assessment.* John Wiley and Sons, NY, NY.

Haas, C.N. 2002 On the risk of mortality to primates exposed to anthrax spores. Risk Analysis. 22:(2): 189-193.

Herrmann, J.G, Dee, P.E., and Robiou, G. M. 2004. Water Security Research and Policy: EPA's Water Security Research and Technical Support Action Plan. J. Contemporary Water Research and Education. 3-7.

Jernigan, JA, Stephens, DS, Ashfor, DA, Omenaca, C., Topiel MS, Galbraith, M. et.al. 2001. Bioterrorism-related inhalational anthrax: the first 10 cases reported in the United States. Emerg. Infect. Dis. 7:933-944.

Khan, A.S., Swerdlow, D.L. and Juranek, D.D.. 2001 Precautions against Biological and Chemical Terrorism directed at Food and Water Supplies. Public Health Reports, Jan.-Feb. 116: 3-14.

Rose, J.B. 2002. Water Quality Security. *Environ. Sci & Tech.* June, 247A-250A.

Torok, T.J., Rauxe, R.V., Wise, R.P., Livengood, J.P., Sokolow, R., Mauvai, S., Birkness, K.A., Skeels, M.R., Horan, J.M and Foster, L.R. 1997. A large community outbreak of salmonellosis caused by intentional contamination of restaurant salad bars. JAMA 278 (5):389-395.

Public Health Security and Bioterrorism Preparedness and Response Act of 2002. United States Congress. 2002 Public Law 107-188.. http://www.epa.gov/safewater/watersecurity/pubs/security-act.pdf

National Strategy for Homeland Security 2002. The Whitehouse Office of Homeland Security. 2002 http:/www.whitehouse.gov/homeland/book/nat_strat_hls.pdf

FINDINGS, CONCLUSIONS AND RECOMMENDATIONS

The goals of the workshop included a discussion of the a) state of the science in b) identification of new research and approaches for; and c) communication of the management of water pollution and sustainability of water resources.

The FINDINGS, CONCLUSIONS and RECOMMENDATIONS presented herein are a result of the scientific papers, presentations and discussions which followed.

Frameworks for addressing the science and management strategies

The integration of scientific information regarding the types of hazards the environmental fate of the chemical/biological, exposure pathways and human and ecosystem impacts may be implemented from both a qualitative or descriptive approach or using a more classical quantitative risk assessment paradigm..

While for both intentional and accidental water pollution a framework which focuses on a reactive mode is most often implemented, a similar framework can be used for preventative approaches and thus may be more proactive as well as have some ability to forecast particular adverse outcomes. In addition out of these types of assessments and the lessons learned come programs for early warning systems and better systems for monitoring or enhancing wastewater/industrial discharges and drinking water treatment.

Thus the frameworks for assessing the risk and managing the risk may be seen as

- Preventive
- Early Warning
- Responsive

G. Dura et al. (eds.), Management of Intentional and Accidental Water Pollution, 343–355.

Findings:

Dr. Veska Kambourova (Bulgaria): presented a descriptive framework to address the relative vulnerability of water supplies and systems from the source and raw water to the treatment facility through to distribution systems and storage facilities. Biological pollution often occurs at the source and chemical pollution occurs due to accidental releases and treatment plant mistakes. Thus this understanding enhances appropriate management strategies.

Dr. Gyula Dura presented a classical quantitative risk assessment (QRA) framework for addressing the response to chemically contaminated sites in Hungry. In addition to the understanding of the chemical nature of the hazard (solubility and toxicity) site assessment (soil characteristics) and the geographical specificity of the situation are important parameters for consideration in the risk. In this case the framework was used in a PREVENTATIVE approach for the explicit protection of groundwater supplies with pesticides.

Dr. Ferenc Lazlo presented a case example of cyanide and heavy metal contamination. Hydrogeological considerations were key to understanding both ecological and human health impacts that were observed. Clearly two areas were identified as factors associated with the accidents: 1) Management of the treatment and storage systems, and 2) climatic factors, heavy rainfalls. Changes to improve the management of the risk in the future included, development of an industry inventory, spill notification, development of action plans (enhancing dilution and flushing capacity of the water reservoirs) and finally the development of an early warning system with in-situ automatic water quality monitors. This example along the Tisza river demonstrated the need for multinational agreements on water quality monitoring, protection and response plans.

Dr. Hans-Martin Mulisch also presented the use of QRA for addressing military sites. The assessment of the site and the substance must be accomplished in concert. Prioritization of risks, assessment of relative risks and potential risks for over a two to 4 year time frame. The communication with two different Ministries was critical to success Ministry of Health and Ministry of Environment.

Dr. Mihail Kochuboski followed up this presentation regarding the development of similar protocols for addressing metal contamination via a Transboundary agreement. Communication with three Ministries Health, Agriculture and Environment was important to success. The long term monitoring program made it possible to follow progress in remediation and agreements about use and protection of the waters from industrial discharges.

Risk management approaches gleaned from agriculture experiences

The agricultural field has had extensive experience with pesticides and nitrogen as the primary hazard of concern which may possibly impact surface and ground waters. With support of a risk assessment frameworks and extensive modeling efforts both PREVENTATIVE and RESPONSE driven management strategies can be addressed.

Findings:

Dr. Domenica Auteri presented the QRA framework with similar elements addressing environmental exposures (fate, stability and transport) as well as effects assessment. Catchment scale modeling and monitoring the appropriate spatial and temporal scale is a key conclusion. A tiered approached was useful and both ecosystem and human health were addressed. Natural systems and buffer zones can be established using a science-based risk analyses.

Dr. Carol Riparbelli demonstrated the translation of the QRA to implementation via a decision support system (Supplying Sustainable Agricultural Production), which could be used for nitrogen management as well as pesticides. The Land use (vulnerability) could be identified with modeling efforts that examined recharge estimates and meterological conditions. Geostatistical modeling is recommended and improvements with better data bases are needed.

Dr. Giovanna Azinorti presented that a strategy to enhance multinational cooperation, consensus and harmonization of data and models (FOCUS; Forum for the Coordination of Pesticides fate models and their Use), using the previous models scenarios which incorporate climatic conditions can be evaluated for a PREVENTATIVE risk assessment method for pesticides which can go from the multinational to the national and regional level.

Biological hazards and the biological nature of water

The hundreds of biological hazards are as diverse as the list of chemical pollutants and represent groups belonging to algae, diatoms, bacteria, helminthes, parasites, and viruses. The sources include sewage and animal wastes as well as organisms in the natural water environment that can cause infections or produce toxins. Exposure pathways are complex, recreational waters and drinking waters (at the source, at the treatment plant, in groundwaters and distribution systems) are at risk and these organisms also impact the food chain. In addition, the natural occurring biological integrity of the water is key to ecosystem health and impacts of pollutants can be observed by examining the aquatic microbial populations of a system.

Findings:

Dr. Joan Rose (U.S.) presented the role of sewage as one of the most important sources of microbial contaminants in water. As for the chemicals the QRA framework is used, and while a single fecal indicator system is currently used, better monitoring for a number of indicators, source tracking host-specific markers and pathogens is needed.

Dr. Andrea Torokne' (Hungary) presented the progress in Hungary addressing the EU legislation for indicator organisms including criteria for sewage and biosolids (helminth, distribution systems (iron and manganese bacteria, sulfur bacteria and *Psuedomonas*) and ambient surface waters (toxic algae, *Cyanobacteria*). The toxic algae represent an emerging risk as many of the toxins have not been identified. In fact while some of the indicator standards are more stringent in Hungary than in the EU, community waterborne outbreaks have been documented (Calicivirus). In regard to sewage/industrial discharges particularly addressing ecological health of aquatic systems, appropriate bioassays for addressing toxicity are now being tested. A tool box of many tests will be necessary and could be developed for evaluation of intentional contamination of drinking water.

Dr. Hamid Taleb presented the risk to coastal waters, recreational uses and the food chain to increasing blooms of hazardous blooms of organisms producing an array of marine toxins. The complexity of identifying these hazards was exemplified by the toxin structures, modes of action and distribution in water. Monitoring was emphasized as the key to understanding these hazards which supported the conclusions of the previous presenters.

Dr. Zdenek Filip presented a case-study of the microbial flora of groundwaters impacted by organic pollution. One must monitor and assess the biogeochemical transformation processes under aerobic and anaerobic conditions in the sub-surface to fully understand the risks and the appropriate management strategy for clean up. The temporal conditions needed for recovery is of great interest as was presented for the previous metal contamination above. Finally, interestingly enough a new approach could develop by monitoring the development of resistance within the microbial flora related to the ability for attenuation of the contaminant.

Water Terrorism and Intentional Acts of Sabotage

Intentional contamination of water supplies is as old as the 6th Century B.C. - poisoning of water supplies, yet more recently, government agencies have begun to address water security specifically under current and/or new water safety management approaches for identifying vulnerabilities and the necessary responses if an event should occur. The list of agents which could be used to impact drinking waters is limited to chemicals, toxins and biologicals and the potential and relative risks are influenced by the same set of parameters used in the QRA presented previously.

Findings:

Dr. Herman Dieter presented an overview of the chemicals and toxins that may be used as chemical weapons in the intentional pollution of water. A QRA approach is useful for developing priorities associated with acute exposures and influenced by stability in water, susceptibility to treatment and finally toxicity.

Dr. Alfred Bernard confirmed that the approach presented by Dr. Dieter was appropriate and that for chemical poisoning of the water the stability and solubility of the contaminant and it’s resistance to treatment were key considerations in the development of the risk and vulnerability assessment. However, in addition, dual-use chemicals must be included on the list as the access to large quantities is a key issue. An approach which examined the vulnerability of water systems by access, dilution and water treatment demonstrated that the storage reservoirs were at the most risk.

Dr. Rose presented the framework for the biological agents which could be used as terrorist tools for impacting water. Like the chemical QRA, stability and resistance to treatment and potency were the key parameters influencing the vulnerability. The ability to rapidly monitor if a credible threat is identified is a key part of the response plan.

Water Ethics

Water Ethics should frame the principals for the development of assessment and management strategies for water pollution prevention and control.

Findings:

Dr. Petro Smalko (Ukraine) presented the key social aspects regarding water use and management. The privatization of the water industry needs to be done not only with efficiency in mind but with strong regulatory system that allows for open data access and integrated water management.

Dr. Magdy Hefny (Egypt) presented the need for institutional frameworks that take into account cultural norms, behavior and shared visions which could promote action plans for including value-laden decision making and social responsibility using the Arab Network for Water Ethics as an example.

Dr. Ioan Boscan addressed the importance of education and training in the decision making process. This must include K-12 as well as the continuing education of professionals.

Their collection knowledge provided a list of key considerations in the development of principals for a water ethics program.

- Provision of safe water should be viewed as a right and an obligation of the environmental health and water community of scientists.
- Valuing and sharing water data [including water quality within the hydrologic context] will be focused on providing better and sufficient data within a common risk assessment approach.
- There is an implicit obligation to examine new potential risks and contaminants as well as better approaches for treatment/management.
- Water (quality) should be valued in light of our future generations.
- Public participation and inclusion of user groups will be allow for access.
- Education, training and communication programs toward a Learning strategy should be implemented.
- Shared responsibilities by the various Ministries and regions and countries should be recognized.
- The human right to water and the goal of a safe and secure water also means that the poor and vulnerable groups must be attended to.
- The fair and beneficial allocation of water, recognizing human health and welfare and the benefits of ecosystem services and goods shall become a part of hydrologic mission.

Acceptable risk within the risk assessment/management frameworks:

There was much discussion regarding the setting of acceptable (safety goals). While on the one hand the global guidelines and standards provided by agencies such as WHO and EU lay a minimal level of risk as part of the beginnings of a level playing field, it is clear that part of the society discussion on management needs to include the issue of acceptable risk. While no single target may be set for all safety goals, principals which include shared values and incorporation of the water ethics issues above will guide the costs and benefit analysis that may be undertaken. Recognizing that prevention goals may be more stringent and restoration goals may be time dependent. Geographic and societal characteristics should be considered.

Vulnerable populations

Drinking water goals and standards are there also to protect that percentage of sensitive and vulnerable populations (due to increased risk of severe outcomes associated with exposures to key contaminants).

Findings:

Dr. Olga Sivochalova addressed reproductive health as a key consideration for approximately 13 identified chemicals. This is clearly a means to protect the next generation. WHO global guidelines have precipitated action and have lead to a decrease of the concentrations of these compounds in drinking water. Recommendations have lead to a requirement for greater storage capacity of water and improved disinfection to help avoid accidental contamination that could cause these effects.

Dr. Anna Potapenko presented the mechanisms of action of chemicals and biologicals particularly on pregnant women and the fetus. These investigations complete our understanding and justify protection of our drinking waters.

Addressing Emerging Science, contaminants and technologies

There is an obligation to continue research into the betterment of humankind and improve public health protection. Research, using the risk assessment frameworks with the goal of prevention that investigates emerging contaminants and potential risks to our waters is warranted. In addition, one must examine and improve both pollution control and contaminant management from the wastewater and drinking perspectives.

Findings:

Dr. Fina Kaloyanova presented an example of the risks associated with persistent organic pollutants, particularly PCBs. Which remain present in sediments, soils and waters and have the potential for bioaccumulation into the food chain.

Dr. Bogdana Koumanova addressed the nitro phenols and demonstrated that bentonite mined from Bulgaria has the potential to reduce these contaminants through adsorption mechanisms via enhanced wastewater treatment.

Regional Water Experiences: Problems and Solutions

The exchange of information and knowledge of the pollution concerns that each country may need to address and the various approaches for management allows for the building of data bases and universal goals to achieve minimum levels of access to safe water. The unique geography and hydrology, land use and climate of the various regions require flexible management strategies that can be tailored to address the priorities for each country while keeping the global goals in view.

Findings:

Dr. Vladimir Bencko presented an overview of the problems and improvements made in the Czech Republic. Surface waters have improved due to decreases in phosphorus loadings and there is a decrease in pesticide contamination. Wastewater treatment has increased yet wastewater reuse based on aquaculture led to infestation of plants with *Salmonella* which moved the aquatic system to herivores. Recycling within industries has been implemented and water conservation in general has led to notable decrease in consumption. Here prioritization of research and management is needed on:

- Improving disinfection processes (balancing DPB and pathogen control)
- Tertiary sewage treatment to further nutrient reductions (also allow for improved pathogen reductions).
- The handling of sewage sludge.
- Land-based natural wetlands systems for wastewater treatment

- Monitoring of emerging chemical and biological contaminants.

Dr. Matyas Borsanyi presented an overview of water safety in Hungary. Fragmentation of water management is being addressed using WHO guidelines and food safety management approaches including HACCP (hazard analysis critical control points). HACCP allows for a system which can aid in identifying water quality targets and establishing controls and monitoring programs which will identify and demonstrate control of the hazards to drinking water from the watershed to the tap. The challenges in Hungary include management of surface water and ground water resources. While bank filtration is used along the Danube. Attention to the following areas is suggested:

- Arsenic and ammonium contamination of ground water
- Improving disinfection and the reduction of DBPs while maintaining pathogen control
- Improved monitoring (accession to EU means for example that parasite monitoring may be needed).
- Address distribution system integrity particularly biofilms and occurrence of *Psuedomonas*.

Dr. Nicolae Opopol addressed water management in Moldova. Water quality is seen as the number one issue for environmental health. The large percentage (90%) of the rural population continues to rely on Phreatic shallow ground waters. Improvement of the water quality at the individual well, home and for the small community is the challenge and pollution has increased due to the nature of water use and return flow/infiltration.

Pollution problems include:

- Bacteria (indicators of pathogens)
- Nitrogen
- Hardness

Dr. Livia-Daniel Galatchi, presented the water management challenges in Romania. Due to the multifunctionality and the hydrology/geography of the country there is uneven distribution of water. The Ministries goal is to minimize the use of the Danube river and enhance it's protection. In addition, multinational conventions exist which govern water flows or quality or both?. Treatment is inadequate and thus the key recommendations have included

- More sewage treatment
- Investigation into more secondary and tertiary treatment
- Address aging infrastructure

- Improve water storage

Dr. Galina Gopina presented the impact of the drought in Bulgaria . Climate was shown to play a significant role in the quality of life and impacted both the agricultural community and city dwellers as well as the ecosystem (forest fires). The Iskar reservoir supply was mixed with mountain water as the precipitation and river flows decreased 77 and 46%, respectively. Problems included bacterial contamination.

- Greater storage is now recommended
- Attention to greater treatment in times of drought.

Conclusions and needs:

1. Indicators are needed for monitoring the system from source to tap, including aesthetic changes, water quality indicators, suspicious activity, changes in water pressure and illness in the community.
2. Action plans for management of both accidental and intentional pollution with biologicals and chemicals should include a base line understanding of the vulnerabilities and baseline quality.
3. Triggers for action must be put in place: spill notification, rainfall, raw water turbidity, fecal indicators and public health indicators.
4. The physical/chemical/biological and geological nature of the water system under study must be considered. Site assessment is an important component of the risk/management framework.
5. Integration of inventory of risks to the watershed, along with climate prediction factors and the monitoring of the raw ambient water quality are critical.
6. Monitoring recovery after contamination events is essential, this will require that baseline data sets are available.
7. Climatic factors and meterological data continue to show a pattern associated with water quality impacts (during floods but even droughts) and are often associated with treatment and management failures. Thus meterological data, weather forecasting and climate prediction scenarios should be integrated in the development of any assessment and management strategy.
8. Emerging contaminants will need to be monitored.
9. Increased sewage treatment is needed to enhance pathogen, nutrient, emerging contaminant reductions and enhance possible wastewater recylcing

10. Attention to ground water quality is paramount.
11. Enhance environmental buffers and ecosystem services.
12. Education stays a vital skill to keep informed/ updated general population and specialists too on risks and their management. Bioethical approach of managerial interventions is needed.
13. The role of the pathogens should include the studies on fate (infectivity, survival and pathogenicity) of the pathogens in groundwater.
14. The ecology of infectious disease and population dynamics of the disease are important aspects of the processes and should be addressed.
15. Each microorganism has a specific survival time. Several groups will emerge: those that we can tie to an outbreak; those that are identified as emerging microorganisms and their significance as emerging pathogens will need to be addressed. The final group of microorganisms will be those identified and detected in water. Both opportunistic and pathogenic microorganisms should be categorized as well as their relative risk and capacity of pathogenicity.
16. Tourism and travel are now more common and extensive. Thus individuals may travel all over the world. The local population and their immunity does not reflect the risk to the visitors. Thus similar biological quality of waters globally is the goal.
17. Marine biotoxins will be of emerging interest for those communities using marine waters as a source of drinking water for desalination, as little is known about removal of many of these toxins via membranes. The health effects need to be better studied and the potential bio-transformations.
18. Molecular genetical methods are needed to prove the causative agents for use in molecular epidemiology in outbreaks and in intentional incidents using biological weapons as well as for detection of emerging microbial waterborne pathogens.
19. The biological agents serve roles directly as risk indicators, indicators of fecal pollution and as tools for quality improvements.

Recommendations:

1. It is recommended that such QRA frameworks be adopted for addressing water safety so that hazards and specific risks can be identified, quantified and prioritized. The risk assessment framework works well for chemical and biological agents, including inorganics, organics and microorganisms. This may be used in both the preventative mode and

well as in a responsive mode, however it must be kept in mind that the safety goals (acceptability of the risk) may be different under the various situations.

2. Use and Improvement of models are recommended including geospatial models. Models and data on transport and fate are critical to the development of the risk assessment. This must include the microbial contaminants of interest.

3. The use of new biological tracers/indicators are needed and recommended for defining transport and fate in groundwater as well as distribution systems (eg. resistance to chlorination/disinfection).

4. Use of multinational "Forums" for the coordination of scientific risk based models is recommended. This will enhance communications and harmonization on methods and tools that can be used.

5. More decision tools are needed which can take parameters used to define the QRA and translate into management strategies for prioritization.

6. Development of Water Safety Plans incorporating HACCP is recommended.

7. Create a database of updated information on educational issues related to management of intentional and accidental water pollution. Continuously updated academic/educational support is needed. Data base of information provided by/through an international network. Creating/using appropriate forms of education addressed to the general population and post-graduate continuous education as well as addressed to specialists.

8. It is recommended that an international network on early detection, reporting and warning for waterborne disease is created.

9. The development of a waterborne disease genetics program is recommended.

10. Decisional tree of responsibility and communications are recommended.

11. Early warning systems should be developed (systems in place for marine biotoxins could inform similar appropriate models for drinking water contamination).

12. The risk assessment be integrated and cover impacts on health and the environment and cover the *complete life cycle of the products*.

13. The benefits of chlorination/disinfection are irrefutable and thus it is recommended that in order to maintain microbiological water safety that any changes to these disinfection programes be fully evaluated.

14. Surveillance (water quality), maintenance (technological and engineered), interventions and response (emergency preparedness, including timely communications) are required for the distribution systems.