Björn Berg
Charles McClaugherty

Plant Litter

Decomposition, Humus Formation, Carbon Sequestration

Third Edition

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Preface to Third Edition

When starting our work on this book we intended to summarize and synthesize the new information that had developed in the past 20–30 years in the field of plant litter decomposition. It turned out, however, that the main part of more recent work was directed toward boreal and temperate forest systems and therefore, with a focus on these ecosystems we finally concluded a synthesis that has a similarity to a case study. Still, we hope that a deeper insight into the behavior of a limited number of litter species will be of value for a generalization and also for the identification of process systems that deviate from those presented here.

We have written the book focusing on the transfer from newly shed litter to recalcitrant humus, describing and explaining the system of chemical changes taking place in the process both on a mechanistic basis and on a more general and regional level, considering different climates and species.

As a synthesis, this book gives some new aspects on decomposition that to some may be controversial. Thus, the fact that we emphasize the dominant role of microorganisms in the process may be disturbing to many readers, as well as the strong emphasis we give to the fact that humus layers actually do grow over millennia and that at a considerable rate, and thus really sequester, e.g., C and N.

This book is based primarily on data and conclusions made from field studies. We have focused on undisturbed forest systems in an attempt to create a basic understanding and basic mechanisms for the decomposition and transformation processes. Its emphasis is on boreal systems for the obvious reason that there appeared to exist more data about these systems that could be synthesized. The information from temperate systems has rather supported and extended the conclusions, suggesting that the synthesis so far may be applicable to at least both types of systems.

In the topic of litter decomposition and transformations, we can not yet identify different schools of thought; it appears that this field of research has not yet developed far enough. We would rather consider different directions of the research work. Thus, some scientists have attempted to understand mechanisms for the degradation whereas several groups have searched for indices for prediction of long-term decomposition rates.

The synthesis that we present has clearly taken impression of the work by a smaller group of scientists and research groups that we want to mention. Thus, the papers emerging from the group around Dr. Marie-Madeleine Couteaux, CNRS, Montpellier has been important to us, like those from Prof. John Aber, University of New Hampshire, and Dr. Jerry Melillo, The Ecosystems Center, MBL, Woods Hole.

Many other persons have been helpful in the process of collecting and developing the information that makes up the backbone for this book. We want to thank all of them and hope they understand that all cannot be listed here.

New and valuable data have appeared from the large US project Long-Term Intersite Decomposition Experiment Team (LIDET) and from the Canadian Intersite Decomposition Experiment (CIDET). The new analytical methods using ^{13}C-NMR for determining organic compounds in decomposing litter, developed in Canada, Italy, and Japan have provided us with new insights and may change older theories about the process of litter decomposition.

For the first edition the support of the Brumbaugh Center for Environmental Science, University of Mount Union, Alliance, Ohio is also gratefully acknowledged. Good and substantial financial support from the BITÖK institute, University of Bayreuth, Germany and from the Commission of the European Union, through the CNTER project (QLK5-2001-00596) is acknowledged.

For the second and third editions we have used much of the data and the views on regionalization to different climates that have been developed by Prof. Vernon Meentemeyer, University of Georgia, Athens, have been extremely valuable. Likewise, the recent papers of Dr. Chunjiang Liu, School of Agriculture and Biology, Shanghai Jiao Tong University and Key Laboratory of Urban Agriculture (South), Ministry of Agriculture, Shanghai have contributed to the synthesis.

We have been allowed to use unpublished data and express our thanks to Drs. Cecilia Akselsson, Maj-Britt Johansson, Anna Hagen-Thorn, Per Gundersen and Åke Nilsson. We also want to thank Prof. Egbert Matzner, BITÖK, University of Bayreuth, Prof. Carl-Johan Westman, Department of Forest Ecology, University of Helsinki and Prof. Amalia Virzo De Santo, Dipartimento Biologia Strutturale e Funzionale, University of Naples Federico II, for their extensive support for this book.

Now when the third edition has been finished we want to express our appreciation of the valuable help and support we have received. Finally, before handing over this book to the reader we would like to once again thank each other for an excellent cooperation.

Uppsala and Helsinki, April 2013 Alliance

Charles McClaugherty

Björn Berg

Preface to Second Edition

When starting our work on this book we intended to summarize and synthesize the new information that had developed in the last 20-30 years in the field of plant litter decomposition. It turned out, however, that the main part of more recent work was directed towards boreal and temperate forest systems and therefore, with a focus on these ecosystems we finally concluded a synthesis that has a similarity to a case study. Still, we hope that a deeper insight into the behavior of a limited number of litter species will be of value for a generalization and also for the identification of process systems that deviate from those presented here.

We have written the book focusing on the transfer from newly shed litter to recalcitrant humus, describing and explaining the system of chemical changes taking place in the process both on a mechanistic basis and on a more general and regional level, considering different climates and species.

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This book is based primarily on data and conclusions made from field studies. We have focused on undisturbed forest systems in an attempt to create a basic understanding and basic mechanisms for the decomposition and transformation processes. Its emphasis is on boreal systems for the obvious reason that there appeared to exist more data about these systems that could be synthesized. The information from temperate systems has rather supported and extended the conclusions, suggesting that the synthesis so far may be applicable to at least both types of systems.

In the topic of litter decomposition and transformations, we can not yet identify different schools of thought; it appears that this field of research has not yet developed far enough. We would rather consider different directions of the research work. Thus, some scientists have attempted to understand mechanisms for the degradation whereas several groups have searched for indices for prediction of long-term decomposition rates.

The synthesis that we present has clearly taken impression of the work by a smaller group of scientists and research groups that we want to mention. Thus, the papers emerging from the group around Dr Marie-Madeleine Couteaux, CNRS, Montpellier has been important to us, like those from Prof John Aber, University of New Hampshire, and Dr Jerry Melillo, The Ecosystems Center, MBL, Woods Hole. Many other persons have been helpful in the process of collecting and developing the information that makes up the backbone for this book. We want to thank all of them and hope they understand that all cannot be listed here.

For the second edition we have used much of the data and the views on regionalization to different climates that have been developed by Prof Vernon Meentemeyer, University of Georgia, Athens, has been extremely valuable. We have been allowed to use unpublished data and express our thanks to Drs Cecilia Akselsson, Maj-Britt Johansson, Anna Hagen-Thorn, Per Gundersen and Åke Nilsson.

Now when the second edition has been finished we want to express our appreciation of the valuable help and support we have received. Thus, we want to thank Prof. Carl-Johan Westman, Department of Forest Ecology, University of Helsinki and Prof Amalia Virzo De Santo, Dipartimento Biologia Strutturale e Funzionale, University of Naples Federico II, for their extensive support for this book. The support of the Brumbaugh Center for Environmental Science, Mount Union College, Alliance, Ohio is also gratefully acknowledged. Substantial financial support for the first edition came from the Commission of the European Union, through the CNTER project (QLK5-2001-00596) and is acknowledged.

Finally, before handing over the book to the reader we would like once again to thank each other for an excellent cooperation.

Helsinki and Napoli, June 2007 — Björn Berg
Alliance — Charles McClaugherty

Contents

Chapter 1
Introduction

1.1 Overview of Plant Litter Decomposition

Decomposition and photosynthesis are processes that account for a huge majority of the biological carbon processing on planet Earth. Photosynthesis has been studied extensively at levels ranging from biochemical to ecological. Relatively speaking, photosynthesis is well understood. Its importance to the functioning of the biosphere, as well as its agronomic significance, is well established. Furthermore, photosynthesis occurs in above-ground tissues in organisms that are often large and esthetically pleasing.

Decomposition accounts for the transformation of nearly as much carbon as does photosynthesis. However, it occurs mainly on or below ground. As such, decomposition is largely out of sight. It is carried out primarily by bacteria and fungi and is sometimes associated with products that are unappealing. The biochemistry of decomposition is very irregular when compared to the biochemistry of photosynthesis. Thus, it should be no surprise that decomposition is the less well studied of the two major carbon-transforming processes on the planet. In the last two decades, the need to have a better understanding of decomposition has become apparent. Decomposition of organic matter is responsible for huge amounts of the carbon dioxide returned to the atmosphere. It is also responsible for the formation of humic substances that contribute to soil fertility as well as the long-term storage of carbon. Decomposition is closely tied to nutrient cycling and is essential for the regeneration of organically bound nutrients.

Decomposition is more difficult to define than photosynthesis. Broadly defined, decomposition includes physical, chemical, and biological mechanisms that transform organic matter into increasingly stable forms. This broad definition includes physical fragmentation by wet–dry, shrink–swell, hot–cold, and other cycles. Animals, wind, and even other plants can also cause fragmentation. Leaching and transport in water are another important physical mechanism. Chemical transformations include oxidation and condensation. Biological mechanisms involve ingestion and digestion, along with extracellular enzymatic activity. Much of decomposition is ultimately accomplished by aerobic

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metabolism. The process is far from linear, and many meta-stable products are created and accumulated during decomposition.

Scientists have long been familiar with negative exponential models. They describe the extinction of light intensity at increasing depths in a water column. They define the decline in radioactivity of a radioactive isotope over time. They have also been used to describe the loss of mass from decomposing organic matter in natural systems. As much as we would like Occam's razor to prevail, the simple linear decay function is not universally applicable to the decay of organic matter, though it often provides an excellent first approximation, especially during the early stages of decay. Equation 1.1 is the basic exponential decay with time (t) as a variable

$$X_t = X_0 e^{(-kt)} \tag{1.1}$$

Unfortunately, neither the total biomass nor the constituent nutrients of decaying organic matter follow this simple function well enough to make it predictive. As a result, decomposition studies have taken two basic tracks. In one track, scientists have relied on mathematical abstractions and a variety of models, both theoretical and empirical, to predict, or at least simulate, the decomposition process. In a second track, the intention has been to study decomposition experimentally in the field and in the laboratory, in an attempt to extract general principles of the process. Both approaches have merit, yet neither has been able to completely explain the complex process of decomposition.

Decomposition is so complex that it requires the attention of numerous scientific disciplines. Studies on litter decomposition and humus formation may encompass different branches of science and include, for example, chemistry, microbiology, climatology, geology, and systems ecology.

The objective of this book is to illustrate the importance of decomposition as a major ecological process and to review and summarize the current understanding of the decomposition processes in natural systems. We start with recently shed litter and follow the decomposition process until we may discuss carbon sequestration. We rely heavily on work that has been done in temperate and boreal forests, but we also refer to other ecosystems.

1.2 A Short Retrospective

In 1929, Tenney and Waksman postulated that decomposition rates of soil organic matter (SOM) are controlled by four distinct factors: (1) the chemical composition of the substrate; (2) a sufficient supply of nitrogen for the decomposer organisms; (3) the nature of the microorganisms involved; (4) environmental conditions, especially aeration, moisture supply, , and temperature. As a general statement concerning factors that control decay, this is still valid more than 80 years later.

During the intervening 80 years, we have begun to understand many of the details of decomposition. We have gained a deeper insight into the effects of substrate quality and environmental factors, both on a local scale and on a regional scale. Studies have begun to show us more about the implications of decomposition on nutrient cycling. We have learned something about the microbial enzymes involved in degrading complex organic substrates. Moreover, we have begun to think of decomposition as more than just the breakdown of organic matter, but also as the formation of stable humic substances.

In 1970s, several scientists reviewed the state of knowledge relating to plant litter decomposition. Singh and Gupta (1977) reviewed studies on plant litter decomposition with a focus on soil respiration. Schlesinger (1977) approached decomposition from the perspective of carbon balance and brought together a large body of literature that described carbon pools and fluxes in ecosystems of the world. His review emphasized the importance of long-term carbon storage in soils. At about the same time, Swift, Heal, and Anderson (1979) produced a book that reviewed what was then known about decomposition in terrestrial ecosystems.

Mindermann (1968) was among the first to challenge the idea of simple negative exponential kinetics. He proposed that as litter decomposes, the readily decomposable materials would disappear first, leaving the more recalcitrant substances behind. As a result, decay should occur at a decreasing rate, rather than at a constant rate. As we will see, even this approach is not entirely correct, but it is closer to reality than the simple, constant rate, loss model.

Nitrogen and lignin, often analyzed as acid unhydrolyzable residue (AUR), were soon recognized as major variables that influence the rate and pattern of decomposition (Fogel and Cromack 1977; Melillo et al. 1982). During the 1980s, numerous investigators focused on the role of these two compounds in regulating the decomposition process. These studies laid the foundation for our current understanding of the decay process and are described extensively in the subsequent chapters.

1.3 The Ecological Significance of Litter Decomposition and the Formation of Humus

At the biosphere level, an understanding of decomposition is important for two main reasons. First, significant amounts of carbon dioxide, methane, and nitrogen-based gases are released as products of decomposition. These so-called greenhouse gases are of great interest currently because of their roles in potential global climate change. Factors that increase the rate of decomposition could serve to increase the amounts of carbon-based gases in the atmosphere. Second, soils represent a major sink for carbon. To the extent that carbon is stored in soil as humus and related stable organic compounds, it is not being circulated through the atmosphere. Thus, an understanding of the factors influencing the amount of humus formed and the stability of that humus are also important in predicting global atmospheric carbon budgets (Schlesinger and Andrews 2000).

At the ecosystem level, decomposition is important for somewhat different reasons. Nutrient cycling is clearly related to decomposition. The availability of nutrients in a given soil is due in large part to the decay dynamics of the organic matter in that soil. In addition, the accumulation of organic matter in soil can greatly increase the cation exchange capacity and have positive impacts on the nutrient-holding capacity of that soil. Decomposition can influence the pH of soil; pH may be increased if plants pump basic cations up from the mineral soil to be released during the leaching and decay of litter. Soil pH can be lowered through the release of CO_2 and the formation of carbonic acid. Finally, during the initial stages of decay, nutrients are immobilized, taken out of the general circulation for a while, thereby temporarily reducing nutrient availability.

Another impact of decomposition is on diversity and stability of the ecological community. Entire food webs are based on decomposition. In fact, detrital food webs process more carbon and energy than do the better-known grazer food webs. Only a small amount of primary production is grazed by herbivores and passed to higher trophic levels. In contrast, all ecosystem production ultimately becomes detritus.

The ecological significance of decomposition and humus formation can also be viewed from the perspective of microbial ecology. The decomposition of the litter substrate can be divided into phases, in which different parts of the substrate give energy to different groups of the microflora. This process supports diversity in the microbial population by supplying a rich set of intermediate degradation products and serving as energy and nutrient sources for different microbial subpopulations.

Decomposition influences other soil processes. For example, part of the litter forms humus and organic acids which in part are responsible for weathering in the mineral soil, thus supporting the supply of plant nutrients. Humus may also act as a carbon source for microorganisms that subsequently produce acids and contribute to weathering. Nutrients are stored in humus. In practice, this creates a reserve of nutrients for plants that may be mobilized through a variety of mechanisms, such as fire or by stress signals from the trees to their mycorrhizae.

In addition to weathering, decomposition and humus formation are involved in storage and controlled release of nutrients to the plant and microbial communities, as well as the storage dynamics of carbon compounds including the sequestration of greenhouse gases. Further, the decomposition of litter and humus may also produce precursors for pathways other than the common one that leads to carbon dioxide. Well-known examples would be the fermentations that produce methane and the ones that produce organic acids.

1.4 Factors Influencing Decay and Humus Formation

Decomposition begins with complex plant detritus and produces carbon gases and humus. The process can be characterized by the rate of mass loss and the rates of nutrient immobilization and release. In addition, the chemical composition of

decaying litter changes during decay. These changes are not, in all cases, linearly associated with mass loss. Neither are the changes in composition the same for similar litter substrates decomposing under different environmental conditions. Thus, there is a complex and interacting set of factors that regulate mass loss, humus formation, nutrient dynamics, and patterns of change in chemical composition of decomposing plant litter.

Factors that influence either rates or patterns of decay will be examined: litter chemical composition, climate, nutrient availability, communities of soil organisms, and site-specific factors. The relationship between human activities and decomposition will be presented. Although there is an emphasis on boreal and temperate ecosystems reflecting the relatively large amount of data from these systems, we have attempted to create a basic image for decomposition and dynamics of plant litter/(SOM).

The chemical composition of litter differs among plant species and tissue type, thus creating unique environments both as regards the larger chemical components and as regards the nutrient composition. The importance of these substances in regulating decay varies among litter types, under different climates, and on different sites. These possibilities increase drastically when we consider a wider range of nutrients (e.g., N, P, S, K, Ca, Mg, Mn, Cd, Pb, Zn, and Cu). In addition, litter pH may have a regulating effect, directly on the microorganisms involved in the decomposition processes and indirectly on the solubility and thus availability of the individual nutrients. Nikolov and Helmisaarii (1992) listed 58 dominant tree species for boreal Eurasia and North America. Of these, 14 species dominate in Fennoscandia and Russia/Siberia and 15 in North America. We know the chemical and nutrient composition for only a few of these species, so it is difficult to generalize to entire forest communities.

1.5 Accumulation of Humus and Nutrients

The nature, rate, and amount of carbon storage vary greatly among ecosystems. We know, for example, that anaerobic environments conserve their carbon compounds in peat or humus, and we normally find more carbon stored there than in drier environments. Thus, anaerobicity may be one factor, but is it the dominant one? Could the chemical composition of the litter also have an influence? Even among aerobic systems with similar vegetation, we can find varying amounts of stored humus from almost bare mineral soil to layers nearly 150 cm thick. Therefore, there may be mechanisms for long-term humus accumulation that can explain the wide range of accumulated humus. Disturbances such as fire, harvesting for forestry or agriculture, and cultivation can clearly reduce SOM content. A natural question is as follows: What could such a mechanism be, is there just one or does a series of coincidences rule whether and to what extent humus will accumulate?

A humus layer of 150 cm accumulated over c. 3,000 years in a boreal environment (Wardle et al. 1997) means, on average, an annual accumulation of c. 17 g of humus m^{-2}. Such a powerful mechanism for storage of C could mean a long-term storage of 0.1–0.3 Pg (Petagram = 10^{15} g) $year^{-1}$, considering the whole boreal forest zone of 1–2 billion ha (UNECE/FAO 2000), which accounts for 10–20 % of the currently estimated 1–2 Pg unidentified sink for carbon (Woodwell et al. 1998; Houghton 2001).

There is often a rather resistant part of the litter remaining, a part that may be stored on a long-term basis (e.g., millennia) and be regarded as humus. This long-term storage encompasses both carbon and nutrients. For carbon, amounts of the magnitude of 50–108 kg of humus m^{-2} have been found in the form of organic layers (Berg et al. 1993c; Wardle et al. 1997). For nutrients such as N and P (see Chap. 11), amounts of 760 and 39 g m^{-2}, respectively, have been measured. A long-term storage in such amounts raises doubts about the concept of a steady state as suggested by a number of authors, such as Schulze et al. (1989).

Plant litter contains nutrients at differing concentrations and is thus a carrier of nutrients that are largely released when the organic matter is being decomposed. The release of nutrients may take place in different ways, depending on the type of litter. Foliar litters may leach nutrients with especially mobile ones such as K being leached to a high extent. Other nutrients may be partially leached, a release that may depend on their concentrations in litter. The major nutrients, such as N, P, and S, can be partially leached immediately at litter fall. This immediate leaching may be followed by an accumulation or a net uptake of nutrients to the litter with a later net release. The release of such structural nutrients is often in proportion to litter mass loss and thus regulated by the same factors that regulate the rate of litter mass loss. Normally, all nutrients are not released. Available studies indicate that some components, such as most heavy metals, are not released from litter, even in clean, unpolluted systems, but rather accumulate so that when the decomposition process becomes extremely slow, close to the humus stage, the remaining part has a rather high concentration of such nutrients.

The boreal forest has a multitude of different storage forms for carbon, most of which are types of dead organic matter. The dead organic matter exists in numerous different chemical compounds of which we will never know more than a fraction, but also on a large scale, as different niches in the ecosystem. On an even larger scale, we may distinguish between living forests with soil systems that are more or less aerobic and more or less anaerobic. Both soil system types would be expected to store carbon on a long-term basis unless disturbed by, for example, fire, ditching, or site preparation.

1.6 The Contents and Organization of the Book

This book brings together much of the current understanding of the decomposition process as it occurs in forested ecosystems, using examples primarily from boreal and temperate forests. The book begins with a presentation of decomposition as a

process (Chap. 2). Terminology related to decomposition is briefly introduced including litter, humus, mineralization, and immobilization (also see Glossary). The overall process of decomposition is reviewed from the input of fresh litter through the dynamics of microbial and physical decay to the formation of metastable humic substances. An examination of litter quality includes a presentation of the cellulose, hemicellulose and lignin structures and the enzymes attacking them. A simple conceptual model is introduced that illustrates the decomposition processes and identifiable functional steps. The model, which is used as an organizing principle, encompasses three stages of litter decomposition with contrasting functional properties. We also compare traditional analytical techniques for organic compounds with the now well established one using ^{13}C NMR. A short review to different analytical methods for lignin and AUR is given in Appendix III.

The book then moves to examine the biological agents of decay (Chap. 3). The most important groups of decomposer organisms are fungi and bacteria, which in boreal coniferous forests may be responsible for more than 95 % of the decomposition. Their importance in deciduous forests is somewhat less (Persson et al. 1980). Even in tropical forests and grassland communities where herbivores may consume larger proportions of net primary production, they are notably inefficient and microorganisms are still the major decomposers. This chapter, therefore, has an emphasis on the microflora. This chapter emphasizes functional roles of organisms rather than their taxonomy. The main groups of fungi and some bacterial genera will be mentioned but with an emphasis on function and activity.

With this biological background, the next two chapters (Chaps. 4 and 5) examine the importance of initial and changing chemical composition of decaying litters. The initial substrate for decomposition is newly shed litter. Its chemical composition determines both the composition of the microbial community and the course and pattern of the decomposition process. Both the organic and the nutrient compositions of litter vary with species and with climate and site properties. Generally, deciduous foliar litters are richer in nutrients than coniferous ones. Organic components are also highly variable; lignin/AUR concentration may vary from a few percent in some litters, up to about 50 % in some others.

As the decomposition process proceeds, chemical changes take place in the decomposing litter. For example, do concentrations of some nutrients and most heavy metals increase as decomposition proceeds. The concentration of the organic component lignin/AUR increases too, whereas the changes in concentrations of the main carbohydrates vary. Of the nutrients, we have given N and Mn special attention due to their roles in lignin degradation. A basic pattern of chemical changes is given as well as an overview of how such changes vary depending on the initial chemical composition.

In Chap. 6, the attention is shifted to the influence of changing litter quality on the decay processes. This chapter shows that the influences of selected litter components change dramatically during the process, sometimes even reversing the direction of the effect. For newly shed litter, differences in initial N, P, and S levels influence the rate of the decomposition process. In the later stage of decay, the increasing levels of AUR have been related negatively to litter mass-loss rates in

ways that interact with concentrations of N and Mn as well as with climate (Chap. 7). Finally, the decomposition process normally reaches a stage at which decomposition goes so slowly that the stage may be approximately described by an asymptote or a limit value. Factors that influence this limit value are reviewed and evaluated.

Decomposition occurs in a natural environment where climate (Chap. 7) and other site factors (Chap. 10) can have a profound influence on the decay dynamics. Climate is a powerful regulating factor for litter decomposition as shown on a larger scale using actual evapotranspiration (AET; Meentemeyer 1978) and will directly influence litter decomposition rate, especially that of the newly shed litter. This effect of climate will decrease as decomposition proceeds and concentrations of AUR increase. We will use the conceptual model introduced in Chap. 2 and developed in Chap. 6 to describe how the effects change with the phase of decomposition.

The other major environmental factors that influence decomposition are edaphic, soil texture, nutrient availability, and soil chemistry. For example, a site factor that may have an influence is the parent rock material. Granite parent material, being nutrient poor, gives a poor litter substrate, whereas one of limestone often increases the nutrient content of the litter. We have reviewed available data on this in Chap. 4. The texture of the soil (sand and clay content) influences nutrient mobility and hydrology, which can affect the decomposition rate both indirectly and directly, and in Sect. 11.5.1, we discuss this.

Some litter types, notably wood and roots, behave differently from foliage, and these substrates require presentation in a separate chapter (Chap. 8). Woody debris and roots may represent a large proportion of the total litter input into an ecosystem. The decay of these substrates is often very different from that of foliar litter, and the course of the decomposition process is directly dependent on whether the wood is attacked by white-rot or brown-rot fungi. Although much less data are available on these litter types than for foliar litter, it appears that the attack by white-rot or brown-rot fungi is an important factor for determining both the rate and course of decomposition and for the long-term accumulation of SOM.

As knowledge of decomposition has grown, scientists have created a number of models to describe or predict decay (Chap. 9). These models vary in intent and complexity. Simple mathematical models have been used (e.g., simple exponential ones) that can describe the process, including rates of decomposition, and which are in agreement with conceptual models. Four such models are discussed: single exponential model, double exponential model, and two asymptotic models. They are discussed and evaluated with regard to recent findings. Many ecosystem properties and processes influence decomposition pattern and some main models, and we discuss this in Chap. 10 as well as influence of litter nutrient levels on type of model.

The book concludes with two chapters (Chaps. 11 and 12) that focus on carbon sequestration rates. Chapter 11 reviews local case studies based on gravimetric determinations. This is a logical step before discussing the accumulation of organic matter on a regional basis which we do in Chap. 12. New data appearing in

recent years make it possible to present different approaches to calculate carbon sequestration in forest soils. We describe and compare these two approaches and validate them relative to independent studies on carbon sequestration. We also place these values in the context of other studies of carbon dynamics in forest soils.

Topics closely related to decomposition include SOM formation and carbon sequestration and efflux. A major rationale for studying decomposition is the strong link to carbon and nutrient cycling and storage. Large amounts of nutrients may be stored in the SOM of an ecosystem, both as integral components of the organic residues and as attached ions on the organic colloids. In addition, the role of humus in soil structure and function and the potential importance of forest soils for long-term carbon storage are discussed.

The terminology used in decomposition studies is sometimes confusing or even misleading. In order to make our text as clear as possible, we have provided a glossary that explains and defines terms used in this book. We have also provided an appendix (Appendix IV) that gives Latin names together with English names for all vascular plant species that we discuss. We have used the plant names as they were given in the original articles. As some species have different common names in American and European English, we have given both names. Further, considering the new, now well-established ^{13}C NMR analytical technique, we have included an appendix (Appendix III), giving some basics about different analytical techniques with the focus on lignin. Finally, Appendix II gives a summary on collected experiences as regards planning of field experiments in litter decomposition.

1.7 Motives for the Present Synthesis

We hope this book will help aim research efforts toward furthering our understanding of decomposition. During the past several decades, numerous investigators have studied many aspects of the decomposition process. At the same time, both scientists and the public have become concerned about the increasing concentrations of carbon gases in the atmosphere and the implications for global climate change. As a result, we felt the need to compile existing recent information on mainly boreal and temperate forest litter and humus, with the aim of giving a new basis for understanding what regulates the buildup and stability of humus. Much of the book focuses on the processes and controls of the early stages of decay, but these early stages influence the long-term carbon dynamics of each ecosystem. A number of basic questions are raised, including

- Is there a long-term buildup of humus?
- Do forest systems exist with very high or very low humus buildup rates?
- Can we influence the humus buildup rate?
- Are there any large-scale threats to the natural course of the humus buildup process?

This book is based primarily on data and conclusions made from field studies. We have focused on undisturbed forest systems in an attempt to create a basic understanding and basic mechanisms for the decomposition and transformation processes. The book focuses on boreal systems for the obvious reason that there were more data about these systems available for analysis. Of course, we have used information from temperate systems when applicable and there have not been any conflicting conclusions, suggesting that the synthesis so far may be applicable to both kinds of systems.

When it comes to the topic of litter decomposition, we have not identified different schools of thought, as it appears that this field has not yet developed far enough. We would rather consider different directions of the research work. Thus, some scientists have attempted to understand mechanisms for the degradation, whereas several groups have searched for indices for prediction of long-term decomposition rates.

1.8 New Developments Included in the Third Edition

Since the first edition was written, the interest in carbon sequestration and the release of carbon gases with relevance for global climate change have both increased. Additional studies on the factors that regulate the decomposition process have allowed us to develop a number of sections.

The importance of manganese as a factor that influences lignin decay has become more obvious. In Chap. 2, we develop a new section on the role of Mn and also expand our conceptual model to include a role for it in the decomposition of plant litter. It appears that Mn may play a role for carbon sequestration, possibly related to litter species/genus. New findings about the relationships between the contents of N and lignin/AUR of litter and N content versus climatic variables on a global scale have been added to Chap. 4. This allows us to extend to a nearly global scale some of the observations described in the first and second editions. We have developed and extended the discussion on models as well as an analysis of factors that may influence decomposition patterns (Chaps. 9 and 10). In Chap. 11, we have added a discussion on local carbon accumulation in forest floors relative to tree species and soil properties of the site. Finally, Chap. 12 is updated and demonstrates the potential for carbon accumulation in forest soils using two different case studies from Sweden.

Chapter 2
Decomposition as a Process: Some Main Features

2.1 Litter Decomposition: A Set of Different Processes Including Synthesis

Decomposition of plant litter involves a complex set of processes including chemical, physical, and biological agents acting upon a wide variety of organic substrates that are themselves constantly changing. Due to the immense diversity of possible factors and interactions, decomposition in a natural setting can be described in general terms only. In spite of this complexity, several major processes are involved and general trends can be outlined. However, new promising research has created new views that in part may seem contradictory to the traditional one.

Litter is in its simplest state when shed by the plant. From this initial state, litter composition changes, with some litter components disappearing rapidly, some slowly and some begin to disappear only after a time delay. Perhaps non-intuitive, but very significant, is the fact that some substances, particularly nutrients, are imported into the decomposing substrate, and new organic compounds are synthesized during decomposition. Due to the heterogeneity in both litter composition and factors influencing decay, decomposition of litter is far more complex than decay of, for example, a radioactive isotope.

A complication in the analysis and understanding of these processes has been the chemical analytical methods for the main organic components. Gravimetric methods for lignin determination have included not only native lignin but newly formed products, to some extent similar to lignin, chitin from fungi as well as ash, unless that has been analyzed. A recent development using ^{13}C-NMR has allowed us a new view on plant litter chemistry during decomposition and given more detailed as well as more specific, and correct information. Further, it allows us to draw new conclusions about the main process, giving us a new starting point for our thinking. Some recent work is that of for example Preston et al. (1997, 2009b), Ono et al. (2009, 2011), and De Marco et al. (2012).

The bulk of plant litter consists of varying amounts of several major classes of organic compounds. The relative proportions of these compounds vary with plant part (for example, leaves, stems, roots, and bark) and among species (see Chap. 4).

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7_2,

These major groups of compounds can be classified according to their molecular size, their solubility, and their primary constituents. Some materials, notably sugars, low molecular weight phenolics, and some nutrients, are readily lost from litter through dissolution and leaching combined with the action of rapidly growing opportunistic microorganisms. Larger macromolecules, including cellulose, hemicelluloses, and lignin, are degraded more slowly. During decay, condensation of phenolics and lignin-degradation products, combined with the import of nutrients, results in the net accumulation of newly formed substances. The relative magnitudes of the main flows (Fig. 2.1) are thus different not only among litter types and species but are influenced by litter chemical composition (see Chap. 6).

We regard 'litter mass loss' or 'decomposition' as the sum of CO_2 release and leaching of compounds, including both C compounds and nutrients. Leaching is simply the loss of nutrients and incompletely decomposed organic compounds transported out by water from the remains of decomposing litter (see Glossary).

The interpretation of mass-loss data during the initial stages of decay may be influenced by a high leaching rate of water-soluble material that is not physiologically modified by microorganisms until after leaving the litter (McClaugherty 1983). These dissolved materials may be lost from litter to subsequently sequestered by humus or clay particles. In such cases, the materials are lost from a particular substrate but are retained in the soil ecosystem.

Under aerobic conditions, microbial decomposition results in a release of CO_2 that leaves the system. Under more anaerobic conditions, such as a temporarily waterlogged organic matter layer, anaerobic decomposers may produce organic acids instead of CO_2. This may also happen with aerobic decomposers that suffer

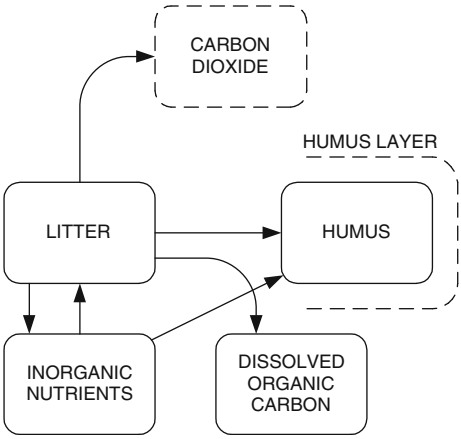

Fig. 2.1 Generalized pathways for transformation of litter to humus and inorganic C. When the litter is shed and its decomposition has started, the microorganisms begin forming carbon dioxide, and soluble compounds that are initially present may be leached out. Newly formed compounds that are stable but water-soluble are also leached out (dissolved organic carbon—*DOC*), and long-term stable remains, including newly formed products form humus

from a lack of oxygen. For example, acetic acid may be released instead of CO_2 and either be decomposed outside the cell or be stored and fulfill another role (see Sect. 10.3.3).

In some cases, the rate of decomposition approaches zero. In 1974, Howard and Howard estimated limit values for the decomposition of some species of leaf litters that were incubated in an animal-free environment. Using litter decomposition data from nutrient-poor forest systems, Berg and Ekbohm (1991) also estimated such limit values, indicating a stage at which the decomposition rate nears zero (Fig. 2.2).

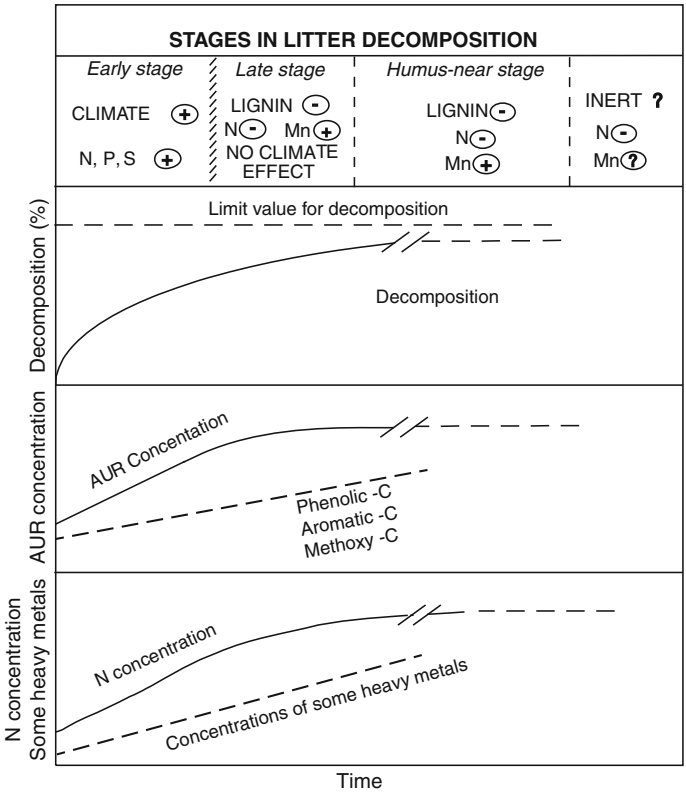

Fig. 2.2 As decomposition proceeds and the accumulated mass loss increases, the rate may decrease and a limit value for decomposition is reached which often is less than 100 % mass loss. Please note - that the rate at the limit value is calculated to be close to zero does not imply that the formed humus is biologically undegradable. The limit value rather identifies a litter fraction that may decompose very slowly. With decomposition, some main chemical changes take place. Thus, concentration of nitrogen increases, which appears to be general over most litter species. The concentration of AUR (gravimetric lignin) increases, in part possibly due to new products registered as gravimetric lignin. Also, concentration of some specific lignin-related bonds increases (cf Appendix III). Further, some heavy metals (e.g., Fe, Al, Cu, Pb) generally appear to increase in concentration

This chapter describes the principal microbial processes associated with litter decomposition that result in mass loss or CO_2 release. We present basic principles about the microbial degradation of the main components of litter such as cellulose, different hemicelluloses, and lignin/AUR using information mainly from Scots pine needle litter and the genus *Pinus*. We thus focus on litter from Scots pine and pine spp. to develop an existing conceptual model. Two main analytical approaches are being used, an earlier, using gravimetric and gas chromatographic determinations and a new, using ^{13}C-NMR, resulting in somewhat different pictures of the process, and we cannot exclude that we in part may need to reevaluate existing decomposition models that are based on older analytical techniques (below).

We also comment on Acid Unhydrolyzable Residue (AUR, 'gravimetric lignin'), degradation of native lignin and synthesis of new products, which increase in concentration and in later stages become more abundant in the residue. These are probably synthesized in the early stages of decomposition.

The process of litter mass loss is described in its main, general features, thus what appears to be patterns in common for the so far studied foliar litter species with focus on *Pinus* spp. We may call these basic and general subprocesses in decomposition. Details in decomposition are different, not only as regards methods but also on the level of species. In the later chapters, we will analyze more in-depth process patterns for different species/genera as far as information exists. We organize our description using a conceptual model that separates the decomposition process into different phases. As litter passes through these phases, the factors that regulate the decay process change. The model connects the developmental processes that occur, beginning with newly formed litter and continuing to the formation of humus. In this chapter, we have included a section discussing the synthesis of new products and their role in the existing models as well as in a new hypothetical model. Differences in the importance of substrate properties (for example, the influence of Mn and N) as well as the possible roles of native lignin and new compounds as the decay process unfolds are emphasized. Recent development has allowed us to revise and develop a former model (Fig. 2.3) into a somewhat more detailed one. We develop this discussion in Chap. 6 introducing studies on specific litter species and genera.

2.2 Definition of Litter Decomposition

Litter decomposition may in part be defined by the method used to study it. A very common method is the litter bag, used for incubations in the field or in laboratory microcosms. Another variety of direct incubation is tethered litter. A further one is the mass of 1.000 m of litter, specific for needle litter (Kurz et al. 2005). With these kinds of measurements, decomposition is measured as loss of mass and studies normally do not distinguish between what is respired as carbon dioxide and what is leached out of the litter or lost due to fragmentation, unless those processes

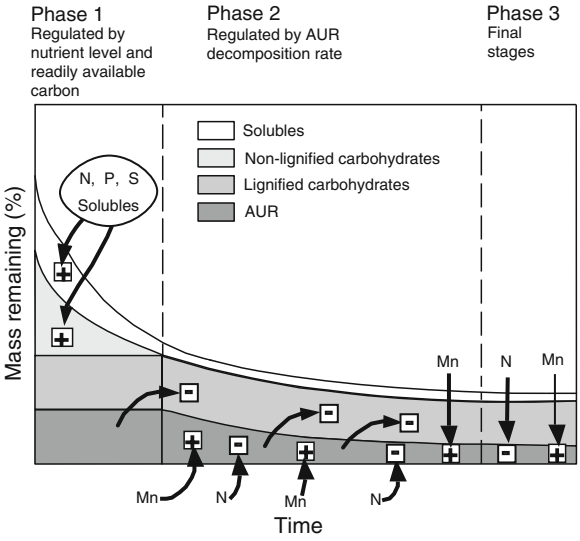

Fig. 2.3 Some main stages in decomposition of pine needle litter. The decomposition of water-soluble substances and unshielded cellulose/hemicellulose is stimulated by high levels of the major nutrients (early stage—phase 1). When degradable solubles and unshielded holocellulose are decomposed, only lignin-encrusted holocellulose and lignin remain as well as newly formed stable products. The early phase has been observed to last up to about 25–30 % accumulated mass loss in Scots pine needle litter. In the late stage (phase 2), the degradation of lignin (often measured as AUR) rules the litter decomposition rate. Nitrogen hampers the degradation of lignin, and higher N concentrations suppress the decomposition whereas higher Mn concentrations appear to have a stimulating effect on the degradation of lignin. Finally, in the humus-near stage (phase 3), the accumulated mass loss reaches its limit value at which the litter decomposition rate is close to zero. Figure modified from Berg and Matzner (1997)

are investigated separately. In terms of mass, net release of mobile nutrients such as K and Mn is also part of the loss. The ingrowth of microbial biomass and the transport of nutrients into the litter result in the movement of mass into the litter that was not there originally. Thus, what is often called 'litter mass loss' or 'decomposition' is a *net mass loss* although the ingrowth of mycelium normally is negligible from the point of view of mass. As we will see later, the in situ incubation of intact litter is, from several points of view, preferred to laboratory incubation methods, but it still to some extent may be compared with laboratory studies.

When litter decomposition is measured as respiration, only part of the mass-loss process is quantified. No specific term has been suggested for this more specific process, but terms such as 'release of CO_2,' 'C-mineralization,' and 'litter respiration' are used. We will use 'litter CO_2 release' (see Glossary in Appendix I) in this book. Thus, the two processes of 'litter CO_2 release' and 'leaching' together should correspond to 'decomposition' as the term is used today (Fig. 2.1), although loss to fragmentation could influence mass-loss measurements.

Distinguishing litter-based respiration from other respiration in the field is difficult. Methods to separate other sources of respiration, for example, root and faunal respiration which is not directly associated with litter decomposition need further development although some first steps have been taken (cf. Högberg et al. 2001).

In boreal forest systems, microorganisms carry out more than 95 % of the litter decomposition (Persson et al. 1980). Before litter falls, some microorganisms are present on the litter. Most of these are not involved in decomposition unless they are pathogens. After litter fall, fungi are generally the first invaders, penetrating the leaf through openings and thus invading the fresh substrate. The less mobile bacteria come later and there is also a succession of fungal species with different physiological properties depending on the decomposition stage and thus the substrate quality of the litter.

2.3 Ash Dynamics

The ash content of litter can vary between litter types and over time. Ash content in, for example, needle litter of Scots pine and of other pine species is initially low, often around 1 %, and in the course of decomposition, it may increase to 2 %. In a study, ash contents in sugar maple leaf litter were initially 11.3 % of dry matter, increasing to 19.5 % after 1 year of decay, and to 26.6 % after 10 years of decay (McClaugherty unpublished). Ash is normally defined as the fraction of matter that stays after heating a sample to, for example, 400 °C for 2–3 h, which means that all organic C and N disappears and components that are neither burnable nor volatile remain.

The concept ash is complex and ash may include, for example, silicates and nutrients such as Ca, Mg, K, and P. It may also include particles such as clay that have entered the litter during incubation. If not considered, high ash contents could affect the calculation of the percentage of mass loss, and concentration of N and other substances relative to that of less ash-rich litter types. Mass-loss and litter-nutrient contents should thus be related to the litter organic matter, rather than to the whole litter, something that is done inconsistently.

2.4 Degradation of the Main Groups of Organic Compounds in Litter

Although there are differences among litter species and genera as regards, chemical composition and arrangements of compounds in fibers there appear to be some general patterns that may be organized, and at present, we may see one main pattern for pine spp. as regards mass-loss and rate-regulating factors. Organic compounds may be degraded in a sequence, which possibly may differ among

litter species and we have organized the sections below accordingly. However, we have made separate presentations for proximate analysis and those based on ^{13}C-NMR (see also Appendix III).

2.4.1 Degradation and Leaching of Soluble Organic Substances

Foliar litter may contain considerable levels of soluble substances. For example, concentrations of water-soluble substances between a few percentage in lodgepole pine needle litter and c. 30 % in gray alder leaves have been recorded (see Chap. 4). Part of these substances may be leached out of the litter (Bogatyrev et al. 1983; McClaugherty 1983) and part may be degraded in the litter structure. So far we have seen four principal groups of soluble organic material in litter: sugars, phenolics, hydrocarbons, and glycerides. The soluble sugars are predominantly mono- and oligosaccharides that were involved in metabolic processes of the plant. The soluble phenolics are low molecular weight compounds that serve either as defensive agents against herbivory, lignin precursors, or waste products; hydrolyzable tannins are a common example of soluble phenolics. Phenolics are highly variable in their solubility and many have a tendency to condense into less soluble forms or to react with larger molecules (Preston et al. 2009a,b). A nutrient like N may be found in soluble and insoluble organic compounds and may be insolubly bound into organic complexes such as condensed phenolics (Fig. 2.4).

Few attempts have been made to follow the degradation of simple soluble components in litter and it should be pointed out that most studies describe net disappearance only. The soluble fraction is challenging to study, due to the complexities of tracing the formation of new solubles during decomposition and the disappearance of the same solubles due to leaching or metabolism. For example, glucose, which is present initially in newly shed litter, is also produced from decomposing remains of starch and from cellulose and is thus found even in

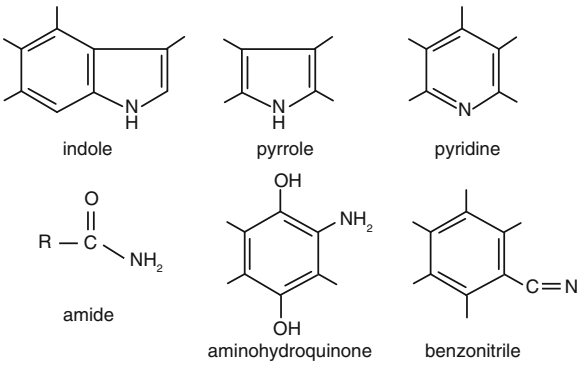

Fig. 2.4 Products detected by ^{15}N-NMR after reaction of ^{15}N-labeled ammonium hydroxide with humic material after oxidative ammonolysis of lignin model compounds. Figure from Knicker (2004)

Table 2.1 The time for onset of net mass loss of different organic chemical components and their relative degradation rates in decomposing Scots pine needle litter

	AUR	Cellulose	Mannans	Xylans	Galactans	Arabinans
Onset (days)	726	376	376	545	Immediate	Immediate
Rate (% day^{-1}) (0–726 days)	–	0.1041	0.0647	0.1077	0.0633	0.1461
Rate (% day^{-1}) (>726 days)	0.0418	0.0393	0.0526	0.0461	0.0375	0.0449

The rates given refer to two stages of decomposition, namely the early stage when the unshielded polymer carbohydrate components and solubles are degraded independently of AUR degradation and the late stage when the degradation of carbohydrate components is regulated by the degradation of AUR, and all components have similar rates (cf. Fig. 2.5). Data from Berg et al. (1982a)

the later stages of decomposition. The same applies to the simple sugars of hemicelluloses. Also several phenolic substances are found in newly shed litter, but are also produced during the degradation of both native lignin and AUR.

Berg et al. (1982a) found that compounds such as simple sugars, for example, glucose and fructose, or ones related to simple sugars such as glycosides and pinitol, were also degraded very early and at a high rate. Also groups of triglycerides and hydrocarbons disappeared quickly whereas fatty acids and diterpene acids remained.

2.4.2 Degradation of Non-Lignified Organic Substances

The ingrowth of microorganisms, mainly fungi, into the litter, may begin prior to litter fall, but the ingrowth of decomposers takes place when the litter has reached the ground. The more fast-growing microorganisms start invading the litter, with part of the litter C becoming microbial biomass and part CO_2. Although the microorganisms degrading the polymer carbohydrates and lignin may be partly the same, the physiology of the degradation of celluloses and lignin is different as are the induced enzyme systems, as previously described. It would therefore be reasonable to use this physiological background for a definition of different steps in the decomposition process, based on substrate and nutrient availability. Raised nutrient levels, in particular N, P, and S, that are normally the main limiting nutrients for microbial growth, stimulate microbial degradation of cellulose, hemicelluloses, and many solubles.

The degradation of solubles and the early degradation of hemicelluloses and cellulose are rather rapid processes, and the measured early-stage rates in a field experiment were at least twice as high as in the late stage. The relative degradation rates of the polymer carbohydrates are relatively high and range from 0.063 to 0.146 % day^{-1} (Table 2.1). In the late stage, the rate of decomposition of the same components can range between 0.038 and 0.053 % day^{-1}. The higher rate of disappearance of arabinan may be due to this hemicellulose being more easily

hydrolyzed and/or less protected. Thus, the cellulose and hemicelluloses were degraded rather quickly until the unshielded portions were consumed. Investigations of the changing patterns of enzyme activities in decomposing litter also support this division in phases (Fig. 2.2). The cellulolytic enzymes appear relatively early, reach a maximum, and decrease before peroxidase (part of the lignolytic system) appears.

The majority of studies on litter decomposition present results from the stage when the litter is recently shed, where normally positive relationships are seen between litter concentrations of N, P, or S and factors such as the mass-loss rate or litter CO_2 release (Taylor et al. 1989; Berg et al. 1997). Also, climatic factors have a strong influence on the turnover rate in newly shed litter (Jansson and Berg 1985; Berg et al. 1993a). For fresh litter with only lignified tissue, this phase should not really be distinguishable.

The simplified but incorrect picture is that climate regulates the rate of decay in early stages on a regional scale and substrate quality on a local one (Chap. 7). This picture holds in a few cases but is far from general. We discuss the basic model with this reservation, while recognizing that local climate and nutrient availability appear to dominate the early stage of decomposition.

2.4.3 A Pattern of Degradation of the Main Organic Compounds in Pine Needle Litter

Some general and common patterns. It appears today that although there are differences among litter species as regards decomposition patterns, there are some main common features, which may be best described using a conceptual model (Fig. 2.2; see also Chap. 6) and we give some main points below. We start with some observations and groups of components that are not affected by the two analytical approaches and continue with these in separate sections.

Decomposition often follows a sequential pattern with different classes of organic compounds dominating the decay process as it proceeds and it appears that this may be related not only to the relative composition of compounds such as cellulose and lignin but also to the synthesis of new compounds as the decomposition process proceeds. Further, it appears that we may be able to describe models, specific for litter genera or groups of genera and species. Such differences among models may be due to a high variability not only in initial chemical composition but also in environment.

The degradation pattern probably is related to the arrangement of the components in the fiber (Fig. 4.2). Microorganisms may first attack and degrade those carbohydrates that are located on the more available and exposed outer structures. Whether this is observed or not may be related to intensity in sampling and analysis/analytical approach.

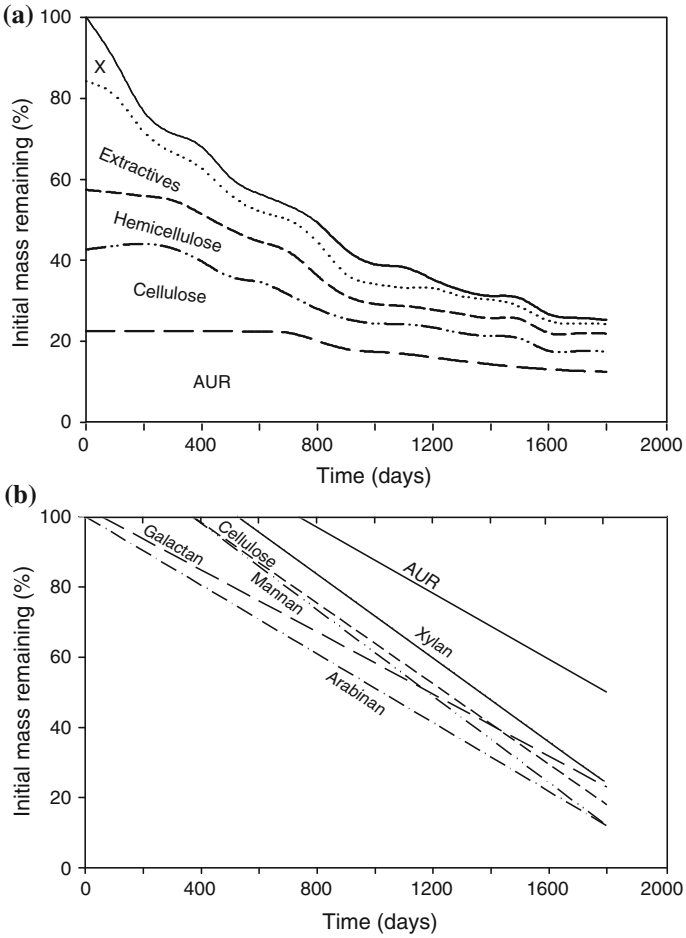

Fig. 2.5 The disappearance of some main organic components from decomposing needle litter. **a** Remaining amounts in decomposing Scots pine needle litter. **b** Onset of decomposition of the different polymer carbohydrates and AUR, showing the different rates of decomposition in the early and the late phases. Decomposition rates are given in Table 2.1. Data from Berg et al. (1982a)

A practical consequence of this is that after onset of decomposition, the degradation of different components may start at different times (Fig. 2.5). Further, the relative degradation rates of the different components may be different at least initially.

Some chemical changes that may be in common for foliar litter over species/genera. As decomposition proceeds, the mass-loss rate often decreases and the accumulated mass loss approaches a limit value, often less than 100 %. With several mass-loss determinations over time, such limit values may be determined with precision (Fig. 2.2; see Chap. 9).

A general phenomenon is that litter N concentration increases, often even linearly to accumulated mass loss (see Sects. 5.3.1, 5.4.2) both for litter with low initial concentrations, for example, 0.3 % as well as for those with higher initial levels, even 3 %. We may expect that N is in the form of microbial biomass, proteins, nucleic acids, and to a certain extent in newly formed compounds (Thorn and Mikita 1992).

Several heavy metals appear generally to increase in concentration (e.g., Fe, Al, Pb, Cu; see Sect. 5.3). In all decomposition studies we have found concentrations of Pb and Cu increase with accumulated litter mass loss. These patterns have been developed for litter in mainly boreal and temperate regions.

AUR. Analyses of AUR ('gravimetric lignin') so far have given one main pattern (Fig. 2.2), namely an increase in concentration. Recent results using ^{13}C-NMR technique have provided new information on the behavior of true lignin, which may resolve and develop the pattern created by AUR. We present available data followed by an attempt to synthesize the information.

2.4.4 Pattern for Main Organic Compounds Based on AUR: Gravimetric Analyses of Lignin

The conceptual 3-stage model (Fig. 2.3) illustrates a typical pattern. When a net loss of AUR begins, there may be little or no easily available carbohydrate and the microbial community must change to one that degrades the AUR complex (see Glossary). The net loss of AUR appears to start after the other groups of compounds have started to degrade. In our example (Fig. 2.5; Table 2.1), the rate of net loss of AUR from the start of year two until the end of year five was about 0.04 % day^{-1}. When we compare to the degradation rates of the carbohydrates during the same period, they were similar in magnitude to that of AUR. This suggests that once the AUR degradation has started, these components are degraded at the same rate because they are so well mixed in the fiber structure that they cannot be degraded separately. Newly formed recalcitrant products may support this pattern.

It thus appears that we may see at least two different groups of carbohydrates: those for which degradation starts immediately after litter fall, namely hemicelluloses dominated by arabinans and galactans; sometimes remaining starch may be included in this group; the second made up of mannans, cellulose, and xylan for which degradation starts later. This could mean that the second group of components is less available than those in the first group as a result of being more dependent on AUR mass loss. So far, there is just one reported detailed pattern (Scots pine) and we cannot exclude a different order or pattern at least for genera other than pine.

Using AUR (sulfuric-acid lignin) and gas chromatography, it was possible to see that onset of decomposition, and the degradation of different components may start at different times (Fig. 2.5). Further, the relative degradation rates of the

different components are different at least initially (Table 2.1). Part of this observation may change using the ^{13}C-NMR approach.

AUR (*gravimetric lignin*) increases in concentration as decomposition proceeds. This is a consequence of its late start and the preferred decomposition of other compounds. The AUR may include some newly synthesized products. We may note that the concept AUR is based on different groups of compounds, namely native lignin, cutin, suberin, waxes as well as recombination products formed during the decomposition process (e.g., Preston et al. 2009a).

2.4.5 ^{13}C-NMR Analysis Applied onto Decomposing Foliar Litter

Recent publications using ^{13}C-NMR have given an alternative analytical approach to apply on decomposing litter. This approach may be used to describe chemical composition and to quantify the disappearance of chemical components in decomposing litter. Some recent work, for example, Preston et al. (1997, 2009a, b), Ono et al. (2009, 2011) and De Marco et al. (2012) have followed decomposing litter and analyzed for changes in chemical composition as well as disappearance of specific bonds (Fig. 2.6). A difference to traditional analytical approaches is that the ^{13}C-NMR does not identify specific molecules such as glucose, arabinose, or native lignin but rather types of chemical bonds, specifically C bonds. To identify a specific compound, we thus may need to identify at least one and more likely several specific bonds belonging to a given compound (Appendix III). Thus, we will obtain information on concentration or amount of, for example, the O–C–O (*Di-O-alkyl-C*) bonds or the O–C (*O-alkyl-C*) bond typical for carbohydrates, which means that cellulose and some hemicelluloses give a common peak or signal (Preston et al. 2009b).

A certain terminology has developed relating to the compounds of which the bonds are part. Thus, the term *O-alkyl-C* mainly encompasses carbohydrate carbon, namely cellulose and hemicelluloses, but it also gives side chains of lignin (those going from carbon 1; see Fig. AIII.2b). At the present development stage, the change in concentration or decomposition of a chemical compound is given as concentration or amount of a certain C-bond. A bond is identified as response in a certain frequency interval (Fig. AIII.3; cf Table AIII.1) and we may expect such responses to be complex. For example, bonds in native lignin molecules may respond to different areas of the spectra (*aromatic-C, phenolic-C, methoxy-C, and alkyl-C*; cf Table AIII.3).

Alkyl-C. Also called aliphatic-C. This frequency interval indicates long chains with $–CH_2–$ units. Further, a side chain, in hemicellulose, namely an acetate group belongs here as well as C in side chains of lignin.

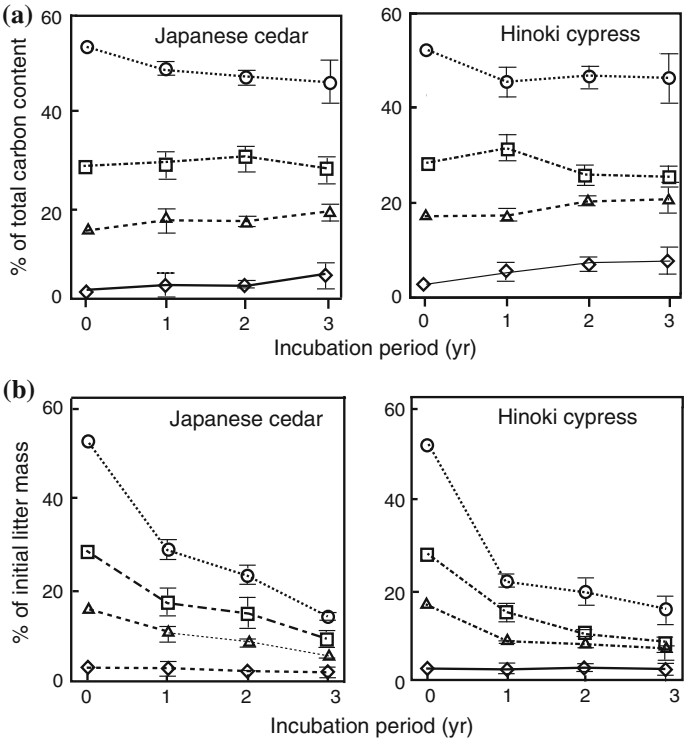

Fig. 2.6 Decomposing needle litter of Japanese cedar and Hinoki cypress investigated using ^{13}C-NMR, litter sampled over time. **a** Concentrations of some C bonds. **b** Remaining amount of C bonds as related to remaining carbon. (◇) carbonyl-C, (Δ) aromatic-C, (◯), O-alkyl-C, (□) alkyl-C. From Ono et al. (2011)

O-alkyl-C mainly encompasses carbohydrate carbon, namely in cellulose and hemicelluloses, but also side chains of lignin (those going from carbon 3, Appendix III). Further, some signals from tannins come in this interval.

Di-O-alkyl-C mainly encompasses cellulose plus hemicelluloses, thus carbohydrate carbon but shows no difference between the different carbohydrates.

Methoxy-C shows the methoxyl carbon in lignin (cf Fig. 3.3; Appendix III, Fig. AIII.2a). This frequency interval also includes the alkyl carbon bound to N in proteins.

Aromatic-C. Also called Aryl-C. The intensity in this interval (112–140 ppm) comes from the aromatic carbon in both lignin and condensed tannins. It may also show the guaiacyl group of lignin.

Phenolic-C. The intensity in this interval comes from phenolic-C (140–165 ppm) in both lignin and condensed tannins. It may also show the syringyl group of lignin.

Carboxyl-C. This region includes carboxylic acids, amides, and esters.

The ratio alkyl-C/O-alkyl-C is sometimes used as an index for degradation of decomposition and is increasing with accumulated litter mass loss. Some authors call it 'humification.'

An investigation by Ono et al. (2011) encompassing Japanese cedar and Hinoki cypress gives concentrations and amounts of 4 types of bonds (Fig. 2.6). A heavy decrease in amount of O-alkyl-C may mean a fast decomposition of cellulose and hexose-based hemicelluloses (Fig. 2.6b). Some signals from tannin may be part of the loss. We may see that also the concentration decreases (Fig. 2.6a). A less fast decrease in aliphatic-C (alkyl-C) may mean a loss of mainly fatty acids, but may also include a side chain in lignin. We may see a decrease in amount of aromatic-C from the start, which indicates that aromatic structures are degraded. This may mean tannins as well as lignin. Tannins are more readily degraded than lignin and may be degraded from the start of the incubation. Further, they do not have the methoxy group (methoxy-C), which makes them possible to distinguish from lignin.

2.5 Factors Regulating Degradation of Lignin/AUR

2.5.1 Potential Effects and Possible Interactions on Lignin/AUR Degradation

Some nutrients have been found to influence the degradation and dynamics of lignin and AUR. We may apply findings from fungal and bacterial physiology as well as from laboratory studies and we discuss a few such ones below. The relationships we discuss on the level of litter decomposition are ones that we have applied and confirmed in the sense of significant relationships as far as data allow. As such we may rather consider them as theories, as an investigated specific relationship between, for example, litter mass loss and a nutrient does not automatically exclude influences of other ones. Still, the relationships we forward in this chapter for mainly Scots pine needle litter have been confirmed in that sense. As we will discuss later, influences like those from Mn and N may have opposite effects (e.g., Fig. 2.2) and interact. However, what is possible today is just to present and comment on the potential effects of single nutrients. We may remember that if an effect is shown for native lignin, it does not automatically apply to the more crude AUR fraction, which is based on several components. As effects on AUR/lignin degradation have been related to both nutrients, we discuss both of them here, well aware of that the effect is potential and may vary among litter species. What we may rely on for support is the shown effects on the AUR fraction. Interaction effects between Mn and N may need to be confirmed in future studies. We have related effects of both nutrients to mass loss for Scots pine litter and to that of AUR.

2.5.2 *Effects of Litter Mn Concentration on Lignin/AUR Degradation and Litter Mass Loss*

The discovery of the enzyme manganese peroxidase (MnP) was important for the science of litter decomposition. The enzyme appears to be produced by the majority of all wood-degrading basidiomycetes which cause white-rot, as well as by various soil-litter-colonizing saprotrophic fungi. Among the lignolytic enzymes, MnP is probably the most widely spread peroxidase produced by these fungi (Hofrichter 2002).

Manganese is essential for the activity of MnP, and enhances its production (Perez and Jeffries 1992). Mn is also involved in the regulation of other lignolytic enzymes, including laccase (Archibald and Roy 1992) and lignin peroxidase (Perez and Jeffries 1992). In a large number of laboratory studies, it has been shown that this nutrient is essential for formation and activity of lignin-degrading enzymes and thus for degradation of lignin.

Manganese peroxidase is a glycosylated heme protein, which is secreted by the fungi into their environment. It oxidizes Mn^{2+} ions, which are found in plant residues, wood and soil, to highly reactive Mn^{3+} ions. These ions in turn are stabilized by organic acids also produced by these fungi. Organic acids, such as oxalic or malic acid, chelate Mn^{3+} ions and prolong their lifetime until the enzymes attack the phenolic structure of lignin or humic acids.

How we should measure the effect of Mn on lignin degradation as part of litter decomposition is still not clear. Annual litter mass loss for several species has been related to Mn concentrations, but the variation in its concentration in litter, both during decomposition and among litter species, has so far not allowed any general conclusions. That there is an effect of Mn on the degradation of pine litter in late stages of decomposition has been demonstrated using litter in the late stages of decomposition (Fig. 2.7).

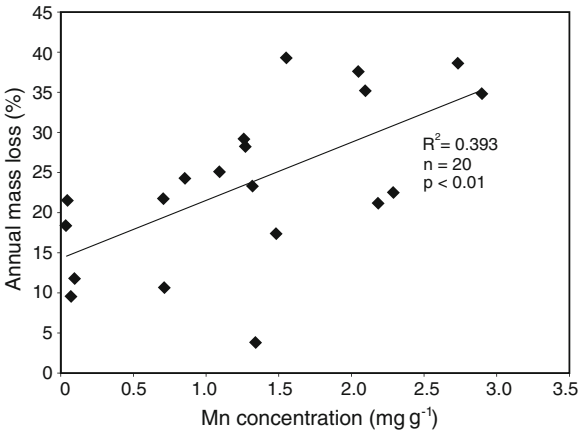

Fig. 2.7 Annual mass loss for pine needle litter (*lodgepole* pine, *Aleppo* pine) in the late stage plotted versus Mn concentration at the start of each one-year period. Data from Berg et al. (2007)

2.5.3 *Effect of N on Lignin/AUR and Late-Stage Litter Degradation*

As litter decomposes and the level of AUR/lignin increases, that of total N also increases (Fig. 2.2). This is a well-known and general phenomenon in decomposing litter. We emphasize this because of the important role of N in the degradation of lignin and the formation of humus (Stevenson 1982; Nömmik and Vahtras 1982; Eriksson et al. 1990; Keyser et al. 1976). In more recent papers, Thorn and Mikita (1992) and Knicker (2004), using NMR, report numerous compounds formed as a consequence of reactions between fulvic and humic acids and ammonia/ammonium.

For the increase in nitrogen concentration, there is no really clear border between the early, the late, and the humus-near or the limit-value stage of decomposition. The rate-retarding effect normally ascribed to the increasing AUR/lignin concentrations (e.g., Fogel and Cromack 1977; Berg and Lundmark 1987) is probably in part due to the associated high concentration of N which, (1) may have a suppressing effect on formation of ligninase and thus on lignin mass loss (see below, Biological mechanisms) and (2) may form complexes with organic compounds (Stabilized compounds, below). Thus, it may not be the lignin concentration per se that is rate retarding, but lignin in combination with N concentrations above a certain and so far unknown level.

We may, as an extreme case, imagine that with low enough N levels and thus no suppressing effect, a higher degradation rate for lignin and for litter may result and probably no raised lignin concentration. There is indirect evidence for this based on experiments in wood decay as wood is extremely low in N. Based on litter-bag studies in Black Hawk Island (WI, USA), wood chips of red maple and white pine lost more mass (88 %) than any of ten other litter types including leaf litter, needle litter, bark, and fine roots after 10 years of incubation on the forest floor. The initial N concentration in these wood samples was 0.09 % for red maple and 0.04 % for white pine (Aber et al. 1990; McClaugherty unpublished). A similar finding was made in the CIDET project using wood blocks (Preston et al. 2009a).

Much remains unknown about the roles of AUR/lignin and N during the late and final stages of decomposition. We do not know whether the rate-retarding effect ascribed to lignin, or the combination of lignin and N in aging litter is due to the level of N, the number of different recombination products or the formation of specific compounds. Several suggestions exist (below). What is the role of the initial N in litter and of that taken up during decomposition? The N transported through fungal mycelia into the litter is one easily available source of N from outside the decomposing substrate (e.g., Berg 1988), but inputs from atmospheric deposition may become increasingly important in some systems. Possibly both internal and external sources are influential, but this requires further investigation.

An evident question is whether the declining rate of decomposition observed in the late stage of decay is due to the suppression caused by N or a combination of (high) N and (low) Mn. The suppressing effect of N on the degradation of lignin, as

well as on the decomposition of whole litter, has been observed in studies with different levels of resolution. The suppression of ligninases in white-rots has been described in reviews by Eriksson et al. (1990) and Hatakka (2001). An effect, possible to ascribe to N has been observed directly, producing different AUR-degradation rates in decomposition experiments (Berg and Ekbohm 1991). That study did not exclude other possible agents, though. Recent studies using N additions to decomposing litter has shown a clear suppression (Sect. 6.3.2; Hobbie et al. 2012; Perakis et al. 2012).

Stabilized compounds. Stabilization of litter residues is a consequence of an enrichment of stabilized compounds, for example, macromolecules. Some different pathways have been suggested (e.g., Knicker 2004).

The N-fixation process involves ammonia, not the ammonium ion, and therefore, the reaction is faster at higher pH values. Also, amino acids react at higher rates at higher pH values for the same reason. Broadbent and Stevenson (1966) demonstrated that close to pH 9 the reaction was 10–20 times as fast as at pH 6 and below. The higher the level of N (or the higher the degree of humification) the lower was the NH_3-fixing capacity of the organic matter studied. For Scots pine needle litter, Axelsson and Berg (1988) largely confirmed these findings and estimated a fixation rate three times higher at pH 9 as compared to pH 5. They also found that Scots pine needle litter that had reached a higher accumulated mass loss and thus higher N concentrations, adsorbed/fixed less ^{15}N. In a more recent investigation, Thorn and Mikita (1992) found that N concentration in a natural fulvic acid preparation increased from 0.88 to 3.17 % after fixation with ammonia. This may be a potential increase.

Using ^{15}N-NMR and natural fulvic and humic acids, it has been possible to follow *pathways for mineralized N*. Thus, Thorn and Mikita (1992) found an array of new compounds, namely after recovering the ^{15}N in a set of compounds (Fig. 2.4). In contrast to earlier investigations, they did not find any quinones. This may be a first step in the humification process. Of refractory N compounds in soils, melanins have been suggested as a precursor.

An alternative suggestion is the *depolymerization—recondensation pathway*. Naturally occurring macromolecules are degraded to smaller units. A small fraction of these may recombine by random reaction (condensation) to insoluble and refractory structures with a more long-term stability. An example on stabilization for N compounds suggests that carbonyl (C=O) in lignin reacts with NH_2 groups of proteinaceous material forming Schiff bases (see the review by Knicker 2004).

The selective preservation pathway suggests that refractory biopolymers may resist biodegradation and accumulate. Such compounds are produced by plants and by bacteria.

Thorn and Mikita (1992) identified and listed 24 compounds, mainly aromatic ones, found in 3 fulvic and humic acid samples. Such chemical transformations may result in structures that are not easily degradable by the soil microorganisms.

Several pathways have been suggested for the reaction of NH_3 with, for example, humic and fulvic acids and several mechanisms are reasonable, possibly related to the nature of the organic matter and the ecosystem, although several

mechanisms are reasonable. Methoxyl groups are removed from the lignin aromatic ring, forming phenolic groups which then may react with and bind NH_3. A fixation mechanism has been suggested involving quinones, which are formed during lignin degradation as side products from laccase or peroxidase acting on diphenol rings (Nömmik and Vahtras 1982). These latter, by reacting with ammonia, could be transferred to heterocyclic polymeric compounds finally resulting in a polymerization into quinones. A newer study (Fig. 2.4) gives a more varied spectrum of compounds than the quinones found by Lindbeck and Young (1965).

In their review, Nömmik and Vahtras (1982) point out that prolonged exposure of organic matter to NH_3 under aerobic conditions leads to degradation of humic acid polymers by hydrolytic and oxidative processes, which results in the formation of soluble low molecular weight soluble compounds (see also Sect. 6.5; Guggenberger 1994).

Biological mechanisms. Raised N levels may suppress the formation of lignin-degrading enzymes, the degradation of lignin (Keyser et al. 1978; Eriksson et al. 1990; Hatakka 2001) and consequently also the decomposition rate of litter (Berg et al. 1987; Berg and Ekbohm 1991; Berg and Matzner 1997). This simply means that the higher the level of available N, the stronger the repression of the formation of lignolytic enzymes in the population of lignin-degrading organisms (see also Chap. 3). The ability of several fungal species to degrade lignin was heavily suppressed when N was added to the culture medium at concentrations of 2.6–7.8 mM, corresponding to 0.0036–0.0109 %. The level of N in solution in a pure fungal culture is not directly comparable to those in litter, where the N will be bound in different compounds and will be much less mobile than in solution. However, trends apparent in culture may stimulate speculation as to possible mechanisms in litter. With an N concentration of 0.4 % in our case-study litter, N concentration is 100-fold greater than in the fungal laboratory culture system. In both cases, the status of the N changes over the course of the experiment. In liquid pure culture, the N becomes bound in microbial biomass and thus less available. In the litter substrate, there may be a mineralization and degradation of proteins, thus converting a fraction of the bound N to more available N, possibly in concentrations high enough to suppress decomposition.

2.6 Proposed Model for Decomposition from Newly Shed Litter to the Humus Stage

In the section above, we demonstrated that the decomposition patterns for organic chemical components not embedded in lignin (early stage) were different as compared to those of the same components in tissue that was either lignified already in the newly shed litter or had become embedded in newly formed resistant products in the late stage. This may be a general basis for considering rate-regulating factors, but the fraction of lignified tissue may vary among litter species

in the same genus and possibly also within our model species, for example, among stands and locations.

We cannot exclude that rate of formation as well as properties of newly formed resistant products may vary with species and environment. A given litter may have only a certain fraction of its holocellulose embedded in lignin, while that of another species may have its holocellulose completely embedded, which may change both decomposition pattern and rate-regulating factors.

We used information obtained from pure culture and physiological studies on microorganisms, compared this to the degradation of different components and organized a three-stage conceptual model based on AUR analysis (Fig. 2.3). It has been recently shown that as further litter species are investigated, the original three-stage model (based on AUR analysis; Berg and Matzner 1997) can be further developed and modified, and we can now see differences in length of the early stage, possibly due to the level of lignification of the holocellulose. We develop this in Chap. 6.

It is possible that we in the future will see separate models related to plant genera or to groups of genera. In the present case, we give explanations for the different stages, which are connected to in situ decomposition experiments for litter and humus. Although each stage can be uniquely described, the process is more accurately described as a continuum in which transition points cannot be defined precisely.

The reasons for dividing the decomposition process into different stages are rather straightforward. On the level of plant cells, the polymers lignin, cellulose, and hemicelluloses are structurally organized (see Fig. 4.2) and the main part of the cellulose and hemicelluloses are found in the primary cell wall, whereas lignin is distributed in the secondary wall and in the middle lamella (Eriksson et al. 1990). A result of the distribution in the cell wall is that there is a separation of carbohydrates into those that are not lignified and those that are encrusted in native lignin. Microorganisms that are not lignolytic may degrade only the former.

We discuss the possibility (Chap. 4) that newly shed foliar litter of some litter species may have a structure with a much higher level of lignified tissue, which may explain the very short early phase and the fact that the litter cannot decay to a significant extent until the onset of lignin degradation, often recorded as AUR degradation. Thus, the early stage is missing or simply too short for us to measure. Still today, it is not clear if this lignification is due to species-related differences or properties related to, for example, the balance of nutrients in the soil that may influence, for example, the formation of lignin (cf Sect. 4.7).

The model is divided into three main phases, describing the decomposition of litter toward humus. The process may be divided into functionally defined stages: (1) newly shed litter—early decomposition stage; (2) late stage for partly decomposed litter; and (3) humus-near stage or limit-value stage, where litter is close to becoming stable humus. These are the main stages that we have described and connected. The model considers the effects of climate, the effects, and roles of nutrients in the early phase and of AUR, N, and Mn in different substages of the late phase, as well as effects of Mn concentration on the level of the limit value. It

also accounts for theories for formation of a stable fraction (humus formation-humus-near stage, Sect. 2.6.3). In recent work, it has been possible to subdivide the stages by adding a transition stage, in which the effects of nutrients are less clear (B. Berg and J. Kiønaas, unpublished).
We will discuss these stages more in detail, referring to the denominated model stages including what factors that may regulate the mass-loss rate (Fig. 2.2).

2.6.1 The Early Stage

The model (Fig. 2.2) was constructed using Scots pine as a model substrate and is a development of the original 3-stage model (Berg and Matzner 1997). Information so far available has indicated that the early phase may encompass different fractions of litter mass, for Scots pine ranging from c. 25 to 28 % accumulated mass loss, and for lodgepole pine, about 20 %. For black pine, De Marco et al. (2012) suggested 28 % accumulated mass loss as the end of the early stage.

The duration of the early stage measured as accumulated mass loss is likely to vary, possibly in some proportion to lignin/AUR concentration. It has been documented that raised concentrations of, for example, N, P, and S are positively related to an increased litter mass loss (e.g., Berg and Staaf 1980). Also increased site MAT or AET has a positive effect, (e.g., Johansson et al. 1995) on mass-loss rate. The existence of an early phase may depend on our ability to measure it. Thus, a very short phase of say 10 % accumulated mass loss or less may simply pass unnoticed in an environment with a high mass-loss rate (see also Sect. 6.3.1).

The definition of this early stage was originally 'the amount of organic matter that is not lignified,' viz. the material that could be decomposed without any degradation of AUR/lignin. We may revise this somewhat to 'the fraction of organic matter the degradation of which is not dominated by that of lignin.' We cannot exclude that ^{13}C-NMR analysis may give mainly the same result but that the fraction of lignin will be smaller than that for AUR, which again may alter the definition (see also Sect 6.3.2).

2.6.2 The Late Stage May Have Substages

An intermediate stage. We may not expect a sharp transition from the early stage to the late one. Using Scots pine needle litter, Berg et al. (201Xa) calculated annual litter mass loss using litter that had decomposed to >30 % accumulated mass loss and thus was at the end of the early stage. They subdivided the dataset (75 annual mass-loss values) into groups of annual mass loss, based on accumulated mass loss subdivided into 10 %-units, namely 30–40, 40–50, 50–60, 60–70, and 70–80 % accumulated mass loss. Using annual mass loss (see the Glossary) for litter in each one of these groups, they investigated for any significant

relationship between factors potentially regulating lignified tissue and annual mass loss, namely MAT, MAP, AUR, N, and Mn.

They identified a zone in which there was a certain influence of MAT ($p < 0.1$), and none of N, AUR, or Mn and interpreted this as a transition zone between the early and late stages. There was no significant effect of anyone of the four factors.

Further substages or simultaneous influences of Mn and N? We have commented on the effect of Mn and on different effects of N in the late stage. One question is whether these two nutrients exert their effect on degradation of lignin and litter simultaneously over the late stage or in a sequence. Using the approach of annual mass loss grouped as described above, Berg et al. (201Xa) found a simultaneous effect of Mn and N throughout the late stage with Mn-stimulating and N-retarding decomposition. Whether the relative effects were related to the relative concentrations of the two nutrients is today not known. At this late stage, there was no relationship to climate. Berg et al. (201Xa) used data from a climate gradient with MAT ranging from −0.7 to 6.8 °C.

2.6.3 The Humus-Near or Limit-Value Stage

Literature that describes the functional transfer from partially decomposed litter to a stable phase or humus is rare. Nonetheless, moderately decomposed litter, the humus-near stages, and humus have at least some properties in common. One example including pine needle litter was that the estimated N concentration at the limit value was found to be almost the same as that in the FH or H layer of the same stand (Berg et al. 1999b). Further, Couteaux et al. (1998) measured rates of litter CO_2 release close to the limit value and in the humus layer from the same Scots pine forest (Table 2.2) and found them to be very similar.

We may also connect litter mass-loss rate to the concept humus. It has been possible to adapt mathematical functions to accumulated mass loss of litter and with good statistical precision estimate how far the decomposition should proceed before we may estimate the rate zero. The rate zero may be found at different

Table 2.2 Compartments of different stability in decomposing Scots pine needle litter and humus in a Scots pine forest

Labile comp. (%)	K_L (% day^{-1})	Intermediate comp. (%)	K_{IN} (% day^{-1})	Recalcitrant comp. (%)	K_R (% day^{-1})
Needle litter incubated in litter layer for 16 months					
4.09 (0.39)	0.124	17.01 (2.41)	0.0087	78.52	<0.0001
Brown needle litter from forest floor					
4.67 (0.61)	0.124	21.91 (1.54)	0.0087	74.93	<0.0001
H layer particles <2 mm					
0.00	0.124	9.80 (1.32)	0.0087	91.20	<0.0001

The sizes of the compartments were estimated and the rate constants were based on respiration measurements. Standard deviation in parentheses. (Couteaux et al. 1998)

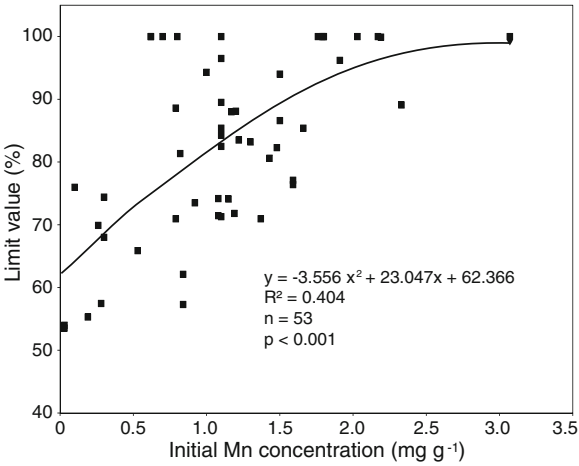

Fig. 2.8 The level of the limit value, given as accumulated mass loss. The limit value for needle litter of pine spp. appears to be related to litter Mn concentration. Decomposition studies from four litter species (mainly Scots pine) were combined into a climatic gradient and limit values estimated using litter accumulated mass loss. A backward elimination procedure removed insignificant factors. Of MAT and MAP and eight substrate-quality factors, Mn was selected as the single significant factor. Data from Berg et al. (2010)

values for accumulated litter mass loss (Fig. 2.8), which also means that a variable fraction of very slowly decomposing material is left (cf Fig. 9.2).

A number of such investigations have been carried out using our case-study litter (Scots pine). Within a given forest plot, there is a certain repeatability of limit values. For example, Berg and Ekbohm (1993) found some homogeneity among limit values within groups of studies on decomposing litter of Scots pine and lodgepole pine. They also found that the limit values of the two groups were significantly different. Berg et al. (1999b) published data for 11 studies on Scots pine litter decomposition in one forest system and found that the limit values ranged between 76.0 and 93.2 %, giving an average of 84.7 % (SE 1.57). In other words, on average, 15.3 % of the initial litter became stabilized as very slowly decomposing residue. For the same litter type, Couteaux et al. (1998) using release of carbon dioxide calculated a mass-loss rate that was less than 10^{-4} % day^{-1} for the recalcitrant fraction (above; Table 2.2).

The variation in limit values using litter from different pine species (genus *Pinus*) was investigated over a larger region using 56 decomposition studies and litter from four pine species with Scots pine dominant. Eight litter-quality factors such as initial concentrations of nutrients and AUR were evaluated as well as MAT and MAP and resulted in Mn as the single significant factor (Berg et al. 2010; Fig. 2.8). With the support of the causal relationship for the role of Mn in degradation of lignin, the result appears reasonable. In that study, they used local litter, which means that the litter was incubated at the same site as where it was

harvested. Further, they identified limit values for pine spp. litter ranging from 100 % accumulated mass loss to c. 50 %. Using backward elimination and available substrate-quality factors, they found that Mn was the sole remaining factor. They used mainly Scots pine needle litter as a model substrate, and the average limit value for Scots pine was 82.7 % accumulated mass loss. We may use part of the dataset of Berg et al. (2010), namely that for just Scots pine ($n = 34$) and comment on that also for this limited dataset, a quadratic function was significant ($p < 0.05$) and similar to that in Fig. 2.8.

The role of animals in the decomposition of litter toward a limit value is unclear. Most of the studies that are used to estimate limit values for pine litter have been carried out in forest soils containing relatively small numbers of animals that would influence litter decomposition. However, other studies have indicated that decomposition may have a limit-value pattern also in systems in which soil animals are found in higher numbers. At present, there appears not to be any study in boreal and temperate forests actually showing an influence of animals on the limit value. We cannot exclude that the existence of limit values and their levels in these studies may in part be ascribed to the absence of soil animals.

Although it is possible to estimate significant limit values for litter decomposition, we do not conclude that such limit values necessarily indicate a completely recalcitrant residue in the humus-near litter (e.g., Table 2.2). The estimated values may illustrate a fraction that is stabilized and thus decomposed at a very low rate or possibly not at all. Even if this is the case, the phenomenon is no less interesting or useful, especially if we can connect this resistance or recalcitrance in litter to its properties, for example, to the concentration of lignin or some nutrient, or climate. We cannot exclude that a limit value may indicate a point of transformation from decomposing litter to stable humus.

Just the fact that allophanic (see Glossary) humus exists shows that an 'eternal' storage is possible. Although allophanic organic material may be regarded as an extreme case, the level of stabilizing components (for example, aluminum and iron ions) necessary to stop the decomposition process is not known (Paul 1984). The fact that the use of limit values allows us to reconstruct a humus buildup over a period of 3,000 years also indicates that at least in some forest systems, the litter has a long-term stability (below). We may speculate about what factors that could disturb the litter/humus accumulation process. That wild fire will cause a severe disturbance appears clear, especially if repeated with some frequency. Forest management such as soil preparation is a factor as well as drainage.

What further influences may cause the decomposition to cease? Although Mn was well related to the limit value, the model suggested by Berg et al. (2010) could 'explain' less than 35 % of the variation. Although we have presented results from a study dominated by Scots pine that excluded other factors than Mn, we cannot conclude any generality, not even within the genus *Pinus* (Fig. 2.8) and we discuss their influence in this sense. They are thus potential factors also for pine litter. Although 8 substrate-quality factors were investigated (Berg et al. 2010), none of them was a heavy metal such as Pb, Cu, Hg, or Cd. Further, all factors were substrate-quality ones and there was none related to the soil.

Heavy metals. We must consider these as a group for which there are too few studies to allow any conclusion about their effect on decomposition under ambient conditions.

It appears that the effect of heavy metals on litter mass-loss rate in non-polluted environments has been little studied and few studies have recorded dynamics of the main heavy metals. Some appear to increase in concentration with accumulated mass loss (e.g., Pb and Cu) as judged from available information, whereas other ones are highly variable. For example, Cd mobility is related to pH. Still, there are several unknowns about increasing *vs* decreasing concentrations for different heavy metals. We have seen for Scots pine needle litter that Fe, Zn, Cu, Pb, and Cd increase heavily (Laskowski and Berg 1993). Such a general increase may influence decomposition in the late stages and at the limit value.

Chapter 3
Decomposer Organisms

3.1 Introduction

The dominant primary decomposers in boreal and temperate forest soil systems are the microorganisms, encompassing both fungi and bacteria. Both these main groups of microorganisms can degrade cellulose, hemicellulose, and different lignins. This chapter will emphasize the functional roles of organisms (e.g., cellulolytic and lignolytic) rather than their taxonomy. The concepts white rot, brown rot, and soft rot and what they stand for functionally in terms of degradation processes will be presented.

Many microorganisms degrade cellulose and hemicellulose in nature. These organisms have in common the production of extracellular hydrolytic enzymes that are either bound onto the outside of the cell or released into the surrounding environment. Polymer carbohydrates may be degraded both aerobically and anaerobically, but a complete degradation of lignin (white-rot type) requires the action of aerobic organisms (fungi and/or aerobic bacteria). Partial lignin degradation (brown-rot type) may also be carried out by anaerobic bacteria, but is mainly found among fungi and aerobic bacteria.

We have used the functional concepts white rot, brown rot, and soft rot as a basis for the discussion of degradation of litter. Although the terms originally seem to refer to visually different types of lignin degradation, it now appears that the degradation of cellulose and hemicellulose is also different among the groups (Worrall et al. 1997). The terms refer to the type of rot rather than to a group of organisms, but we have adopted the common use of the terms and refer to fungi when using the terms white rot, brown rot, and soft rot. As regards degradation by bacteria, it is described and discussed as such.

The composition of the microbial population (e.g., cellulolytic versus lignolytic) may vary with general properties of the soil/litter ecosystem, such as nutrient status and pH. A specific functional property that may discriminate among systems and populations is their sensitivity to N concentrations in litter and humus, which may be either stimulating or suppressing. Such sensitivity is not universal, but common in species of both white-rot and brown-rot organisms.

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By tradition, soil animals, such as collembola, mites, and earthworms, have been considered important for litter decomposition. Such groups have different roles in decomposition, although those roles are not always clear. The decomposition by free-living microorganisms has also been considered important, but the relative influences of soil animals and soil microorganisms have not been apparent, thereby indirectly supporting studies of the more easily studied visible component, namely soil animals.

In recent decades, it has become increasingly clear that for some systems, at least boreal and temperate coniferous ones, the microbial component is of absolute dominance. For example, Persson et al. (1980) estimated that at least 95 % of the energy flow goes through the microbial population. The implications of this proportion are considerable, and we could express this in a somewhat simplified way by stating that the decomposition of litter in a given system is determined by conditions and limitations that are valid for the microbial community of that system, which may be quite different from those of the soil faunal community.

Considering that the focus of this book is directed toward boreal and temperate systems, which have a decomposition process dominated by microorganisms, we have described both the microbial population (Sect. 3.2) and the microbial enzymatic degradation mechanisms (Sect. 3.3). This chapter will describe those properties of the organisms that are important in the degradation of cellulose, hemicellulose, and lignin. The main combined effects on the decomposition of whole litter are given in Chaps. 2 and 6.

Mycorrhizae have been found to turn into aggressive decomposers under certain circumstances and may decompose humus that has been considered as stabilized. Such a degradation can take place at a high rate. This phenomenon may be related to nutrient stress in growing trees. The role of mycorrhizae in decomposition in general is still under dispute, and we present observations here without taking part in that dispute (Sect. 3.4).

The ecology of decomposer communities can influence the pattern of decay. The changes in the community and its function during the decay process and the cyclic nature of the successional process in the soil will be addressed. The effects of moisture and temperature on the activity of the microbiological decomposition process are presented later, in Chap. 7.

3.2 General Properties of a Given Microbial Population

The two main groups of litter decomposers are bacteria (including the filamentous bacteria that earlier were called actinomycetes) and fungi: two groups that appear to include some of the same basic physiological properties when it comes to degradation of fresh litter polymers. Still, the fungi are generally considered the most important group, and we know more about their litter-degrading properties and enzyme systems. Each of these two groups may be divided into functional subgroups with different properties, degrading different groups of chemical

Table 3.1 Some of the general properties of main groups of bacteria and fungi

Property	Bacteria	Fungi
Mobility	+	+
Spore-forming ability	+	+
Can degrade cellulose/hemicellulose	+	+
Can degrade lignin completely	+	+
Can degrade lignin anaerobically[a]	+	–
Can degrade intact fiber walls	+	+
Species with N repression of the ligninase system	?[b]	+
Species without N repression of the ligninase system	?[b]	+

[a] Incomplete degradation to be compared to the brown-rot type
[b] Not known

components. The taxonomy of both fungi and bacteria is complex and is beyond the scope of this book.

The bacteria include both aerobic and anaerobic organisms, which distinguishes them from the exclusively aerobic fungi. Both groups have organisms able to degrade all the main polymers: lignin, cellulose, and hemicelluloses. There are also organisms able to degrade woody tissue where all these components are combined into fibers. Complete degradation of lignin appears to be carried out by a small number of the fungi and aerobic bacteria. Some of the general properties of main groups of bacteria and fungi are listed in Table 3.1.

The biological diversity in the soil microbial community is high. The potential species diversity is evident just by comparing crude numbers of identifiable species. For just 1 m^2 of a given soil system, we may estimate that for bacteria, there may be 1,000–5,000 species and for fungi perhaps 100 dominant species.

The high density of bacteria in, for example, an organic soil creates a high potential for invading a new substrate, such as newly shed litter. Estimates of 10^9 bacteria g^{-1} organic soil in either an active or a resting stage are common when made by direct light microscopy counting. This figure is conservative since there are numerous bacteria that are simply too thin to be detected with light microscopy and have to be counted using electron microscopy. In the same soil, total mycelial lengths have been estimated to reach ca. 2,000 km L^{-1} of humus, of which perhaps 10 % would be live mycelium. Microorganisms will only be actively dividing and growing when environmental conditions are favorable. When the conditions cannot support growth, the microorganisms will be in some kind of resistant, resting stage, or spore form. Wind and animals easily transport fungal and bacterial spores. This means that spores may be transplanted among ecosystems and that a given ecosystem may have a passive gene bank able to quickly produce active microorganisms that can attack a particular litter type, possibly with new chemical components that are novel in a given environment.

The size of most microorganisms gives them access to different parts of the fiber and tissues that make up litter (Fig. 4.2). For a main part of the bacteria, the diameters range largely from 0.1 to 2 μm and for filamentous fungi from ca. 1 to

less than 20 μm. The lengths of rod-shaped bacteria mainly range from ca. 1 to 10 μm, while those of the fungal mycelia are more undetermined.

Bacteria may be either immobile or mobile, with one or more flagella, a whip-like structure. Fungal mycelia demonstrate mobility in another way, in that they simply grow in one direction and thus move their protoplasm, leaving an empty cell wall structure behind.

The term 'decomposer' microorganism is sometimes used for those microbes that decompose plant litter structures, sometimes for the larger group that decomposes organic matter, thus including the whole group of free-living heterotrophic microorganisms. Free-living in this context simply means those microorganisms that do not live in obligate symbiosis. Here, we will focus on what may be called primary litter decomposers, namely those that attack and degrade (at least in part) the polymer structures to carbon dioxide and/or small, partly degraded molecules. We discuss below the hypothesis that not only free-living microorganisms play a role in the turnover of organic matter but that mycorrhizal fungi may also be important.

3.3 The Degradation of the Main Polymers in Litter

3.3.1 Degradation of Cellulose

Cellulose is degraded by numerous species of both bacteria and fungi. These organisms rely on extracellular enzymes that either are secreted into their immediate surroundings or are located on the cell surface. It is necessary that cellulose be degraded outside the microbial cell (Fig. 3.1), and that the insoluble macromolecules be degraded to monomers or oligomers of a few glucose units (Fig. 3.1), such as cellobiose, that can be taken into the cell and metabolized.

A common feature among all cellulose-degrading organisms is that they produce hydrolytic, extracellular enzymes that attack the cellulose polymer. Part of the cellulose in the plant fiber is arranged in a crystalline form that makes it harder to attack (see Chap. 4) and relatively few cellulolytic organisms have the necessary complete set of enzymes to degrade this structure. Many organisms are able to degrade the more amorphous kind of cellulose (see Eriksson et al. 1990).

The most studied group of cellulose-degrading organisms is the fungi, and no less than 74 species (Eriksson et al. 1990) have been studied in some detail. The traditional division of wood-degrading fungi into three main groups, white-rot, brown-rot, and soft-rot fungi, relates primarily to their mode of lignin degradation, but these groups also differ in the way they degrade polymer carbohydrates.

Perhaps the most studied wood decay fungus is the white-rot basidiomycete *Phanerochaete chrysosporium* Burdsall (previously called *Sporotrichum pulvurolentum* Novabranova). Much of what is known about the decay of lignocellulosic materials in nature is based on studies of this fungus (Ander and Eriksson 1977;

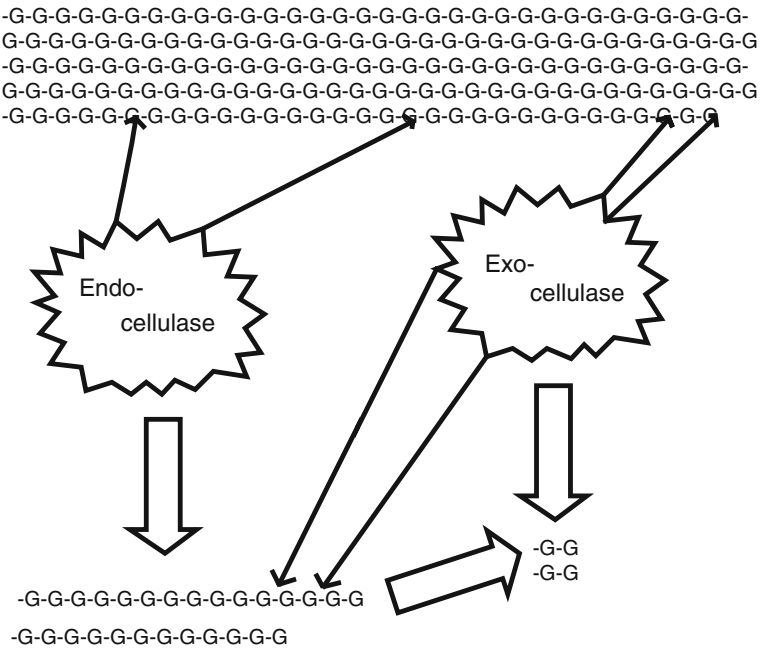

Fig. 3.1 Part of the cellulose fiber is attacked by an endo-1, 4-β-glucanase (endocellulase) breaking the chains and splitting off oligosaccharides in a random manner, including soluble shorter chains with, for example, 3–5 glucose units. An exo-1, 4-β-glucanase (exocellulase) splits off cellobiose units from the non-reducing end of the carbohydrate chains. *G* stands for a glucose unit

Higuchi 1993; Tien and Kirk 1984). Three main hydrolytic enzymes are involved in cellulose degradation; one type of enzyme (endo-1, 4-∃-glucanase) covers the cellulose chain and splits the glucosidic linkages in a random fashion (Fig. 3.1) producing oligosaccharide units of different lengths that may still be attached to the microfibril structure. Another enzyme, an exo-1, 4-∃-glucanase, splits off either cellobiose or glucose from the non-reducing end of the cellulose chain. Finally, 1,4-β-glucosidase hydrolyzes cellobiose and other water-soluble oligosaccharides, such as triose and tetraose, to glucose. One important aspect of this enzyme system is that the different enzymes with different specificities (the endo- and exoglucanases) exert a synergistic action that enables them to degrade both crystalline and amorphous cellulose.

In addition to hydrolytic enzymes, some cellulolytic organisms produce cellobiose dehydrogenase. This enzyme is found in a variety of fungi and appears to have roles in both lignin and cellulose degradation. There was much confusion in the early literature about this enzyme, but recent work has resulted in a renaming of both cellobiose oxidase and cellobiose:quinone oxidoreductase to cellobiose dehydrogenase (Cameron and Aust 2001).

The soft-rot fungi as a group appear to have a cellulose-degrading system similar to that of the white rots. However, in contrast to white-rot fungi, brown rots have not been found to have the synergistic enzymes that are found in white rots and they appear not to have the exoglucanase mentioned above. However, Highley (1988) found several species of brown-rotters that were able to solubilize microcrystalline cellulose. Thus, the generally held conclusion that these fungi merely seem to depolymerize cellulose without producing soluble monomers or dimers may not be entirely correct. Still, no other enzyme has been found to substitute for the missing exoglucanase that splits off soluble units. This has led Eriksson et al. (1990) to conclude that there may be a non-enzymatic mechanism involved. An observation that hemicellulose is virtually absent in wood decayed by brown rots suggests that brown-rot fungi may degrade hemicelluloses. Although the mechanisms for degradation of cellulose are far from clear, work on a basidiomycete (Wolter et al. 1980) suggested that at least for some species, a less specific or multifunctional enzyme that could degrade several different polysaccharides was active, an observation that suggests that this enzyme also has an effect on cellulose.

The ability to degrade crystalline cellulose is also found in many bacteria. Detailed studies on *Clostridium cellulolyticum* show that the organism produces at least six different cellulases, each with slightly different structural and catalytic properties. The cellulases, along with xylanases, are held together in a large structure, the cellulosome, by a scaffolding protein (Bélaich et al. 1997), much as was envisioned by Eriksson et al. (1990). In the anaerobic bacterium *Clostridium thermocellum*, a multicomponent complex of cellulolytic enzymes was named 'cellulosome' in the very early work of Viljoen et al. (1926). A close contact between the cellulose substrate and the organism often appears to be necessary.

The degradation of cellulose by bacteria has been suggested to be hydrolytic, although the mechanisms seem to be different from those found in fungi. For bacteria, the cellulolytic enzymes are arranged in clusters and act in a combined way as described above. There are a few other groups of cellulolytic bacteria that have been studied, including *Cytophaga*, *Cellulomonas*, *Pseudomonas*, and *Cellvibrio*. It appears that these have their cellulolytic enzymes bound to the cell wall, and therefore, a close contact is needed between the cell and the substrate (Berg et al. 1972; Eriksson et al. 1990). This property seems today to be widely recognized (Wiegel and Dykstra 1984).

Actinomycetes, in contrast to some other bacterial groups, appear to degrade cellulose in a manner similar to that of the fungi and can also degrade the crystalline form. Several strains have the ability to degrade the lignocellulose complex. The fungal model for enzymatic attack on the cellulose molecule, namely that an endo- and an exocellulase act synergistically, appears to be valid for actinomycetes, supporting their similarity to white-rot and soft-rot fungi.

The synthesis of cellulases is induced by cellulose, cellobiose, sophorose, and lactose. The presence of cellulose appears to be the best induction agent. On the other hand, the presence of glucose seems to repress the synthesis of the cellulase system. As cellulose is a large and non-soluble molecule, it cannot be absorbed

into the microbial cells and exert an inducing effect. Today, the accepted theory is that the organisms have a constant, basic level of cellulase on their surface. Upon contact with cellulose, low amounts of inducing substances are released from the cellulose, enter the microbial cell, and induce cellulase formation. It is likely that both the type of compounds, for example cellobiose or cellotriose, and a low intracellular concentration of these compounds influence the synthesis of cellulase. There are also theories that metabolic transfer products of glucosyl are active as inducing agents, one of these being sophorose (Eriksson et al. 1990).

3.3.2 Degradation of Hemicelluloses

In wood, the total concentration of hemicelluloses usually ranges from 20 to 30 % (Chap. 4). There are clear differences in the composition and structure of hemicelluloses in softwood as compared to hardwood litters. The composition of hemicelluloses is clearly different between hardwoods and softwoods (Table 4.1). The hemicelluloses are composed of both linear and branched heteropolymers of D-xylose, L-arabinose, D-mannose, D-glucose, D-galactose, and D-glucuronic acid. These individual sugars may be methylated or acetylated, and most hemicellulose chains contain between two and six different kinds of sugars. Hemicelluloses from hardwoods have average degrees of polymerization in the range of 150–200 units, and most hemicelluloses are based on the 1,4-ß-linkage of their main sugars.

Degradation of hemicelluloses requires more complex enzyme systems than are needed for the hydrolysis of cellulose. For example, xylan-based hemicellulose contains both 1,4-ß-linkages and branched heteropolysaccharides, which require a complex set of enzymes for degradation (Dekker 1985). Figure 3.2 shows the possible structure of a xylan-dominated molecule. The xylan backbone is made up of both acetylated and non-acetylated sugar units. On the branches, there are units of glucose and arabinose. The degradation of such a molecule requires the concerted action of several different hydrolytic enzymes (Eriksson et al. 1990).

3.3.3 Degradation of Lignin

Lignin degradation is regarded as a process that differs between the three general groups of decomposers: white-rot, soft-rot, and brown-rot fungi. Although the names are old and refer to characteristics easily seen by the eye, there are also functional differences in the degradation mechanisms, motivating the continued use of the terminology. The names are used in connection with fungi although bacteria are also lignin degraders.

The number of different enzymatic mechanisms of lignin degradation with which organisms operate appears to be large, and only a few are well described. In

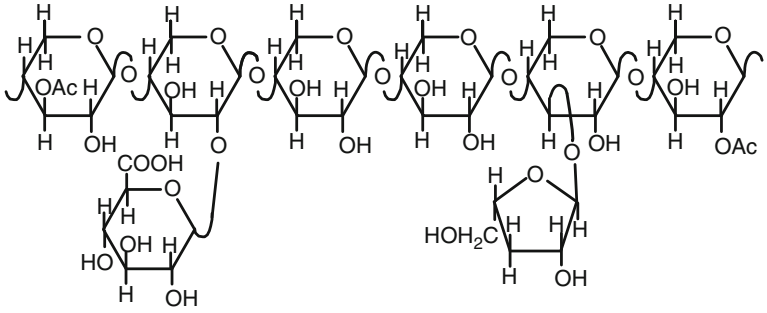

Fig. 3.2 An example of a fragment of a xylan molecule. The backbone of the molecule is made up of xylan units of which part are acetylated (Ac) and part not. The branches in this case are composed of glucose (*left*) and arabinose (*right*) units. The main enzyme attacking the unbranched part of the chain would be an endo-1, 4-β-xylanase, producing oligomers of different lengths. β-xylosidases split the oligomers into simple xylose units. Other enzymes are necessary to split off the side chains as well as, for example, the acetyl substituent. (Eriksson et al. 1990)

fact, today it appears that only one mechanism of lignin degradation is well described, namely that for *P. chrysosporium*, a white-rot fungus. Some characteristics for each of the groups are given below, starting with white rots since these are not only the most studied ones, but also probably the strongest lignin degraders known.

3.3.3.1 Lignin Degradation by White-Rot Fungi

White-rot fungi possess the ability to completely mineralize lignin to CO_2 and H_2O. The result, for wood, is that the entire lignocellulosic complex is degraded more or less simultaneously. A large group of the white rots may even degrade lignin preferentially to cellulose (Hatakka 2001).

The attack on lignin structure has long been considered to start with a removal of the methoxyl group (Figs. 3.3 and 3.4). Newer research has shown that a combination of hydroxylation and demethylation is followed by an oxidative attack on the aromatic ring (Eriksson et al. 1990). The cleavage of the aromatic ring (Fig. 3.4) is an oxygen-demanding step, and the data in Table 3.2 illustrate the importance of the presence of O_2.

The lignolytic enzyme system of our example fungus (*P. chrysosporium*) is synthesized as part of several physiological events that appear to be triggered by N starvation. As described by Kirk (1980), a whole set of enzymes are synthesized under conditions of N starvation (see below). Almost all white-rot fungi produce Mn peroxidase, a fact that may create an ecological niche, based on Mn as a limiting nutrient.

Although we may know more about the lignolytic system of *P. chrysosporium* than those of other white rots, it appears that the lignolytic systems are species

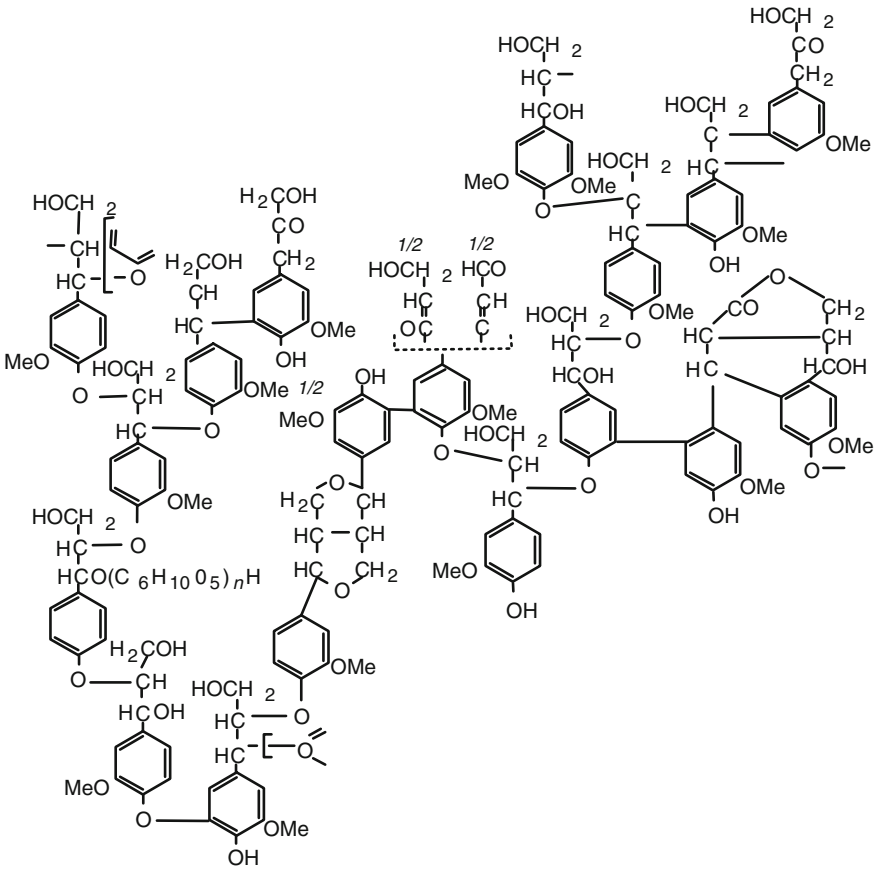

Fig. 3.3 Part of a lignin molecule from spruce

specific and it has been suggested that they depend on the ecological niche of the fungus in question (Hatakka 2001). For example, the white-rot *Ganoderma lucidum* produces Mn peroxidase in a medium with poplar wood but not in one with pine wood (D'Souza et al. 1999). An observation like this latter one may support the finding that white-rot fungi are more commonly found on angiosperm than on gymnosperm wood (Gilbertson 1980).

3.3.3.2 Lignin Degradation by Brown-Rot Fungi

Brown-rot fungi decompose mainly the cellulose and hemicellulose components in wood and have the ability to significantly modify the lignin molecule, but are not able to completely mineralize the compound (Eriksson et al. 1990). They allow for the degradation of cellulose with a relatively small loss of lignin mass.

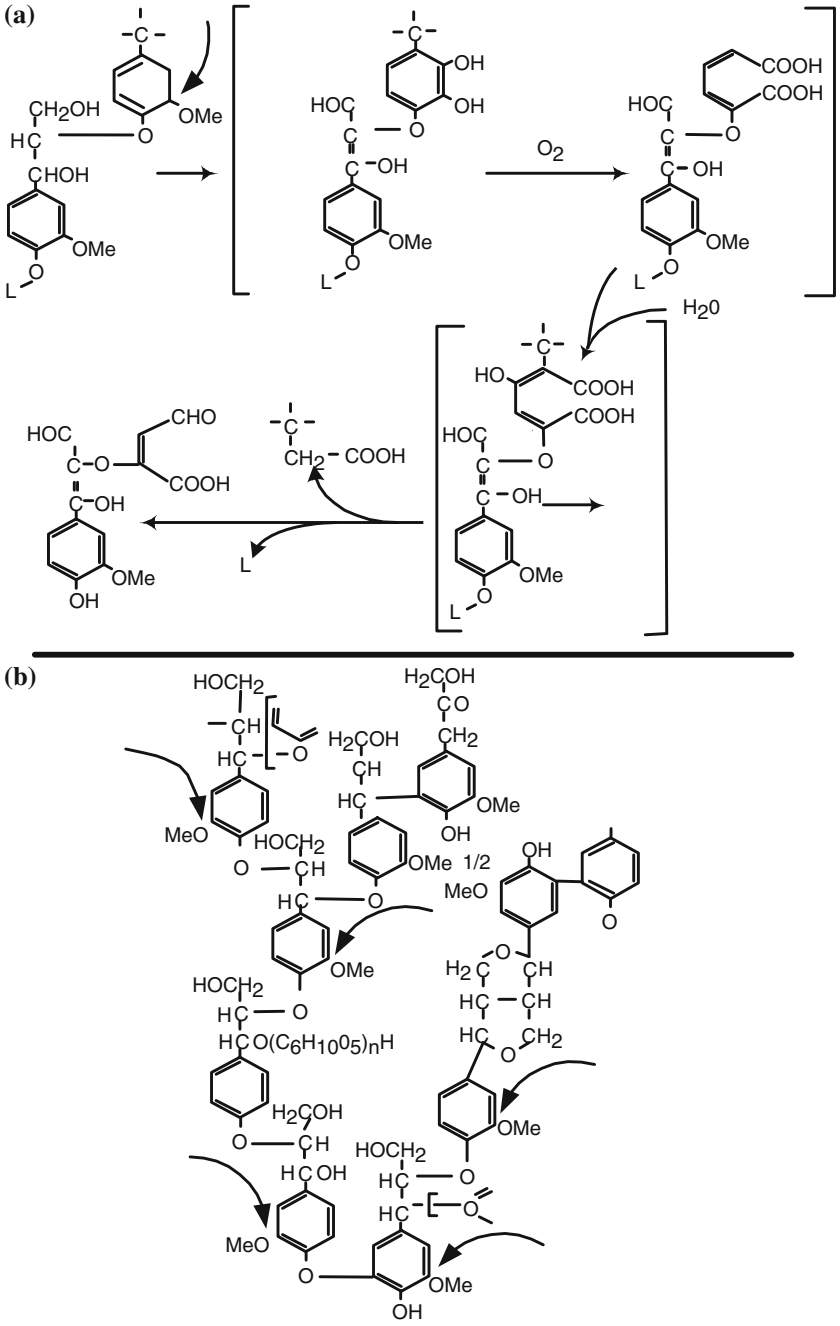

Fig. 3.4 Part of a lignin molecule of spruce during degradation. **a** Under degradation by white rot, demethoxylation and hydroxylation are followed by an oxidative step leading to ring cleavage (from Kirk 1984). **b** The same molecule under attack by brown-rot fungi, resulting in just a demethylation where the methoxy groups (MeO) are replaced by OH groups

Table 3.2 Degradation of aspen wood lignin by different white-rot fungi in the presence of air or pure oxygen

Fungal species	$^{14}CO_2$ evolution (%)		Klason lignin loss (%)	
	Air	O_2	Air	O_2
Phanaerochaete chrysosporium	10.8	35.2	13	40
Coriolus versicolor	14.6	35.5	24	46
Gloeoporus dichrou	9.7	18.1	22	24
Polyporus brumalis	16.6	33.0	19	33
Merulius tremellosus	14.0	22.3	30	40
Pychnoporus cinnabarinus	13.6	22.6	18	37
Lentinus edodes	9.7	18.0	18	41
Bondarzewia berkeleyi	9.0	13.8	25	27
Pleorotus ostreatus	11.7	11.6	17	17
Grifola frondoza	9.2	10.6	8	15

Determinations were made as $^{14}CO_2$ evolution and as Klason lignin. (Reid and Seifert 1982)

Brown-rot fungi are considered to have similarities in degradation mechanisms to white-rot fungi. In both cases, the formation of hydroxyl radicals that attack wood components is important and high oxygen tensions support the degradation (Hatakka 2001). It has been assumed that all brown-rot fungi use the same mechanism for wood decay. However, newer research has indicated that in parallel with white rots, brown-rot fungi appear to have different mechanisms. The initiation of the degradation of both lignin and cellulose appears to be by diffusible small molecules that can penetrate the cell wall. In contrast to white rots, only one brown rot has been found to produce Mn peroxidase.

The radicals formed by brown-rot fungi can remove methoxyl groups from lignin and produce methanol, leaving residues of mainly modified lignin (Eriksson et al. 1990). Relative to native lignin, brown-rotted lignins are structurally modified and have a decreased number of methoxyl groups (Fig. 3.4) and an increase in phenolic hydroxyl groups (Crawford 1981). Brown-rotted lignin is more reactive than native lignin due to the increased content of phenolic hydroxyl groups. Carbonyl and carboxyl groups are also formed (Jin et al. 1990).

3.3.3.3 Lignin Degradation by Soft-Rot Fungi

The traditional view has been that soft-rot fungi do not degrade lignin, but act to soften wood by breaking down the middle lamella of the cell wall (Fig. 4.2). Most soft-rot fungi are ascomycetes and deuteromycetes and are most active in moist wood. Crawford (1981) reviews a number of studies in which purported soft-rot fungi were able to decrease the lignin content of decaying wood.

Today, it has been well confirmed that soft-rot fungi do degrade lignin: In laboratory experiments, up to 44 % was degraded at a wood mass loss of 77 % (Nilsson et al. 1989). In general, they are considered to degrade lignin to some extent.

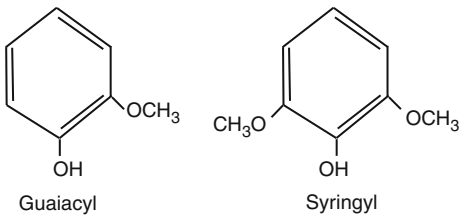

Fig. 3.5 Structures of guaiacyl and syringyl components of lignin

Evidence from a study on the fungus *Daldinia concentrica* may explain why these fungi preferentially degrade hardwoods. This fungus degraded birch wood efficiently but not that of pine (Nilsson et al. 1989). The lignolytic peroxidases of soft-rot fungi do not have the potential to oxidize the softwood lignin which has a high level of guaiacyl units (Fig. 3.5). In contrast, soft-rot fungi readily oxidize the syringyl lignins in hardwoods (Nilsson et al. 1989).

3.3.3.4 Enzymes Directly Affected by Mn Concentration in the Substrate

Manganese peroxidase belongs in a group of enzymes that are classified as phenoloxidases. Manganese is essential for the activity of the lignin-degrading Mn peroxidase (Perez and Jeffries 1992). Although not much was published on this enzyme before 1983, Lindeberg (1944) discovered in the 1930s that *Marasmius sp*. was dependent on Mn for their growth and that a low level of Mn in a substrate hampered the degradation of lignin. This finding was not pursued, and it was not until the 1980s that additional detailed studies followed.

Manganese is also involved in the regulation of other lignolytic enzymes, including laccase (Archibald and Roy 1992) and lignin peroxidase (Perez and Jeffries 1992). The role of Mn peroxidase in lignin degradation is not clear although one of its roles may be to form H_2O_2. The enzyme itself shows no affinity for non-phenolic compounds, which on the other hand are readily attacked by ligninase. Blanchette (1984) found that Mn often accumulates as MnO_2 in wood attacked by white rots, which suggests that Mn peroxidases are important for the degradation of lignin. It has also been found that MnO_2 stabilizes lignin peroxidase.

3.3.3.5 Effect of N Starvation on Lignin Metabolism

Lignin degradation may be repressed by high N levels in the substrate, an effect seen mainly in white-rot fungi but also in brown rots and soft rots. As mentioned above, Kirk (1980) described a set of effects for *P. chrysosporium* that were regulated by N starvation. A drastic effect on lignin degradation was seen when the

Table 3.3 Some fungal species for which raised N concentrations have or, alternatively, have not elicited a repressing effect on lignin degradation

Species	Comments	Reference
Sensitive to N		
Phanerochaete chrysosporium	Isolated from wood	Keyser et al. (1978) Eriksson et al. (1990)
Phlebia brevispora		Leatham and Kirk (1983)
Coriolus versicolor		Leatham and Kirk (1983)
Heterobasidion annosum	Some repression	Bono et al. (1984)
Not sensitive to N		
Pleurotus ostreatus		Freer and Detroy (1982)
Lentinus edodes		Leatham and Kirk (1983)
NRRL 6464 not identified	Isolated from cattle dung	Freer and Detroy (1982)

N concentration in the culture medium was increased from 2.6 to 5.6 mM (Keyser et al. 1978), namely that the lignolytic activity (measured as transformation of ^{14}C-lignin to $^{14}CO_2$) was repressed by 83 %. The same property has since been described for several fungal species in laboratory experiments with pure cultures, although the levels of N and the magnitude of the effect vary. For three species (*Phlebia brevispora*, *Coriolus versicolor*, and *Pholiota mutabilis*), there were effects at 7.8 and 34 mM N in the culture, but not at 2.6 mM N. The magnitude of the effect varied from an almost complete repression in *P. chrysosporium,* to about approximately a 50 % repression in *P. mutabilis*. When using ^{14}C-labeled lignin from red maple wood, there was a clear effect of 20 mM N. There are also several fungi that are not sensitive to N. For example, a white-rot strain isolated from an N-rich environment (cattle dung) showed no sensitivity to raised N concentrations. Table 3.3 lists a number of species investigated for this property.

The results suggest that repression of lignin degradation by N is common but not always the rule. The addition of N to fungal cultures may in certain cases even increase their ability to utilize lignin. We would expect that such fungi, and tolerant fungi in general, would be found in environments with high N concentrations, as in the example given above with cattle dung, whereas most white-rot fungi that grow in and on wood are adapted to low N concentrations. Many of the fungi that have been studied were isolated from wood, and the low N content in wood (with C-to-N ratios in the range from 350 to 500) may explain the generally strong influence of increased N levels.

3.3.3.6 Effect of the C Source on Lignin Degradation

It appears that the presence of a carbon source other than lignin stimulates lignin degradation in several white-rot species including *P. chrysosporium, C. versicolor, Coriolus hirsutus*, *Polyporus sp*., and *Lentinus edodes*. One observation was that

cellulose had a stronger stimulating effect on lignin degradation than glucose, an observation that was ascribed to its *lower* availability; thus, an influence of catabolite repression could be expected (cf. Sect. 3.3.1). The major organic components in litter are normally the insoluble ones such as lignin, cellulose, and hemicelluloses. The latter two normally supply the lignin-degrading organisms with alternative carbon sources.

3.4 Degradation of Fibers

3.4.1 Bacteria

Though bacteria have long been known to be involved in litter decomposition, they have received far less study than fungi. In most cases, bacteria coexist with fungi, particularly basidiomycetes and yeasts, and their presence has been shown to double the rate of fungal growth on wood and increase the overall rate of decay (Blanchette and Shaw 1978). Although it was once thought that bacteria were not capable of degrading lignified cell walls without some type of pretreatment, a variety of fiber-degrading bacteria have now been identified. Three types of bacterial degradation are recognized, based on the manner in which they degrade the cell walls of the substrate: tunneling, erosion, and cavitation (Blanchette 1995). Bacterial decomposition seems to be more common in situations where fungi are under stress. Bacteria have also been found to degrade substrates, especially wood, that are resistant to fungal decay (Singh et al. 1987).

3.4.2 Soft Rot

Soft rots generally occur under conditions that are not favorable for basidiomycetes. However, a key for good growth of soft rots is a high availability of nutrients. It is also generally held that soft rots require moist conditions, though this requirement may not be different from that of basidiomycetes (Worrall et al. 1991). Two forms of soft rots are identified based on the morphology of the degradation they cause (Blanchette 1995). Type I causes the formation of cavities in the secondary wall and is most commonly found in conifers, where lignin-like materials accumulate on the edge of the cavities. Type II causes cell wall erosion, but unlike white rot, it does not degrade the middle lamella (Fig. 4.2). It is possible that the middle lamella is resistant because it contains more guaiacyl propane units. Type II is more common in angiosperms.

3.4.3 Brown Rot

Brown-rot fungi have the ability to degrade holocellulose in plant cell walls without first removing lignin. Brown rots apparently begin their attack on fibers by degrading the hemicellulose matrix because xylans begin disappearing before cellulose (Highley 1987). They do this by first causing a rapid decrease in the degree of polymerization of the holocellulose polymers. The decomposition occurs in a diffuse manner and, in wood, with a rapid loss of strength. These two factors suggest that agents smaller than enzymes are involved (Green and Highley 1997). This initial degradation is generally accompanied by relatively little mass loss.

When attacking fibers, brown-rot fungi appear to attack the S2 layer first, leaving the S3 layer until later (Fig. 4.2; Highley et al. 1985). The reason for this is not known, but Hirano et al. (1997) offer a proposed mechanism that agrees with the observations. They suggest that the brown-rot fungus grows into the cell lumen and releases a low molecular weight substance (1–5 kDa) that diffuses into the S2 layer. Fe(III) is then reduced to Fe(II) and chelates it. The newly formed complex with the Fe(II) catalyzes a redox reaction that produces hydroxyl radicals. These hydroxyl radicals are able to cut canals through the S3 layer large enough for cellulases to penetrate. Clearly, more work is needed to validate this mechanism and to identify the unknown substances required for its operation.

3.4.4 White Rot

White-rot fungi carry out two different types of fiber degradation: simultaneous rot and selective lignin degradation. Some species can carry out both types (Blanchette 1991). In simultaneous rot, the fungi are able to either erode the cell wall adjacent to the hyphae, creating erosion channels, or they generally erode the lumen surface, resulting in an overall thinning of the cell wall. In addition, the hyphae move from cell to cell through pits or by boring through the wall. The other type, selective delignification, often results in cell separation as well as overall thinning of the cell walls. Anagnost (1998) provides numerous photomicrographs that illustrate the various types of decay.

White-rots sometimes seem to have a delay or a lag time of relatively slow mass loss before a period of more rapid mass loss (Fig. 8.1). Blanchette et al. (1997) used a novel biotechnological approach to demonstrate why this might occur. They incubated loblolly pine wood with a white-rot fungus, *Ceriporiopsis subvermispora*. They then placed the wood, in various stages of decay, in solutions containing proteins of known size. Using immunocytochemical techniques, they were able to show that proteins of the size of cellulases and lignin-degrading enzymes could not freely pass through the wood until later stages of decay. After cell walls had been thinned enough to increase their porosity, it was possible for extracellular enzymes to move freely from lumen to lumen, thus initiating the stage characterized by a higher rate of mass loss.

3.5 Mycorrhizae

In undisturbed soil systems, there also appear to be mechanisms that can change the composition of the microflora in ways that enhance its ability to degrade the otherwise stable humus. Hintikka and Näykki (1967) gave a good description of the mycorrhizal basidiomycete *Hednellum ferrugineum* and its effects on the humus layer. The development of thick mycelial mats under the mor layers was described, as well as bursts of soil respiratory activity, followed by a large decrease in the amount of humus in the FH layer. The effect was observed on dry, sandy, nutrient-poor sediment and till soils and could be attributed to plant growth. It appears to be a powerful mechanism driving humus decomposition. Unestam (1991) discussed this effect for certain other mycorrhizal fungi. Further, Griffiths et al. (1990) studied the effects of the ectomycorrhizal fungus *Hysterangium setchelli* on respiration in humus under Douglas-fir and identified patches with very high respiratory activity.

3.6 Ecological Aspects

The composition of the microbial community that invades litter depends on the properties of the litter that falls onto the soil system and the changes in those properties over time. The community of decomposers undergoes many of the same ecological processes that act on communities of primary producers. These processes include succession and competition, while the pathway of decay may be influenced by modifications in these processes.

Microbial succession, the change in community composition over time, occurs as the quality of the decomposing substrate changes, but it also occurs because different organisms invade substrates at different rates. Griffith and Boddy (1990) followed the development of the fungal community on common ash, common oak, and European beech twigs. The primary colonizers included endophytes that were present on the twigs while they were still alive. Secondary invaders were not endophytic and did not show up in appreciable numbers until about 11 months after twig death. They identified a third type of colonizer, the superficial, that appeared on the surface rather early into decay but was not present on the living twig. This pattern is probably similar for all litter types, though of course the species and timing may differ. For example, spruce needles can persist on the twigs for some time after death and decomposition can begin then. However, when the needles ultimately fall to the forest floor, the changing environmental conditions and the availability of a rich variety of inocula result in a change in the microbial community.

In addition to the change in microbial community that occurs along with decay, there are seasonal changes in the microbial community reflecting temperature and moisture. For example, Kayang (2001) followed fungi, bacteria, and selected

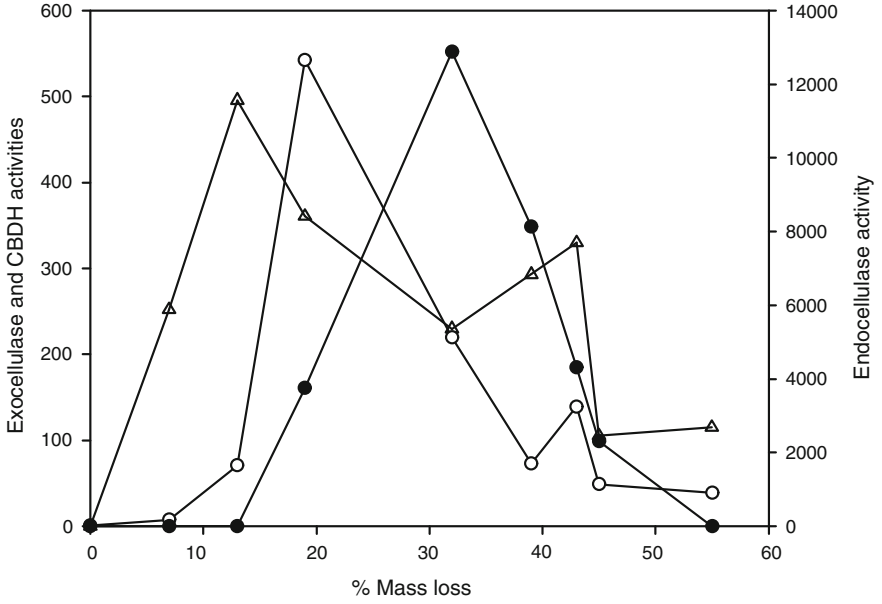

Fig. 3.6 Activities of exocellulase (*triangle*), endocellulase (*circle*), and cellobiose dehydrogenase (CBDH) (*filled circle*) during chestnut oak leaf litter decay in microcosms (Data from Linkins et al. 1990)

enzyme activities in freshly fallen leaves of Nepalese alder in India. The climate was described as subtropical monsoon. The dry season occurred from November through March, with frosts during December and January. The fungal and bacterial propagule numbers varied by a factor of nearly 5 between winter and summer. Enzyme activities (invertase, cellulase, and amylase) reached their peaks before the peak of microbial numbers, between April and June, and then fell slowly. The sequence of peaks suggests a succession of enzyme activities, with invertase, an enzyme involved in sucrose metabolism, peaking first. Amylase, which catalyzes the hydrolysis of starch, and cellulase appear later.

Examining activities of cellulases and cellobiose dehydrogenase on leaf litter in laboratory microcosms, Linkins et al. (1990) observed similar patterns for three different litter species. The species, flowering dogwood, red maple, and chestnut oak, differed in lignin contents and decay rates. However, all three species exhibited an increase in cellulase activity that reached a peak at the same time that cellulose disappearance rate was at its maximum. Cellulase activity then began to decline, and cellobiose dehydrogenase activity began to increase (Fig. 3.6).

As enzyme activities are changing, so are the fungal communities. Osono and Takeda (2001) studied the fungal populations on Japanese beech leaves as they decomposed in a cool temperate deciduous forest. Total and living fungal biomass, estimated using a modified Jones and Mollison (1948) technique (Ono 1998), increased during the first year of decay and then fluctuated for the remainder of the

study period. The percentage of fungi that were basidiomycetes increased for the first 21 months of the study, reaching a maximum of 25–35 % of the total living fungal biomass. They noted that the relative abundance of basidiomycetes was linearly and negatively related to the lignocellulose index (Chap. 2), an index of litter quality equal to the fraction of holocellulose in the lignocellulose. They identified over 100 fungal taxa on the beech leaves during their study and distinguished three groups: an early-appearing group, a late-appearing group, and a constantly appearing group. The early-appearing fungi were present during the period of net nutrient immobilization and the late-appearing fungi increased in number as the litter moved into the phase of net mineralization.

Decomposer populations may work synergistically or in competition. Competition is visible in decaying logs where discrete zones of decay caused by different organisms can be easily discerned. In some cases, the organisms define their boundaries with black zone lines. The interspecies dynamic can change as decomposition proceeds. For example, Bengtsson (1992) found a synergism with no evidence of competition between fungi and bacteria on common beech leaves during their first year of decay in stream microcosms. In comparison, Møller et al. (1999) found clear evidence of competition between fungi and bacteria on 1-year-old beech leaf litter, also in a microcosm study. This difference probably relates to the age, and hence the state of decomposition and the quality of the litter. Though there are not many studies on this phenomenon, it is possible that as litter quality decreases, the competition for the remaining resource becomes more intense.

As decomposition proceeds, the microorganisms themselves can become important substrates for the microbial community. Some fungi, including wood decay fungi, are able to use the cell walls of other fungi or bacteria, presumably as an N source. Some bacteria are able to degrade hyphal walls (Tsuneda and Thorn 1995).

There are many interactions among the organisms involved in decomposition and these interactions change over time. These complex, dynamic systems are not easily described. However, this natural complexity does have implications for the interpretation of pure culture and microcosm studies. Such studies are often the only way to control variability enough to ask a precise question. On the other hand, the behavior of a single, isolated species or of a simple community in a mesocosm may not reflect its behavior in the more complex natural environment.

Molecular microbial ecology promises to be a powerful tool for the study of decomposition and nutrient cycling (Zak et al. 2006). As molecular analytical tools become more available, molecular databases more accessible, and computer systems to analyze them become more powerful, molecular tools will be able to provide information on microbial community structure and function at a level previously not possible. For example, Blackwood and Buyer (2007) have demonstrated the potential of terminal restriction fragment length polymorphism (T-RFLP) to identify microorganisms from a variety of soils.

Chapter 4
Initial Litter Chemical Composition

4.1 Introduction

In forested ecosystems, litter fall is the largest source of organic material and nutrients for the humus layer. The quality and quantity of litter fall influence the nature of the microbial community, including its size, composition, function, and physiological properties. The composition of the microbial community may, in turn, influence the course of decomposition and the chemical changes in the litter during decomposition. With the knowledge about the initial chemical composition of litter and the chemical changes during decomposition, it is possible to predict how mass-loss rates will change even in late decomposition stages. With a close connection between the chemical composition of newly shed litter and the relative amount of recalcitrant residual litter (Chap. 10), we see a direct connection between litter chemical composition and rate of humus (soil organic matter) buildup.

Plants shed not only foliar litter, but, with trees as an example, twigs, branches, bark, roots, flowers, and occasionally cones. Structures such as cones are often quantitatively important and may sometimes exceed foliar litter as the largest component. Several litter types are not 'recently dead' but are recognized as litter after they have been shed and started to decompose and their chemical composition has begun to change. This applies, for example, to twigs, branches, and boles which remain standing after their death and often start decomposing before they fall to the ground and are recognized as litter. Roots die and are 'shed' differentially based on their size and function, and dead roots may remain attached to their parent tree for extended periods. We have collected information about roots and wood in Chap. 8.

The combinations of main chemical components in live vascular plants have general similarities among species and genera. Quantitatively dominant groups of polymer carbohydrates and lignin/AUR are ubiquitous. However, their proportions vary and minor structural differences occur among species.

Similarly, the same plant nutrients are found in different plant materials and in the litter, though in very different proportions. All plant litter contains essential nutrients such as N, P, S, K, Ca, Mg, Mn, and Fe, but the concentrations vary with

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7_4,

the litter species. For example, leaf litter of the N_2-fixing genera such as alder (*Alnus*), leadtree (*Leucaena*), and acacia (*Acacia*) has very high levels of N (often above 3 %); in contrast, pine needle litter is more N poor (often below 0.4 %). Species is thus one dominant factor in determining the nutrient levels in litter, but climate and the composition of the mineral soil, parent material and the humus are also of importance (Fig. 4.1). In undisturbed Scots pine systems as well as systems with other pine species, it appears that the concentration of N in needle litter may be related to climate (Berg et al. 1995a; Liu et al. 2006).

This chapter focuses on the litter fall from trees and aims to give an insight into the present knowledge on the chemical composition of needle litter fall, principally in pine stands, though other conifers and deciduous species are included. Although the emphasis is on foliar litter, we will include some discussion on wood. We have given a certain focus on the fiber structure, being aware of that other factors may be dominant over fiber structure for decomposition. We introduce the characteristics of the main insoluble chemical constituents of plant litter. We also identify factors that may influence litter chemical composition, with an emphasis on climate and soils, although species is an important factor. As data are limited, case studies have been used. The purpose of this chapter is not to explain the chemical composition of litter as based on the physiology of living plants, but rather to take into account the effect of general environmental conditions. As such, we focus on environmental components that appear to have a significant influence on the rate and pattern of litter decay and humus formation.

The new analytical approach using ^{13}C NMR rather shows the frequency of type of bonds between carbon and carbon as well as carbon to other atoms. This means that the approach so far is not directly compatible with the more traditional ones and we have presented it as a separate methodological approach. See also Appendix III.

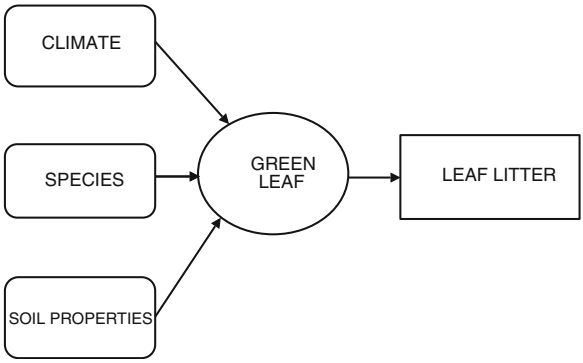

Fig. 4.1 Today, it appears that three main factors determine the chemical composition of foliar litter, namely species, climate, and soil properties. For a given species/genus, this means that climate and nutrient availability in soil have a dominant influence on (1) concentrations of nutrients and heavy metals in the live leaf (2) in the formed litter. Empirical findings indicate that the magnitude of the influences varies among litter species/genera

4.2 Organic-Chemical Components of Plant Litter and Fiber Structure

4.2.1 Organic-Chemical Components

The plant fiber structures are composed principally of lignin, a complex polymer compound formed mainly by esterification of phenylpropanoid structures (Fig. 3.3), and polymer carbohydrates. The quantitatively most common components in plant litter are the different polymer carbohydrates such as cellulose and the main hemicelluloses. Of these, cellulose is the most common compound and is made up of glucose units connected with β-1-4 bonds, forming long chains of molecules organized into fibers. Cellulose may constitute between 10 and 50 % of the litter mass (Table 4.1).

Hemicelluloses are polymers of sugars other than β-1-4 bound glucose that form long and somewhat random chains of monosaccharides (Fig. 3.2) that are incorporated into the fiber. However, they do not provide structural strength in the same way as cellulose.

Hemicelluloses are named based on the simple sugars from which they are synthesized, such as mannan, galactan, arabinan, and xylan. Also, starch, viz. glucose bound by α-1-4 bonds, is sometimes considered a hemicellulose. The proportions of hemicelluloses vary among litter species (Table 4.1). Differences in the major hemicelluloses are primarily reflected in the concentrations of xylose and mannose (Eriksson et al. 1990). Deciduous leaves are lower in mannans, whereas Norway spruce needles have higher levels, and birch leaves are richer in xylans. The ratio of hemicelluloses to cellulose ranges from about 0.7 to 1.2 (Table 4.1) with higher ratios often seen in deciduous litter as compared to coniferous litter. Hemicelluloses may together make up as much as 30–40 % of the fiber and are normally present in between 1 and 10 % each (Table 4.1). In contrast to cellulose, hemicelluloses are often branched.

Table 4.1 Comparison of the major organic-chemical compounds in some boreal litter species. Foliar litter data from Berg and Ekbohm (1991) and Berg and Tamm (1991)

Litter type	Concentration of compound (mg g^{-1})									H:C
	WS	ES	AUR	Glu	Man	Xyl	Gal	Ara	Rha	
Coniferous needles										
S. pine	164	113	231	245	75	23	32	36	3	0.69
LP. pine	103	42	381	254	90	34	46	48	6	0.88
N. spruce	32	48	318	288	105	33	28	40	7	0.74
Deciduous leaves										
S. birch	241	57	330	166	14	77	44	49	16	1.2
G. alder	254	39	264	116	10	30	32	44	9	1.08

WS water soluble, *ES* ethanol soluble, *AUR* gravimetric lignin, *Glu* glucans (cellulose), *Man* mannans, *Xyl* xylans, *Gal* galactans, *Ara* arabinans, *Rha* rhamnans, *S. pine* Scots pine, *LP pine* lodgepole pine, *N. spruce* Norway spruce, *S. birch* silver birch, *G. alder* gray alder, *H:C* hemicellulose:cellulose ratio

Lignin/AUR often makes up between 15 and 40 % of the foliar litter mass. In some extreme cases, litter can have lignin/AUR contents as low as 4 % or as high as 50 %. Native lignin, in contrast to cellulose, is a highly variable molecule. The initial composition of lignin varies with the plant species, and the variation is enough to make the lignin of each species unique. This also rules the terminology. Thus, the native lignin of different plant species may be specified by the name of the species, for example, Norway spruce lignin and aspen lignin. A generalized structure of Norway spruce lignin is illustrated in Fig. 3.3. The terminology pertaining to lignin and its transformation products is, however, not always clear, especially after some degradation has taken place (Dean 1997, see Chap. 2 and Glossary). Thus, also the analytical method may determine not only the terminology but also the basic understanding of the studied component (cf Preston et al. 2009a, b). For 'gravimetric lignin,' we use the common name 'acid unhydrolyzable residue' (AUR). Native lignin as determined using ^{13}C NMR we refer to using the term lignin and sometimes native lignin to avoid misunderstandings.

The AUR/lignin content of deciduous species is generally lower than that of the coniferous ones (e.g., Berg et al. 2013; Sect. 4.5.2, Fig. 4.2), although the variation is large in both groups. Further, the types of lignin formed in gymnosperms and angiosperms are different. Whereas angiosperms (deciduous species) contain varying ratios of syringyl and guaiacyl types of lignin, gymnosperms (conifers) have mainly guaiacyl lignin (Fengel and Wegener 1983) (Fig. 3.5). While some basic structural elements are common over a wide range of species, individual species show variation among a variety of groups such as methoxyl groups and other substituents located at different sites in the molecule.

Litter also contains large quantities of low molecular weight substances, such as amino acids, simple sugars, short-chain fatty acids, and low molecular weight phenolic substances. Complex compounds such as high molecular weight fatty acids and complex phenolic compounds are also found. We may be able to identify some hundred different molecules from these two groups. Often, they are analyzed simply as water solubles for the former group and ethanol solubles or acetone solubles for the latter.

Cutin and suberin are resistant molecules that can influence decomposition and can increase in concentration during decay (Kolattukudy 1980, 1981, 1984). Although present in rather small amounts and seldom identified in litter decomposition studies, these polyesters act as barriers to protect living plants and to delay invasion by microorganisms. Cutin is found on and in leaves and suberin in bark and roots. Both are polymers composed of hydroxy- and epoxy-fatty acids. Kögel-Knabner et al. (1989) extracted these acids from the L layers of common beech and Norway spruce forests. They found that cutin and suberin contributed 12–24 mg g^{-1} of the organic matter. The presence of suberin in root tissues may retard their decay.

The analytical approach using ^{13}C NMR presents frequencies of different bonds (Appendix III; Table 4.2), some specific for a certain compound and some in common for different ones.

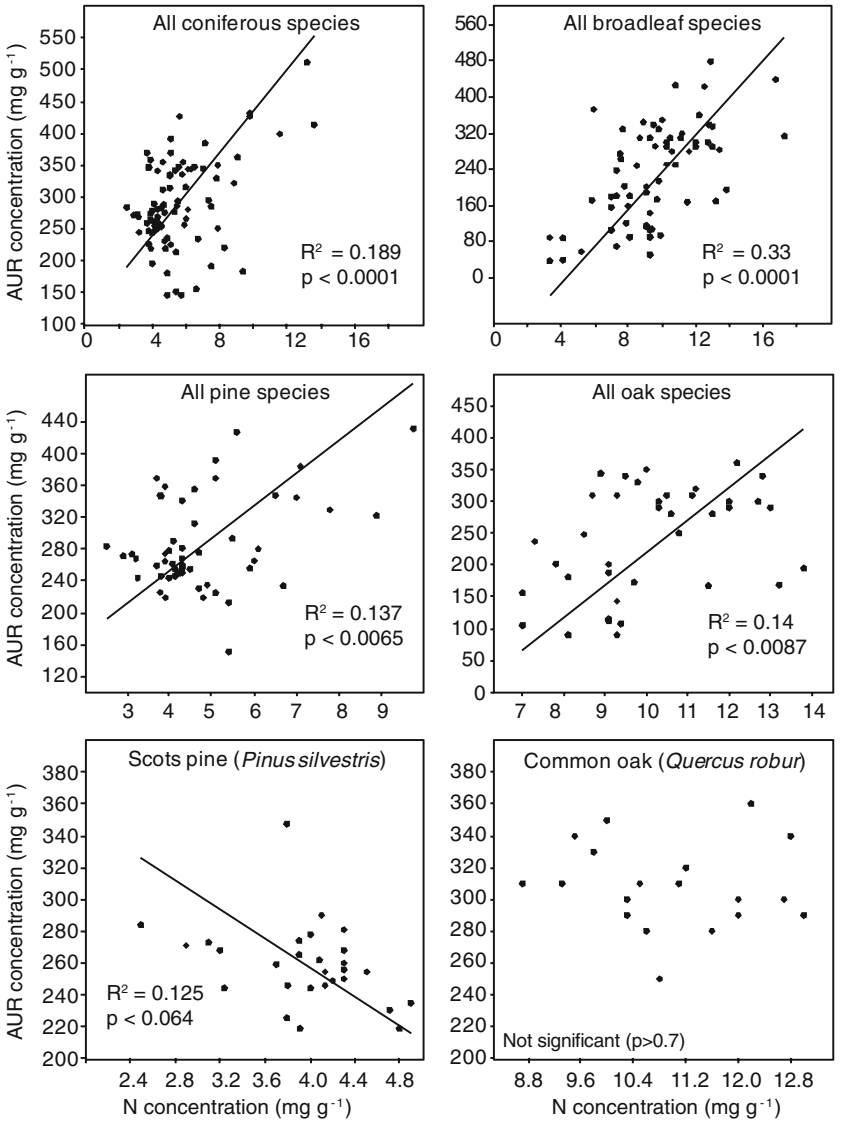

Fig. 4.2 Comparison of relationships between N and AUR concentrations in broadleaf ($p < 0.0001$) and coniferous ($p < 0.0001$) litter as well as in pine species ($p = 0.0065$) and Scots pine ($p = 0.064$) litter. Leaves of all oak species gave a significant relationship ($p < 0.0087$), whereas those of common oak did not (ns). From Berg et al. (2013)

So far, there has not been any standard for this analysis method, and the frequency values such as those given in Table 4.2 are not directly comparable between studies and laboratories. The numbers (Table 4.2) show the frequencies of different, specific bonds, found in one or more molecules. The numbers are not readily comparable with concentrations of known compounds in litter.

Table 4.2 Estimate of the frequency of different bonds in newly shed foliar litter

Species	Alkyl-C 0–50	Methoxyl-C 50–60	O-alkyl 60–93	Di-O-alk 93–112	Arom 112–140	Phen 140–165	Carbox 165–190	Alkyl/ O-alkyl
Jack pine	23.4	2.2	44.8	10.5	8.6	5.9	4.6	0.41
Black spruce	20.5	4.4	39.4	9.9	12.4	6.7	6.7	0.38
Douglas fir	23.2	1.5	45.2	8.7	9.4	6.4	5.5	0.42
Red cedar	26.8	2.1	40.9	11.0	7.1	7.5	4.7	0.50
Tamarack	15.9	1.7	43.3	16.5	8.0	11.1	3.5	0.26
American beech	15.7	3.2	48.7	11.9	9.6	6.0	5.0	0.25
Trembling aspen	22.8	1.5	42.1	12.2	7.3	7.5	6.6	0.41
White birch	25.8	2.4	43.7	11.7	7.1	6.3	2.9	0.45

The numbers give intensity distribution as percentage of total area for the given frequency intervals, which represent different bonds. Data from CIDET project (Preston et al. 2009)

4.2.2 Fiber Structure

Fiber structure appears to be a critical concept for the pattern of decomposition. The fiber's main organic-chemical components may be arranged in different ways, and the arrangements may be of importance for the properties of the fiber as regards decomposition. Thus, a fiber may have holocellulose and lignin separated to a high degree, or the holocellulose and the lignin may be well integrated; the holocellulose has a high degree of lignification. We may even expect that cases occur in which all holocellulose is integrated in or covered by lignin.

Description of one type of fiber. The insoluble components of plant litter are concentrated in the cell wall, a multi-layered structure. The wood cell wall is composed of various layers (Fig. 4.3) and is made up of a primary wall (P) and the secondary wall (S), which has three layers designated S1, S2, and S3. The middle lamella and the primary wall make up the compound middle lamella that is located between the secondary wall layers of adjacent cells (Core et al. 1979). The S3 layer is located closest to the lumen (L). The normally thickest layer (S2) is the middle layer and S1 is the outermost layer of the secondary wall. These layers are distinct from each other because the cellulose is arranged in different microfibrillar

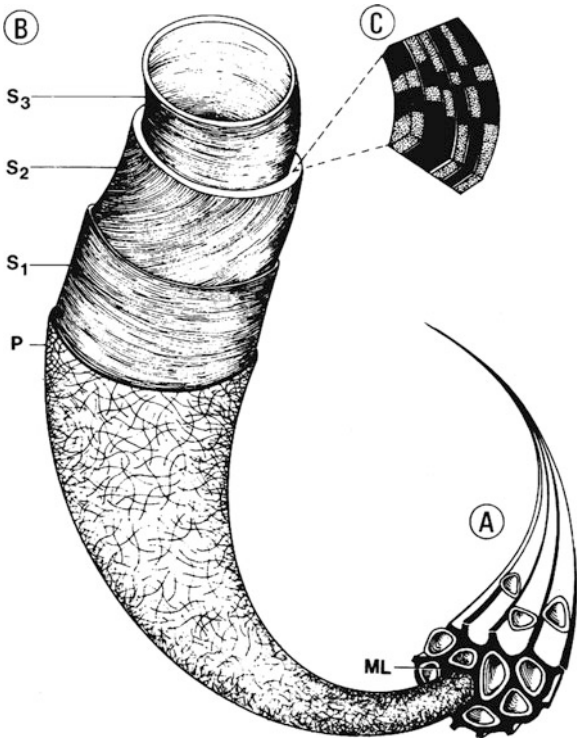

Fig. 4.3 Overview of a plant fiber. **a** Tracheids. **b** Cell wall layers. **c** Arrangements of polymer carbohydrates and lignin in the secondary wall. Middle lamella (*ML*), primary wall (*P*), layers of the secondary wall (*S1, S2, and S3*). The microfibrillar orientation and the thickness are different among the layers, and some species have an additional warty layer over the inner (*S3*) layer. The model demonstrates the distribution of the lignin–hemicellulose matrix (*black*) hemicellulose (*white*) and cellulose fibrils (*dotted*). (From Eriksson et al. 1990)

orientations. A model describing the arrangement of lignin, hemicellulose, and cellulose within the cell wall was proposed (Kerr and Goring 1975, Fig. 4.3). The model shows how a matrix of lignin and hemicellulose encrusts the cellulose fibrils. There is a tremendous diversity in wood structure among the hundreds of hardwood species that grow throughout the world (Panshin and de Zeeuw 1980). Still, the drawing in Fig. 4.3 may serve as a model for our discussion.

In plant fibers, the cellulose, the hemicellulose, and the lignin molecules are not only combined physically, but the celluloses are normally more or less encrusted with lignin. Within the cell wall, cellulose forms microfibrils composed of individual strands of cellulose that are often about 10–25 nm in diameter (Fig. 4.3). Microfibrils group together into larger strands called macrofibrils. These are visible with a light microscope and are about 0.5 μm in thickness.

Of the several cell wall layers, the thickest (S2) normally has a width of 0.5–4.0 μm. In their turn, the walls are constructed of a matrix of cellulose, hemicellulose, and, in many plant tissues, lignin. The thickness of the entire primary and secondary wall complex is highly variable.

The formation of lignin in the fibers (lignification) of the live plant is a slower process than the formation of cellulose. As a result, the last parts of the cell wall to be formed may be very low in lignin and the older parts are rich in lignin. Thus, in wood, lignin is distributed throughout the secondary (S) wall and compound middle lamella, but the greatest concentration is in the middle lamella. The secondary wall makes up a large part of the total cell wall, and most of the cell wall lignin (60–80 %) is located in this region (Musha and Goring 1975; Saka and Thomas 1982a, b). The distribution of hemicellulose parallels that of lignin within the wall (Parameswaran and Liese 1982). The hemicellulose surrounds the cellulose microfibrils and occupies the spaces between the fibrils.

The pattern and extent of lignification of fibers are probably different among tree species and thus also among litter species. This appears to be an area in which we lack good information, although it has a potential importance for the decomposition process. For a fiber in which the lignification is complete or close to complete, the cellulose and hemicelluloses may be completely encrusted in lignin and the structure of the fiber may be very different as compared to those that are less lignified. Such differences may give rise to different properties, for example as regards rate-limiting properties. Thus, fibers with a complete lignification may be very different as compared to those in which it is incomplete or in which the fiber tissue is without lignin (cf. Fig. 6.1 and the discussion in Sect. 2.4). The lignin concentration in litter as such seems not to give enough information to be really useful as regards the level of lignification although we may expect that fibers with a high lignin concentration would have a more complete lignification.

4.3 Nutrient and Heavy Metals' Concentrations in Newly Shed Litter

4.3.1 General Features

The nutrients found in newly shed plant litter have their origins in strictly controlled structures in the live plant parts, and a nutrient like N can be found in membranes, cytoplasmic enzymes, structural proteins, or nucleic acids. In green foliage, ribulose bisphosphate carboxylase/oxygenase (rubisco) may account for the majority of the N. When a leaf dies and foliar litter is being formed, these cellular constituents disintegrate, at least in part. Before a leaf dies, a proportion of the nutrients is translocated into the perennial portion of the plant, leaving the remainder in the dead material, a process that may take place over several weeks. This process is often called retranslocation.

Nutrients, as usually measured by ecologists, are expressed in their elemental or ionic form, generally making no distinction as to the origin of the nutrient within the plant's structure. What is often measured as just a 'mineral nutrient,' for example N, can thus originate from a number of different components in the litter, such as proteins or nucleic acids.

Nitrogen is found in concentrations, normally ranging between 0.2 and 3.0 % in foliar litters. In woody structures, such as branches, the concentration may be as low as 0.02 %. We cannot assume that the total N in different litter species or in different parts of the same species is chemically bound in the same molecules across species, plant parts, and concentration ranges. Phosphorus is bound in nucleic acids and S is found in proteins, among other molecules. Some heavy metals like Mn and Zn have a function in enzymes, for example as coenzymes, whereas any function of other ones in the live leaf such as Pb is not known.

A lack of data prevents us from creating any system for concentrations of litter nutrients. Still, we may distinguish influencing factors and create general relationships that so far are just empirical. However, they may be a beginning (Fig. 4.1). One evident source to variation in litter chemical composition is *species* and concentrations of, for example N may range more than 10-fold among species, other factors constant, and it seems that litter species or genus has a dominant influence (Sect. 4.4). *Climate*, expressed as, for example annual average temperature (MAT), annual precipitation (MAP), or annual evapotranspiration (AET), has been shown to have an influence on concentrations of at least a few nutrients (Sect. 4.5.1). Further, the availability of nutrients and heavy metals in soils has an influence so far observed as an effect within a given species (Sect. 4.7).

When decomposition and microbial ingrowth have started, further changes occur and the distribution of nutrients in compounds, as well as concentrations of nutrients, will be very different from both the living and the freshly senescent materials. In this book, we will not generally discuss the nutrients/heavy metals in terms of the macromolecules they are part of, but rather simply as nutrients.

4.3.2 Nutrient Resorption and Withdrawal Efficiency

The chemical composition of the living plant is reflected in its litter. This applies especially to structural components such as lignin, the relative composition of hemicelluloses and concentrations of nutrients.

Many genera, such as pine, growing on relatively nutrient-poor soils, retrieve the main part of their nutrients before shedding their foliar litter. This 'inner circulation' is a conserving mechanism that has been suggested to be in effect mainly on nutrient-poor soils (Gosz 1981) and for *Pinus* to be related to latitude (Oleksyn et al. 2003). An example at the opposite extreme are the N_2-fixing genera, for example alder or acacia, which produce leaf litter with as high a concentration of N as the live leaves, c. 2–3 %.

Trees also withdraw substances other than nutrients before shedding their leaves and needles. Thus, at senescence, different soluble C components, such as sugars and phenolics, are withdrawn, resulting in a mass loss from the living tissue, and 15–30 % loss of mass has been measured (Table 4.3). This may result in an increase in concentration of those nutrients and heavy metals that are withdrawn to a smaller extent and a decrease only for those that have been withdrawn to a greater extent. Thus, an increase in concentration for some nutrients during senescence may not represent a real increase in amount but rather an increase in proportion as total organic compounds are depleted.

A study on green and senesced leaves from four tree species (Hagen-Thorn et al. 2006) quantifies both the carbon compounds retrieved and the nutrients (Table 4.3) using the leaf and litter mass per cm^2 leaf surface. We may see that of the main nutrients, N, P, and S varying fractions stayed in the shed litter, from c 23 % in lime leaf litter to 59 % in that of ash. A nutrient like Ca was little retained and stayed in the litter to between 90 and 130 %, whereas Mg, Mn, Fe, and Cu appeared to be retranslocated to a higher extent, leaving between 60 and 95 % in the leaf litter. Hagen-Thorn et al. (2006) found significant differences among the species.

A thorough study on leaves of common beech (Staaf 1982) indicates that there was a positive correlation between the withdrawal of nutrients and the concentration of the nutrient in green leaves. This relationship was especially steep for N, showing that a higher initial concentration led to a relatively higher withdrawal. In contrast, the relationship was rather flat for Ca, indicating a lower effect of initial concentration on the withdrawal. Soil pH was related to the withdrawal of Ca, and at sites with a lower soil pH, there was a lower withdrawal. This effect was seen only for Ca.

4.3.3 Nutrient Concentration Change; Green Foliage versus Brown Litter

A comparison was made between concentrations of the main nutrients in green leaves collected at summer in early July as compared to newly shed ones

Table 4.3 Concentrations of some main nutrients in green leaves and senesced (*brown*) leaf litter as calculated on an area basis and concentrations of nutrient or mass in brown litter as a percentage of that in green litter

	Ash	Birch	Lime	Oak
N green	173.8	170.4	235.4	185.2
N brown	103.1	49.6	55.8	72.1
N % in litter	59.3	29.1	23.7	38.9
P green	13.5	23.6	12.5	16.3
P brown	7.17	12.6	4.71	8.92
P % in litter	53.1	53.3	37.7	54.7
S green	35.5	11.2	14.2	12.3
S brown	17.65	5.52	7.45	6.23
S % in litter	49.7	49.3	52.5	50.6
K green	72	65	95.9	82.1
K brown	23.6	31.9	36.5	44.2
K % in litter	32.8	49.1	38.1	53.8
Ca green	152.4	69.7	95.7	68.5
Ca brown	198.1	74.7	90.8	63.9
Ca % in litter	130	107.2	94.8	93.3
Mg green	37.5	22.9	10.3	13.1
Mg brown	22.3	21.4	9.5	10.9
Mg % in litter	59.5	93.4	92.3	83.2
Mn green	0.37	15.5	5.94	5.89
Mn brown	0.28	13.2	5.64	5.28
Mn % in litter	75.7	85.2	94.9	89.6
Fe green	0.66	0.66	0.58	0.79
Fe brown	0.47	0.41	0.53	0.55
Fe % in litter	71.2	62.1	91.4	69.6
Cu green	0.08	0.04	0.05	0.05
Cu brown	0.05	0.03	0.04	0.03
Cu % in litter	62.5	75	80	60
Mass green	8757.9	7239.9	5477.8	7222.4
Mass brown	5903.2	5821.6	4699.2	5347.2
Mass % in litter	67.4	80.4	85.8	74

All concentrations are given in micrograms per cm^2 leaf area. From Hagen-Thorn et al. (2006)

(Table 4.4a). Concentrations of N, P, S, and K were considerably lower in newly shed litter as compared to green leaves, whereas Ca, Mg, and Mn had increased concentrations in the shed litter as compared to the green leaves.

For Scots pine and silver birch foliage, the concentrations of N may decrease to about 1/3 of that in green leaves before the leaves and needles are shed in the autumn. For example, in Scots pine, the concentration may decrease from about 12–14 mg g^{-1} to about 3–4 mg g^{-1} (Table 4.4a). This retrieval process may of course be disturbed, occasionally leading to extreme levels of N (Table 4.5).

Changes in concentrations of remaining P to those in green leaves were found to be of the same magnitude as for N, 15 % for Scots pine and 53 % for silver

birch. For S, less of the nutrient was retrieved and more S remains with concentrations ranging from 38 to 103 % of those in green leaves. For K, there was a difference between coniferous and deciduous foliage litter, with deciduous leaves having clearly higher concentrations when shed, in the range of 40–50 % of the concentrations in green foliage. The newly shed conifer needles had less than 25 % of their summer K concentrations, while pines as a group had even lower levels. For Norway spruce, lodgepole pine, and trembling aspen, the patterns were similar (Berg and McClaugherty 2008).

Calcium was retrieved to a small extent, resulting in an increase in its concentration up to 143 %. This may be explained by the decrease in leaf mass from green to senesced leaves (Sect. 4.3.2). The remaining Mg ranged from 43 to 98 % of the initial concentration. Manganese contrasted with the other nutrients by having increased concentrations in both cases, ranging from 158 to 224 %.

In the very same study (Scots pine and silver birch), heavy metals were investigated (Table 4.4b), giving different patterns. Lead (Pb), barium (Ba), and strontium (Sr) showed heavy increases in concentration in the brown litter suggesting no or low retrieval. Aluminum (Al) gave different patterns for pine and birch, suggesting a heavy retrieval from pine needles and none from birch leaves. Zinc (Zn) may have a similar pattern, whereas Cu apparently was retrieved to a high extent—the concentration in brown litter decreasing to about the half of that in the live leaves (Table 4.4b).

4.4 Factors Influencing Litter Chemical Composition

4.4.1 General Factors

Some factors that influence litter chemical composition have been more investigated than other ones. Below, we have listed three such main influences (Fig. 4.1) and will discuss these using case studies as far as available data allow.

Litter genus and species. A main factor is litter species (Table 4.6). Among species, N concentrations in foliar litter may vary with at least a factor of 10 as far as we know. Concentrations of different nutrients do not covary more than to a certain extent, not even within a genus. Also, the ranges within a genus or species vary. Thus, Berg et al. (2010) found that for 8 species of pine, for example, N concentrations ranged between 2.9 and 5.1 mg g^{-1} and those of Mn ranged from 0.03 to 2.03 mg g^{-1}, with range factors of 1.8 and 68, respectively. We may see (Table 4.6) in a comparison of 11 pine species that N concentrations range from 3.0 to 7.8 mg g^{-1} whereas those of Mn range from 0.03 to 1.79 mg g^{-1}.

Climate appears to be a dominant factor for several nutrients with positive relationships between nutrient concentrations and warmer and wetter climate. Although the database so far has been small, it appears that single genera and species may deviate strongly from a possible general pattern. To compare the

Table 4.4 **a** Comparison of concentrations of some main nutrients in green leaves collected in July and in the corresponding foliar litter collected at litter fall (B. Berg unpubl.). Data for common beech from Staaf (1982). **b** Comparison of concentrations of some heavy metals in green leaves collected in July and in the corresponding foliar litter collected at litter fall (B. Berg unpubl.). N.B. The table compares only concentrations and does not consider retention or withdrawal of nutrients and carbon compounds (Sect. 4.3.2)

a Species	Concentration of nutrient (mg g^{-1})						
	N	P	S	K	Ca	Mg	Mn
S. pine (br)	3.6	0.20	0.44	0.5	5.6	0.34	1.19
S. pine (gr)	12.1	1.36	0.81	5.9	3.9	0.79	0.53
% concn change[a]	30	15	55	8	143	43	224
LP. pine (br)	3.1	0.29	0.44	0.5	8.7	1.06	2.03
LP. pine (gr)	10.5	0.82	1.17	3.8	4.0	0.93	0.82
% concn change	30	35	38	13	220	113	250
N. spruce (br)	4.2	0.41	–	1.0	13.1	0.89	1.32
N. spruce (gr)	8.5	1.32	–	4.0	11.3	1.22	1.07
% concn change	49.0	31	–	24	115	73	123
S. birch (br)	7.7	1.05	0.80	4.7	11.8	3.30	1.23
S. birch (gr)	24.3	1.96	1.54	9.0	9.5	3.37	0.76
% concn change	32	53	52	52	124	98	158
T. aspen (br)	6.8	0.63	1.37	6.3	17.1	2.13	0.15
T. aspen (gr)	24.2	2.12	1.87	14.2	8.4	2.29	0.10
% concn change	28	30	73	44	204	92	150
C. beech (br)	9.1	0.63	1.21	2.7	10.0	1.70	–
C. beech (gr)	22.6	1.44	1.18	5.4	7.7	1.67	–
% concn change	40	44	103	50	130	102	–

b Species	Concentration (μg g^{-1})							
	Pb	Cu	Fe	Al	Zn	Cd	Ba	Sr
S. pine (br)	2.5	1.4	57	280	51	0.2	7	4.6
S. pine (gr)	1	2.8	50	510	43	0.3	3.5	3.0
% concn change	250	50	114	55	119	67	200	153
S. birch (br)	2.6	3.4	61	130	340	0.8	13	31
S. birch (gr)	nd	6.4	53	46	140	0.2	54	16
% concn change	–	53	115	283	243	400	24	194
T. aspen (br)	0	8.6	46.4	nd	126	0.5	nd	nd
T. aspen (gr)	0	8.8	44.0	nd	107	0.3	nd	nd
% concn change	–	98	103	–	118	167	–	–

S. pine Scots pine, *LP pine* lodgepole pine, *N. spruce* Norway spruce, *S. birch* silver birch, *T. aspen* trembling aspen, *C. beech* common beech, *br* brown, *gr* green

[a] Concentration change is expressed simply as the concentration in brown litter as percentage of that in green

effect of climate over a gradient, it may be advantageous to use a limited set of species or possibly just one genus (below).

Influence of soils, within species. Soil chemical composition, including the availability of nutrients, has an influence on the chemical composition of the live leaves and thus also on chemical composition of foliar litter. The chemical

Table 4.5 Annual variation in concentration of solubles, AUR and nutrients of Scots pine (*P. sylvestris*) needle litter collected in a nutrient-poor Scots pine forest in central Sweden (Johansson et al. 1995)

Year	Concentration (mg g^{-1})									
	WS	ES	AUR	N	P	S	Ca	K	Mg	Mn
1973	92	120	223	3.8	0.19	0.42	6.5	0.73	0.38	1.55
1974	145	84	276	4.2	0.22	0.29	5.4	0.71	0.49	n.d.
1975	172	107	238	3.4	0.20	0.32	4.7	0.61	0.39	n.d.
1976	151	89	255	4.0	0.21	0.36	4.9	0.53	0.42	n.d.
1977	202	102	224	4.1	0.19	0.38	6.0	0.87	0.42	1.02
1978	164	96	257	3.8	0.21	0.33	5.5	0.62	0.55	1.00
1979	129	95	288	10.4	0.29	0.78	2.3	0.97	0.39	0.31
1980	180	102	246	3.8	0.18	0.50	6.1	1.72	0.53	0.77
1981	213	94	231	3.9	0.28	0.61	7.1	1.02	0.58	1.17
1982	164	113	231	4.8	0.33	0.55	4.4	1.07	0.49	0.79
1983	178	112	229	3.8	0.30	0.45	5.9	0.9	0.39	1.08
1984	82	116	288	3.7	0.21	0.47	6.3	0.82	0.44	1.12
1985	182	94	241	3.0	0.19	0.45	4.8	0.52	0.38	1.24
1986	170	89	257	4.0	0.23	0.44	5.6	0.58	0.57	1.13
1987	162	100	250	3.8	0.21	0.42	4.9	0.55	0.41	1.18
1988	165	94	247	3.8	0.21	0.39	5.0	0.67	0.38	1.18
1989	n.d.	n.d.	n.d.	3.6	0.17	0.38	4.0	0.59	0.42	0.92
AVG	159	100	249	4.2	0.23	0.44	5.3	0.79	0.45	1.03
S.D.	35	11	21	1.6	0.05	0.12	1.1	0.29	0.07	0.27

WS water solubles, *ES* ethanol solubles, *AUR* gravimetric lignin, *n.d.* not determined, *AVG* average value, *S.D.* standard deviation

composition of the soil and the availability of the nutrients would be two main factors acting either directly or indirectly on the composition of foliar litter.

4.4.2 Nutrients, Heavy Metals and AUR in Needle Litter of Two Conifers, Pine and Spruce spp: Two Case Studies in Climate Gradients

4.4.2.1 The Genus Pinus

Litter and litter fall from pine spp (Pinus) across Europe. Extensive data are available on the initial organic-chemical and nutrient composition of Scots pine needle litter over extended periods of time and a wide geographical area as well as for some other pine species. The genus *Pinus* encompasses between 105 and 125 identified species native to the Northern Hemisphere and with a geographical extension from c 70°N to the Equator, thus over a climatic range where forests may form. Today, pines are introduced and grow over large areas also south of the Equator. We have taken advantage of this for a case study encompassing available

Table 4.6 Concentrations of main nutrients in a selection of foliar litters from Europe and North America with focus on coniferous ones

Litter	Concentration of nutrient (mg g^{-1})						
	N	P	S	K	Ca	Mg	Mn
Coniferous							
Scots pine[d]	4.8	0.33	0.55	1.07	4.4	0.49	0.79
Lodgepole pine[d]	3.9	0.34	0.62	0.56	6.4	0.95	1.79
Maritime pine[a]	6.8	0.54	1.01	1.95	3.1	1.90	0.59
Red pine[a]	6.0	0.36	0.73	1.4	8.9	2.00	0.73
White pine[a]	5.9	0.21	0.68	0.70	7.2	1.10	0.80
Jack pine[a]	7.8	0.64	0.77	2.30	4.0	2.10	0.25
Limber pine[a]	4.3	0.43	0.52	1.10	5.3	1.10	0.21
Stone pine[b]	3.0	0.57	1.36	5.9	7.1	2.4	0.19
Corsican pine[a]	4.7	0.54	0.71	3.5	7.8	1.3	0.50
Monterey pine[a]	5.6	0.22	0.70	1.3	1.9	0.93	0.47
Aleppo pine[c]	4.3	0.38	1.3	1.73	25.2	2.33	0.03
Norway spruce[h]	4.9	0.45	0.73	0.72	17.9	0.65	2.15
Black spruce[g]	7.3	0.67	–	2.69	5.69	0.72	1.94
Western red cedar[g]	6.4	0.39	–	0.77	15.38	0.67	0.15
Tamarack[g]	5.9	0.15	–	3.17	5.30	1.99	0.04
Douglas fir[g]	7.0	0.88	–	1.52	12.15	0.82	0.72
Deciduous							
Gray alder[d]	30.7	1.37	6.12	15.6	12.3	2.32	0.10
Silver birch[d]	7.7	1.05	0.80	4.7	11.8	3.30	1.23
White birch[g]	7.2	0.34	–	3.28	7.24	2.04	1.21
Trembling aspen[b]	8.2	0.93	–	5.1	29.9	2.69	0.53
Ash[e]	8.6	1.96	–	15.3	33.2	2.28	0.03
Mountain ash[e]	7.1	0.31	–	10.8	12.4	2.86	0.30
European maple[e]	5.1	3.15	–	13.1	20.4	1.46	0.12
Common oak[f]	15.9	0.73	–	0.75	7.2	0.68	0.89
American beech[g]	7.1	0.34	–	1.01	8.41	2.14	0.36

[a] C. McClaugherty and B. Berg (unpubl.)
[b] Berg et al. (2003)
[c] Faituri (2002)
[d] Berg and Ekbohm (1991)
[e] Bogatyrev et al. (1983)
[f] Berg (1998)
[g] Preston et al. (2009)
[h] Berg et al. (2000)

data, enabling us to examine the variability of chemical composition within a single stand over time, among stands in a small geographical area and among stands across a climatic gradient. We forward these observations, being aware of that they are empirical and that the causal relationships remain to be found.

In Europe, Scots pine grows mainly from the Barents Sea in the north to the Pyrenees and Northern Greece in the south, although it forms forests to about the latitude of the Alps and the Carpathian Mountains (c. 47–48°N). Starting in

Central and Middle Europe, other species such as Austrian pine/Corsican pine follow, and in the Mediterranean area, stone pine, Aleppo pine, maritime pine, and Monterey pine become dominant, some of them introduced. Pine species may grow on both nutrient-poor granite sand and clayey soils. On a European scale, the magnitude and pattern of litter fall vary with the geographical position and climate.

Litter fall begins relatively early in the north, close to the Barents Sea (c. 70°N), normally in the first week of August. In south Poland (c. 50°N), it may start as late as November. A strong drought may change this pattern and induce an earlier litter fall. A drought that does influence the onset of litter fall is seen in the Mediterranean climate where native pine species shed their needles in July. Introduced pine species, such as Scots pine, when growing in a Mediterranean climate, has adopted the litterfall pattern of the Mediterranean pine species and has its main foliar litter fall in summer during the dry period.

Concentrations of nutrients in a climate gradient and at single sites. The needle litter's chemical composition varies with the site's climate and thus its geographical position (Berg et al. 1995a). A study along a gradient ranging from the Barents Sea in the north to about the Carpathian Mountains (Central Europe) in the south, thus encompassing half the length of Europe, shows a clear trend in chemical composition with climate both for Scots pine and for different pine species combined. Concentrations of N, P, S, and K are positively related to both annual actual evapotranspiration (AET) and annual average temperature (MAT) (Table 4.7). For example, N levels range from about 3 mg g^{-1} in the north (AET c. 350 mm) to about 9 mg g^{-1} in the more southern locations with AET at c. 600 mm.

The observation of Berg et al. (1995a) was followed up by Oleksyn et al. (2003) who used mainly the same climatic gradient with Scots pine and investigated the N concentrations in green Scots pine needles and compared those with brown ones. They suggested a retrieval mechanism with a stronger retrieval of N under colder and drier climates. Also, other studies have shown that the resorption of N from foliar litter in trees is related to climatic factors (Killingbeck 1996). Their suggested mechanism is not contradictory to that proposed for common beech by Staaf (1982) with the relative amount withdrawn being in proportion to the initial amount in the green leaves. We have included both as they seem to complete each other but cannot exclude that for different species, such mechanisms may be different.

Berg et al. (1995a) also found significant relationships between AET and concentrations of P, S, and K. Also, MAT gave significant relationships to N, P, S, and K, whereas none was seen to Ca, Mg, or AUR. Annual precipitation (MAP) did not give any significant relationship (Table 4.7).

We have combined available pine data for Europe from published studies, ranging from northern Finland to North Africa (DELILA III database, (www.eko.uj.edu.pl/deco) using data from 7 pine species and a range in MAT from −1.7 to 17 °C and in MAP from 396 to 1500 mm. With this larger dataset ($n = 62$), we obtained highly significant positive relationships for N, P, and K

Table 4.7 Regression coefficients (r) for relationships between concentrations of litter nutrients and AUR in pine needle litter and the climatic parameters annual average temperature (MAT), annual precipitation (MAP), and annual evapotranspiration (AET)

	N	P	S	K	Ca	Mg	Mn	AUR	Range (mm/°C)	n^a
Scots pine (Europe)										
AET	0.786[b]	0.751[c]	0.771[c]	0.731[c]	ns	ns	ns	ns	350–626	30
MAT	0.787[b]	0.638[b]	0.768[b]	0.645[c]	ns	ns	ns	ns	1.7–10.5	30
MAP	ns	ns	ns	ns	ns	ns	ns	ns	443–1067	30
Pine species (Europe and North Africa)[1]										
AET	0.733[b]	0.479[b]	0.610[b]	0.777[c]	ns	ns	−0.417[b]	0.378	350–654	61
MAT	0.624[b]	0.578[b]	0.680	0.802	−0.377	0.713[c]	−0.606[c]	0.472[c]	1.7–17.0	62
MAP	0.277[c]	ns	ns	0.336[c]	−0.389[c]	ns	ns	ns	396–1500	62
Pine species (Europe and Asia)[2]										
MAT	0.366‡	nd	nd	nd	nd	nd	nd	nd	−0.5–25	79
MAP	0.347	nd	nd	nd	nd	nd	nd	nd	460–2005	79

Only significant values are given in bold with at least $p < 0.01$. Data from Berg et al. (1995, 2010) and from Liu et al. (2006)

[a] A maximum number. For some single nutrients and AUR, n was lower than the given number

[1] 7 pine species were included

[2] 8 pine species were included

[b] Exponential relationship

[c] Linear relationship

ns not significant, *nd* no data

versus AET, and S gave a significant relationship only, possibly due to lack of data. Manganese gave a highly significant and negative relationship over the AET range of 350–654 mm, whereas Ca and Mg did not give any relationship (Table 4.7). Using MAT modified this picture somewhat. Nitrogen, P, S, and K were significantly and positively related to temperature. Calcium gave a significant negative relationship and Mg a positive one. The negative exponential relationship for Mn was emphasized (Fig. 4.4) and highly significant as found by Berg et al. (2010) with a range in Mn concentration from c. 0.03 to 3 mg g^{-1}.

AUR/lignin variation. In newly shed litter, sulfuric acid (Klason) lignin (AUR) gives a rather good quantification of native lignin (Preston et al. 2009a, b). For a European dataset, this gravimetric lignin was found to increase significantly with increasing AET in both gradient studies. There was also a significant positive relationship ($p < 0.05$) between AUR concentration in pine spp and MAT across Europe (Berg et al. 2010). A relationship between AUR and litter N concentration was also significant at $p < 0.05$).

Eurasian—global gradient—nitrogen. In a continental-scale investigation over Eurasia, Liu et al. (2006) used data from eight species of pine (Table 4.7), including Scots pine, lodgepole pine, stone pine, maritime pine, Khasi pine, Chinese pine, chir pine, and Korean pine. Liu et al. (2006) separated the climatic factors with MAT, ranging from c. −1.7 °C to about 25° and MAP from c. 500 to 3,000 mm. Over this gradient with 56 samples, they found highly significant and

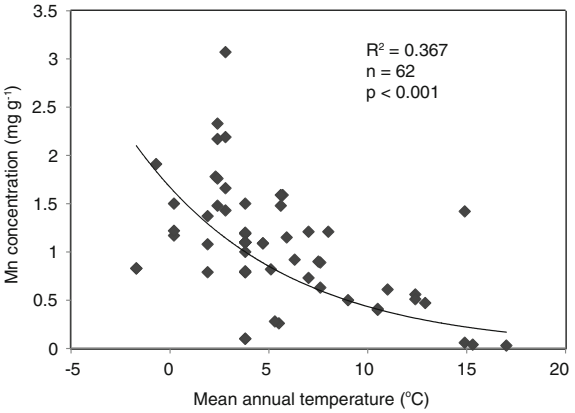

Fig. 4.4 Negative exponential relationship between litter Mn concentration and mean annual temperature (MAT) using data from 62 sites with a range from 70°N (northern Finland) to the Mediterranean area (northern Libya) and the American Midwest. Data from Berg et al. (2010)

positive relationships to MAT and a negative one to MAP. We may note that the single genus *Pinus* investigated by Liu et al. (2006) behaved in different ways as compared to the larger group of different coniferous species as well as to the groups of broadleaf and coniferous litter, and we cannot exclude that single species and genera with their defined ecological niches have different behavioral patterns, for example as regards response to temperature as compared to continuously changing species along a continental gradient.

A combination of our dataset with that of Liu et al. (2006) (n = 79) (Table 4.7) resulted in highly significant relationships between N concentration and MAT as well as MAP. We may comment on that AET may predict litter N concentration more generally than MAT. Using a dataset with sites for which we had both AET and MAT values (n = 61), we obtained a clearly higher R^2 value for AET ($R^2 = 0.596$) than for MAT ($R^2 = 0.388$).

Liu et al. (2006) evaluated the relative influences of temperature (MAT) and precipitation (MAP) on leaf litter N concentration and used 'standardized' data, transforming them using the program Standardize Transform (SPSS Inc., 1997) (see legend to Table 4.8). Using a linear regression, they found a significant difference in response for pine species as regards MAT and MAP. The standardized temperature (STemp) and precipitation (SPrecip) are dimensionless, with a mean of zero and a standard deviation of 1.0. Thus, in a multiple regression equation, the values of the intercept coefficients are forced through zero and the slope coefficients for STemp and SPrecip indicate their relative contributions to the variation in leaf litter N concentration. For a general relationship, they compared the two factors, temperature and precipitation, by using STemp and SPrecip and found that for pine spp temperature appeared to have a stronger effect than precipitation (Table 4.8), with a coefficient of 0.808 as compared to −0.217 for precipitation. This difference was highly significant and separated pine spp needles from the rest of their material. The difference in effect of relative temperature and precipitation was highly significant ($R^2_{adj} = 0.435$; $p < 0.001$) (Table 4.8). We may comment on that such effects possibly are distinguished on species or genus level. For the

broader groups, they found positive relationships for both temperature and precipitation (Sect. 4.5.1).

Eurasian—global gradient—AUR. Using a Eurasian dataset with data for no less than 12 pine species, MAT, MAP as well as litter AUR and N, Berg et al. (2013) found a positive linear relationship ($n = 44$; $p < 0.0065$; Fig. 4.2) for AUR *versus* N concentration. A corresponding relationship for Scots pine litter only gave a negative relationship ($p = 0.064$). It is possible that the single species simply follows another relationship than the genus.

Variation within a stand. With an influence of climate, we may raise the question of variation in nutrients and AUR at one site or within one stand. In a single stand, there is a clear variation in chemical composition of the newly shed needle litter over different years. This is illustrated (Table 4.5; Berg and McClaugherty 2008; Johansson et al. 1995) using an investigation in which some nutrients and AUR in freshly fallen needle litter were measured in 17 consecutive years. The ranges are narrower than within a larger area.

Concentrations of N varied from 3.0 mg g^{-1} up to a high value of 10.4 mg g^{-1}. Compared with other years, the latter value is exceptionally high in relation to concentrations of elements such as P and S in the same year. The frequency of occurrence of such a high value has not been established and may be regarded as a consequence of an unknown extreme event, possibly an early frost.

The concentrations of the main nutrients N, P, and S were in the average proportions of 1:0.055:0.105 (Table 4.5). As we will discuss later, both N and P have been ascribed the role of being rate-limiting for decomposition in the early stage. When we relate both concentrations of P and S to that of N, the relative proportions of P are seen to vary considerably, from 0.028 to 0.079 and for S from 0.069 to 0.156. There thus was a variation in proportions between years that may

Table 4.8 Multiple linear relationships for leaf litter N concentration regressed against annual average temperature (°C) and annual precipitation (in dm) for a dataset of 204 values for N concentrations in litter collected over Asia and Europe

Forest/ litter type	Intercept		Standard temperature		Standard precipitation				
	Coeff	$p<$	Coeff	p<	Coeff	$p <$	n	R^2_{adj}	$p<$
BrdCon	0	1	0.486	0.001	0.326	0.001	204	0.522	0.001
Broadleaf	0	1	0.336	0.001	0.327	0.001	123	0.298	0.001
Coniferous	0	1	0.367	0.001	0.349	0.001	81	0.384	0.001
Pine spp	0	1	0.808*	0.001	−0.217*	0.131	56	0.435	0.001

BrdCon Broadleaf plus coniferous

* Significant difference ($p < 0.001$) between coefficient for standardized temperature and standardized precipitation

The data were also subdivided into the subgroups 'coniferous' and 'broadleaf' as well as pine spp. The data were standardized to allow a direct comparison of coefficients. Coeff thus stands for the slope of the regression equation and can be used as an index within each row to indicate the relative importance of temperature *versus* precipitation for the litter N concentration. Standardized temperature and moisture were calculated using the program Standardize Transform (SPSS Inc., 1997) and mean that the effects of temperature and precipitation can be directly compared. From Liu et al. (2006)

influence which nutrient that was rate-limiting in the early stage (see Chaps. 2 and 6).

A trend analysis did not reveal any significant change in nutrient concentrations over time. The variation in concentrations of water-soluble substances ranged from 82 to 213 mg g^{-1}, with an average value of 159 mg g^{-1}. AUR concentrations ranged from 223 to 288 mg g^{-1} with an average value of 249 mg g^{-1}.

No strong correlation existed among the constituents, and using the Spearman's rank correlation, only three correlations were significant: water solubles and AUR ($r = -0.535$, $p = 0.033$), N and P ($r = 0.546$, $p = 0.029$), and S and K ($r = 0.599$, $p = 0.014$). Ash concentrations in the collections of Scots pine needle litter were relatively low (average value = 20 mg g^{-1}) as compared to those of other tree species (Bogatyrev et al. 1983).

4.4.2.2 The Genus Picea

Using available data for *Picea* litter, we related concentrations of litter nutrients and AUR to the sites' MAT and MAP. We had in all 25 values for Norway spruce needle litter. Nitrogen concentration did not vary with site MAT (range from −1.7 to 8.4 °C) (Fig. 4.5). The observed variation could rather be ascribed to spruce stands being in N pollution zones (encircled values). The average values of the two groups are significantly different. It is likely that an effect of N pollution is more readily seen in Norway spruce needle litter as compared to that of pine. In controlled N fertilization experiments (Sect. 4.7.1), the same dosage of N resulted in considerably higher N concentrations in Norway spruce needle litter than in that of Scots pine.

There was no relationship between climate parameters and concentrations of P, K, Mn, and AUR. We found significant positive relationship between MAT and concentration of Mg and a negative one between MAP and Ca concentrations (Table 4.9).

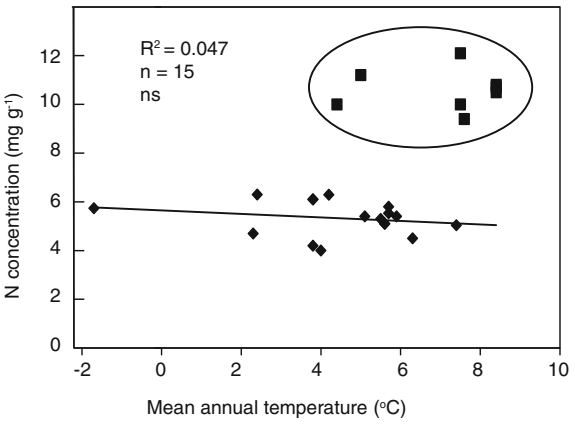

Fig. 4.5 Pattern for nitrogen concentration in needle litter of Norway spruce and Glehn's spruce, when related to site annual average temperature (MAT). The encircled points represent litter collected at sites subject to strong N pollution

Table 4.9 Regression coefficients (r) for relationships between main nutrients and AUR in spruce needle litter and the climatic parameters annual average temperature (MAT) and annual precipitation (MAP)

Forests	N	P	K	Ca	Mg	Mn	AUR	Range (mm/°C)	n
Norway spruce and Glehn's spruce (Europe and Japan)									
MAT	ns	ns	ns	ns	0.528[a]	ns	ns	−1.7–8.4	21
MAP	ns	ns	ns	−0.623[b]	ns	ns	ns	469–1339	21

Data from the DELILA database (www.eko.uj.edu.pl/deco)
[a] quadratic function
[b] exponential function
ns not significant at $0 < 0.05$

4.4.3 Influence of Soil Properties

That nutrient availability has an influence is seen from, for example, N fertilizer experiments (Sect. 4.7) in which different dosages of ammonium nitrate resulted in increases in the N concentration in the needle litter. Nitrogen availability in undisturbed or unmanaged forests may vary greatly across sites dominated by different species (Pastor et al. 1984). However, variations in N availability among natural, undisturbed sites, which are dominated by the same species, appear to be much smaller.

Although the levels of N available to plants in natural soils often are low enough not to influence the litter chemical composition, the levels of other nutrients in litter appear to be more directly dependent on their occurrence in soil. Thus, the concentrations of Ca and Mg in litter appear to increase as their availability in soil increases. Still, we do not know whether this observation is general or limited to a few observed species. These and other nutrients such as Mn are dependent on pH for their mobility. At lower pH values, a better supply of mobile Mn may lead to higher levels in the leaves and needles.

The influence of soil pH is also well illustrated by a study on leaf litter of common beech in 24 stands in a climatically homogeneous area. Ten plots with mull soils had significantly higher average humus pH, and the litter had higher concentrations of Ca (12.0 vs. 8.5 mg g^{-1}, $p < 0.002$) and Mg (1.97 vs. 1.56 mg g^{-1}, $p < 0.0001$) than those with a mor soil, whereas the concentration of N, P, S, and K were not affected. In the same study on Ca in common beech leaves, Staaf (1982) found a clear relationship between the humus (A_0) pH and Ca concentrations in the leaf litter.

Another group of nutrients may give an example of an indirect effect on the chemical composition of litter. For example, a lack of boron (B) will not only be reflected in a lower B concentration in the litter, but will also have an indirect effect by influencing the litter AUR level. Boron has an important role for the formation of an enzyme transporting phenols out from the needles. A lack of B results in an accumulation of phenolics in the needles, which causes increased

lignin synthesis (Lewis 1980; Dugger 1983). Excessively high levels of available Cu have been suggested to have a similar effect.

An empirical finding (Sect. 4.5) giving a general difference in chemical composition between coniferous and broadleaf litter suggests that there is a direct or indirect relationship between litter concentrations of N and AUR/lignin for non-N_2-fixing species. We will discuss this further (below).

4.5 Several Deciduous and Coniferous Leaf Litter Species

4.5.1 Variation in a Eurasian to Global Gradient—Focus on Nitrogen

Litter from tree species other than Scots pine also appears to show variation in chemical composition with climate. Available data for various pine species follow the same pattern as for Scots pine and the genus *Pinus*. Different approaches have been taken to describe this relationship. Thus, Berg and Meentemeyer (2002) related available data for foliar litter N concentrations for Europe to AET, which indicates a more general relationship. Considering this wider range of species, the relationships are weaker than with Scots pine alone (or *Pinus*), but the trends remain the same. For Mn, there was a similar, general negative relationship to AET as that recorded for Scots pine, and no general relationship was found for other nutrients including P, Ca, Mg, and K.

In a large study covering Europe and Asia, Liu et al. (2006) distinguished between MAT and MAP as influencing factors. Their study encompassed 204 datasets with c. 92 species, and the gradient ranged from an annual average temperature of −1.7 to 30 °C and annual precipitation of 500–3,000 mm. Overall, the zone they used extended from north of the Arctic Circle to the Equator. The litter N concentrations ranged from c. 0.1 to c. 3.6 % (in that comparison, N_2-fixing species were excluded). They related N concentrations to annual average temperature and annual precipitation and obtained a highly significant relationship when all species were combined ($R^2_{\text{adj}} = 0.522, n = 204, p < 0.001$). For both coniferous and broadleaf trees investigated separately, the overall concentration of leaf litter N over Eurasia appeared to increase with MAT and MAP (Fig. 4.6). They investigated coniferous and broadleaf trees both separately and combined and found clear relationships between leaf litter N concentration and annual average temperature, as well as between N concentration and annual precipitation (Fig. 4.6).

Liu et al. (2006) evaluated the relative influences of temperature and precipitation on leaf litter N concentration, using standardized data after transformation by means of the program Standardize Transform (see Sect. 4.4.2). They found that for all data combined, temperature appeared to have a stronger effect than

precipitation (cf. coefficient of 0.486 for the former and 0.326 for the latter; Table 4.8).

For all three models tested, that is, (1) broadleaf and coniferous litter combined, (2) coniferous, and (3) broadleaf separately, coefficients for STemp (range 0.336–0.486) were larger (albeit not significantly) than those of standardized SPrecip (range 0.326–0.349). This suggests the possibility of a stronger effect of a change in temperature than of precipitation on leaf litter N, on a relative basis and within their present ranges (Table 4.8).

We may note that for pine spp., the coefficient for SPrecip was negative (Table 4.8), thus differing from the other groups. Liu et al. (2006) also made a separate study of the genus *Quercus* and could subdivide that into a deciduous group and an evergreen group. The deciduous group had a tendency of increasing leaf litter N with increasing temperature, whereas the evergreen group did not indicate such a tendency. The two groups had a similar pattern of leaf litter N along the precipitation gradient. We may note that compared to the larger groups comprising different species, the single genera that were investigated by Liu et al. (2006) behaved in different ways, and we cannot exclude that single species and genera with their defined ecological niches have different behavioral patterns, for example as regards response to temperature, in contrast to continuously changing species along a continental gradient.

4.5.2 Coniferous versus Deciduous Genera/Species and Influence of Species: An Old Concept

The often-seen general statement that deciduous foliar litter is more nutrient rich than coniferous appears not generally correct, and we intend to modify that statement using available information. There appear to be some main differences between the two groups encompassing both organic-chemical compounds and nutrients. Still, considering the size of each of these main groups, we will always be restricted to evaluate available data and to compare genera and species ideally using paired stands.

Organic-chemical components. As regards organic-chemical components, one general difference between deciduous and coniferous trees is that in relative concentrations of hemicelluloses and cellulose (Table 4.1) which can be compared with a ratio. Thus, so far as we know today, the ratio of hemicelluloses to cellulose appears to be above 1.0 for deciduous and below for coniferous. As regards lignin/AUR, broadleaf species in general may have lower concentrations than coniferous ones. However, we may see some limitation and dependence on other factors that make simple statements less valid.

Lignin/AUR is a component that appears to have higher concentrations in coniferous than broadleaf litter. Using 152 datasets, Berg et al. (2013) found significantly different average values for the two groups. Thus, the average AUR

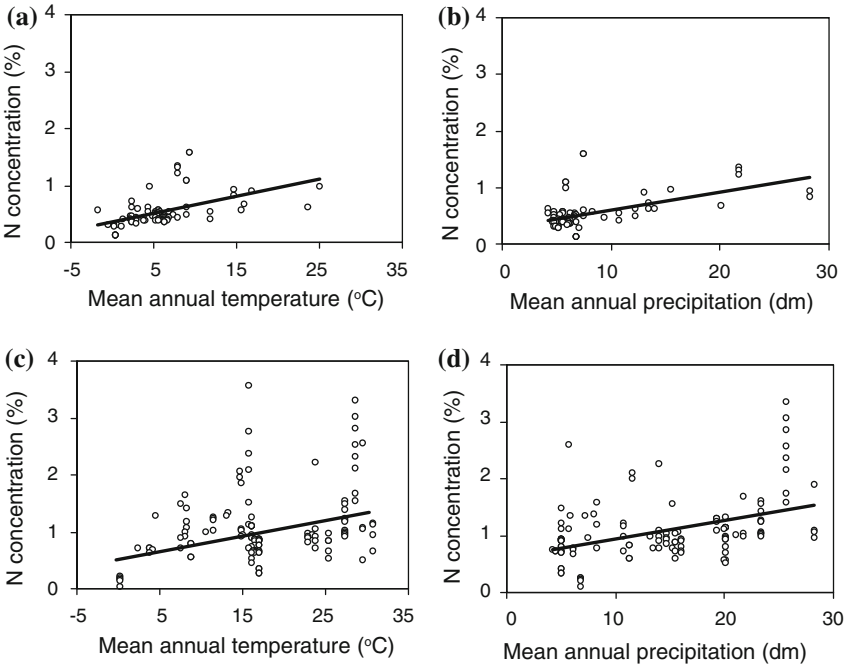

Fig. 4.6 Foliar litter N concentration related to MAT and MAP. Available data of both coniferous **a, b** and broadleaf **c, d** foliar litter with origin from Asia and Europe. The relationships are significant at $p < 0.001$. Cf Table 4.7. From Liu et al. (2006)

concentration for coniferous litter was 292 mg g^{-1} with a range from 155 to 512 mg g^{-1} (n = 73), and for broadleaf litter it was 219 mg g^{-1} with a range from 38.0 to 478.6 mg g^{-1} (n = 79). For both coniferous and broadleaf litters, AUR concentration was related to that of N and with intercepts significantly different. In this comparison, they excluded dinitrogen-fixing species (Fig. 4.2).

There were highly significant and positive relationships between concentrations of N and AUR for both broadleaf and coniferous litters over rather wide gradients (Fig. 4.2). The climatic gradients ranged from 3.8 to 28.1 °C for broadleaf and from −1.7 to 25 °C for coniferous litter. We may see that the intercepts for the relationships to N concentration are significantly different with that for coniferous litter being higher than that for broadleaf (Fig. 4.2).

Nutrients. Nutrient is a wide concept and overlaps with heavy metals. For the most measured nutrient, nitrogen, Liu et al. (2006) showed on a large geographical scale that foliar litter of broadleaf trees generally has higher N concentrations and a larger variation under given climatic conditions in comparison with coniferous trees. They investigated more than 90 species for N concentration, on a continental level using 204 litter samples from the Equator to north of the Arctic Circle covering Europe and Asia. For instance, at an annual average temperature of

10 °C, the average N concentration was about 10 mg g^{-1} for broadleaf foliar litter and only about 5 mg g^{-1} for that from conifers (Fig. 4.6) (Liu et al. 2006).

In a recent study, Kang et al. (2011) presented 482 foliar litter datasets with both N and P analyzed. The data originated from all continents, except for Australia, and indicated that not only concentrations of N but also P were higher in deciduous and evergreen broadleaf litters as compared to coniferous. They also found differences among continents.

There appear to be differences in concentrations of nutrients other than N and P between deciduous and coniferous foliar litters and among species. Coniferous foliar litter generally appears less rich in nutrients such as N, P, Ca, and K than deciduous (Table 4.6). We evaluated data from the DELILA III database (www.eko.uj.edu.pl/deco) (Table 4.6). The 13 coniferous litter species in general had N levels below 7 mg g^{-1}, whereas the deciduous ones generally were above 7 mg g^{-1}. There were large differences in P levels, with deciduous litters averaging three times as much P as coniferous. For Ca, the pine litter generally had low concentrations, with Aleppo pine an exception. Norway spruce had a higher value, and deciduous litter had Ca concentrations that were at least 2–10 times higher than those of coniferous litters, with the average value about 2.5 times higher. Mg and Mn were more similar among species.

A study on concentrations of K in needle litter (Laskowski et al. 1995) encompassed more than 25 boreal and temperate tree species. The full range for K concentrations in the whole dataset was 0.31–15.64 mg g^{-1}, with a large and statistically significant ($p < 0.0001$) difference in average initial K concentrations between coniferous and deciduous litters (1.03 vs. 4.52 mg g^{-1}, respectively). Both these litter types had lower initial K concentrations than those found in the leaf litter of Norway spruce, mixed oak-hornbeam, and silver birch. The highest average K value was that for gray alder leaves (8.26 mg g^{-1}), followed by that for silver birch leaves (5.01 mg g^{-1}). In contrast, leaves of common beech, with 1.67 mg g^{-1}, were in the same range as the coniferous litter. Their investigation also covered temperate forests and covered both the most common litter species found in the forests of north-central Europe and some major North American species.

Heavy metals. Heavy metals are natural components of litter, some as coenzymes, for example Zn and Mn, other ones being found in trace amounts in litter also in unpolluted ecosystems. They may have an ecosystem role (Sect. 10.3.2) although some are not known parts of plant physiological processes. Their concentrations in foliar litter probably reflect their availability in soil which may be related to their occurrence in the parent rock, weathering rate, and solubility, in some cases related to soil pH. 'Natural' concentrations in foliar litter from trees outside directly polluted areas seem to be less known, at least rather few data are published.

We have made a compilation of available data for 6 more commonly analyzed heavy metals using litter samples collected from unpolluted areas. As

Table 4.10 Initial concentrations of some mineral nutrients and heavy metals in a few foliar litter species

Litter species	Concentration (μg g^{-1})						
	Fe	Zn	Cd	Cu	Pb	Al	Lit ref
Stone pine	299	49	0.1	5.0	3	n.d.	Berg et al. (2003)
Scots pine	79	48	0.1	2.6	2	n.d.	Berg et al. (2003)
Scots pine	57	51	0.2	1.4	n.d.	280	B. Berg, unpubl.
Scots pine	60	50	n.d.	2	1	n.d.	Berg et al. (1991)
Lodgepole pine	53	85	0.6	2.8	1	n.d.	Berg et al. (2003)
Jack pine	105	56	n.d.	n.d.	n.d.	505	Preston et al. (2009)
W. red cedar	529	47	n.d.	n.d.	n.d.	662	Preston et al. (2009)
Tamarack	121	35	n.d.	n.d.	n.d.	46	Preston et al. (2009)
Black spruce	345	47	n.d.	n.d.	n.d.	200	Preston et al. (2009)
Douglas fir	570	42	n.d.	n.d.	n.d.	471	Preston et al. (2009)
American beech	97	29	n.d.	n.d.	n.d.	35	Preston et al. (2009)
Silver birch	61	340	0.8	3.4	2.6	n.d.	Berg et al. (2003)
White birch	49	125	n.d.	n.d.	n.d.	34	Preston et al. (2009)
Trembling aspen	46	126	0.5	8.6	0	n.d.	B. Berg, unpubl.
Trembling aspen	118	191	n.d.	n.d.	n.d.	48	Preston et al. (2009)
Common beech	1540	70	0.32	4.1	4.1	n.d.	Hristovski et al. (201X)

concentrations of heavy metals are less known than the main nutrients, too few values are recorded from unpolluted litter to allow any real synthesis (Table 4.10). However, we may give some ranges. Thus, is there a good range in Fe concentrations, viz. from 46 μg g^{-1} in trembling aspen to 1540 μg g^{-1} in common beech. For Zn, the range goes from 29 μg g^{-1} in leaf litter of American beech to 340 μg g^{-1} in silver birch (Table 4.10). Copper ranges between 1.4 in Scots pine and 8.6 μg g^{-1} in trembling aspen and lead from 0 (μg g^{-1}) in trembling aspen to 3 in Scots pine litter.

4.5.3 General (Global) Relationships

The concept 'global relationships' is not always clear. When it comes to relationships possibly generally valid for the planet Earth, we are forced to admit that they do not exist. What can be shown is the latest large dataset encompassing numerous species distributed over the continents. If the number of species or their distribution is important for the concept, global may be considered an open question. In a recent study, Kang et al. (2011) presented 677 foliar litter datasets with N and 482 of them had also P analyzed. The data originated from all continents, except for Australia, and indicated that N concentration increased with MAT and MAP ($p < 0.001$). Phosphorus, on the other hand, had no relationship with MAT but a negative one to MAP ($p < 0.01$).

4.6 Wood and Fine Root Litter

The nutrient concentrations in woody litter are drastically different from those of foliage. Fine root litters, in contrast, are often rather similar to foliage in initial nutrient concentrations, but have different decay patterns. Because of the unique nature of wood and fine roots, discussion of their decay will be treated separately in Chap. 8. Here, we will briefly review the range of values observed for nutrient and organic-chemical composition of wood and fine roots.

Nutrient concentrations are much lower in wood than in foliage litter. We may see that, for example, N concentrations may be a factor of 10 lower for the species Norway spruce, rembling aspen, silver birch, and common beech. Wood is largely made up of cellulose, lignin, and hemicelluloses in different proportions. As a whole, the woody parts of the tree are poorer in nutrients than the photosynthesizing or actively growing parts. It also appears that the levels of water solubles are lower in wood than in the corresponding foliar litters (Table 4.1).

4.7 Anthropogenic Influences on Initial Litter Composition

Human activities can dramatically influence the chemical composition of newly formed litter. These effects may be either direct or indirect. Clearly, fertilization with nutrients can have an effect on the nutrient composition of litter. This is true whether the nutrients (usually including some form of N) are added as part of forest practice or because of atmospheric N deposition. Here, we only examine the effects of selected human activities on initial litter composition, specifically the effects on litter chemical composition of artificial N enrichment and heavy metals deposition.

4.7.1 N-fertilized Scots Pine and Norway Spruce Monocultures

Additions of N to soils have been performed as N fertilization or to simulate N deposition. Such experiments may be done by small daily additions but also by large annual additions. The latter may be useful to interpret the effects, keeping in mind that such heavy additions should be interpreted with care. With experimental dosages as high as 100–500 kg N ha^{-1} $year^{-1}$, it appears that most of the supplied N left the system relatively quickly, with a low percentage, in the range 9–30 %, being recovered from the topsoil (Tamm 1999). This heavy outflow of N can be attributed in part to the fact that the fertilization technique added the full annual dosage of N fertilizer in a period of hours. As discussed by Tamm (1999), the

Table 4.11 Average concentrations of AUR and some main nutrients in Norway spruce and Scots pine needle litter collected at plots with three fertilization regimes, namely control, 50, 100, and 150 kg N ha^{-1} $year^{-1}$ (B. Berg unpubl.)

Species/Dosage	AUR (mg g^{-1})	N	P	S	K	Ca	Mg
Norway spruce							
Control	355	4.9	0.45	0.73	0.72	17.9	0.65
100 kg N	388	15.3	0.54	0.93	1.04	10.0	0.74
150 kg N	402	16.8	0.55	0.98	1.27	7.7	0.76
Scots pine							
Control	270	3.6	0.14	0.25	0.53	5.3	0.50
50 kg N	260	4.3	0.20	0.33	0.52	5.1	0.55
100 kg N	300	5.8	0.25	0.46	0.59	4.0	0.52
150 kg N	380	8.5	0.30	0.49	0.85	2.9	0.38

percentage of added N that is retained in soil depends on the magnitude of the dosage, the number of additions, and the level of saturation. Using the observations by Nömmik and Möller (1981), we can estimate that 12–20 % may be recovered with additions in the range from 150 to 500 kg, meaning that, say 20–60 kg ha^{-1} would remain in the soil, which corresponds to annual N deposition amounts in some areas. Long-term fertilization experiments would thus be of value in illustrating long-term deposition effects.

We have used data from N fertilization studies by Tamm (1991) who carried out extensive work on Scots pine and Norway spruce forests. For both species, there is a clear variation in chemical composition of needle litter between different fertilizer regimes (Table 4.11), especially N (Fig. 4.7). Tamm (1991) initially used annual doses of 50, 100, and 150 kg N ha^{-1}, later reduced to 40, 80, and 120 kg N ha^{-1}. With such dosages given once a year, heavy losses occurred, and the amounts retained were comparable with those of N deposition.

The addition of N, either as fertilizer or through N deposition, will result in increased uptake by the trees and, consequently, in enhanced concentrations of N in the freshly formed litter. This has been observed by Miller and Miller (1976) and later by Berg and Staaf (1980a). The latter, using Scots pine needle litter from a fertilization experiment (Tamm et al. 1974; Tamm 1991), found that N additions at an annual dosage of 80 kg N ha^{-1} resulted in a statistically significant increase in litter N concentrations, whereas the dosage of 50 kg ha^{-1} $year^{-1}$ did not have any significant effect (Table 4.11). A clear relationship was seen between dosage and litter N concentration ($r = 0.949$, $p < 0.001$, $n = 8$). The N concentrations measured over several years at one experimental site ranged from about 3.6 to 8.5 mg N g^{-1} needle litter in control and high-dosage stands, respectively. The variation in N concentration was accompanied by variation in concentrations of other nutrients as well, producing a relatively balanced nutrient composition (Tables 4.11 and 4.12). Thus, P, S, and K concentrations showed positive linear

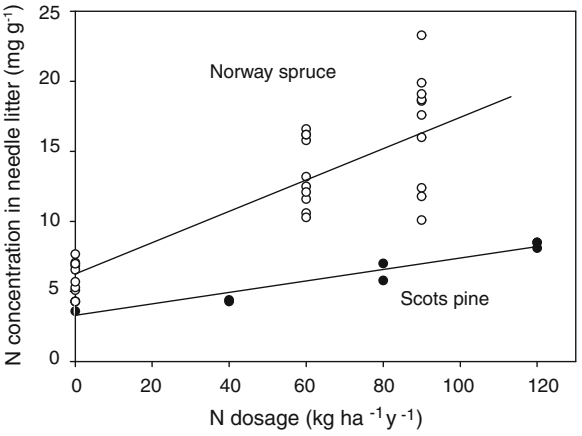

Fig. 4.7 Relationships between dosage of N fertilizer (ammonium nitrate) and concentrations of N in needle litter of Scots pine and Norway spruce. (B. Berg unpubl.)

relationships to the N concentration, whereas Ca showed a negative relationship, and there was no significant relationship found for Mg.

Norway spruce needle litter followed a similar pattern, although litter N had significantly higher concentrations. In general, the concentrations of N, P, and S (Table 4.12) increased with dosage of N fertilizer, although the effect on the concentration of N was more pronounced. The concentrations of N in the litter appeared to be largely in proportion to the dosage of fertilizer, the range being from 4.2 mg g^{-1} in control plots to 18.3 mg g^{-1} in a high-dosage plot (Fig. 4.7). In addition, the concentration of K and Mg increased, whereas Ca concentrations decreased at higher N concentrations. Relative to the dosage, the concentrations of N in Norway spruce needles increased about three times faster than for Scots pine, thus resulting in needle litter considerably richer in N.

It is noteworthy that concentrations of AUR also varied for both Scots pine and Norway spruce, increasing with dosage of N fertilizer (Fig. 4.8). For Scots pine, the AUR concentrations increased with those of N from 270 to 380 mg g^{-1}. For Norway spruce, the increase was similar, with a range of 242 to 407 mg g^{-1} (cf.

Table 4.12 Coefficients of determination (R^2) for linear relationships between concentrations of nutrients, water solubles, and AUR in needle litter of Scots pine subjected to different dosages of N fertilizer A negative relationship is indicated by (−). $n = 19$. (Reurslag and Berg 1993)

	Component			
	N	P	S	Ca
P	0.550^{**}	–	ns	ns
S	0.717^{**}	0.932^{***}	–	ns
K	0.497^{**}	0.901^{***}	0.773^{***}	ns
Ca	$(-)0.596^{***}$	ns	ns	–
AUR	0.517^{**}	ns	ns	$(-)0.728^{***}$
Wsol	0.453^{**}	ns	ns	0.725^{***}

Wsol water soluble, significance levels ** $p < 0.01$, *** $p < 0.001$, *ns* not significant at $p < 0.05$

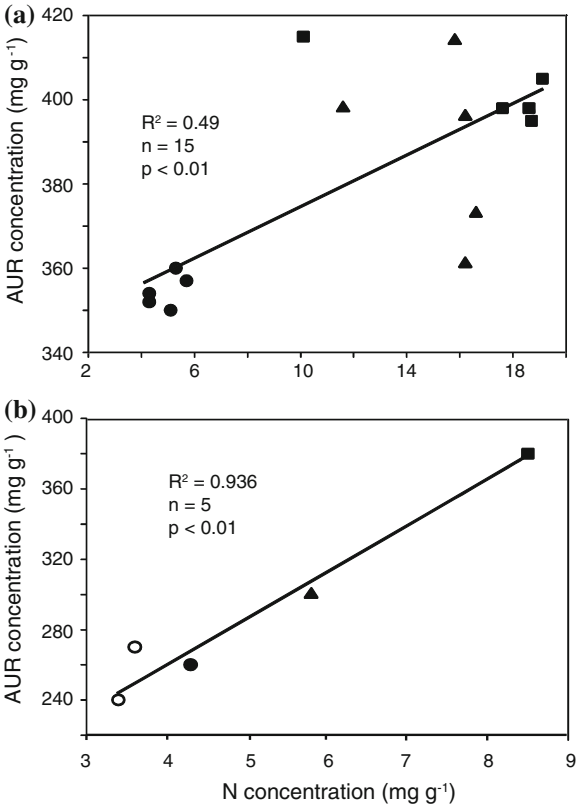

Fig. 4.8 Linear relationships between N and AUR concentrations in needle litter from N-fertilized plots with **a** Norway spruce and **b** Scots pine. Collections were made in 1983 (**a**) and 1976 (**b**). Plots were given 50 kg N ha^{-1} $year^{-1}$ (●), 100 kg N ha^{-1} $year^{-1}$ (▲), and 150 kg N ha^{-1} $year^{-1}$ (■), control (○). Note the different scaling of the X-axis (Berg and Tamm 1991; B. Berg unpubl.)

Table 4.11). This effect on lignin concentration seems to vary with the kind of system and appears to be indirect.

The effect of fertilization on AUR concentration could be related to a lack of B in the soil. The high dosage of N fertilizer may have forced the trees to grow so quickly that the supply of some essential nutrients became lacking, as the mobile pool in the soil was exhausted. Weathering apparently could not give a sufficient supply, leading to a lack of this micronutrient in the plant.

4.7.2 Heavy Metal Pollution and Initial Litter Chemical Composition

Heavy metals can be taken up by plants through their roots or accumulate on their leaf surfaces from atmospheric deposition. In sufficient concentrations, these metals can cause a slowing of decomposition, presumably due to toxicity toward the microbial community.

Table 4.13 Concentrations of plant nutrients and heavy metals in local fresh needle litter of Scots pine sampled at six study plots in a smelter pollution gradient in northern Sweden and needle litter sampled at an unpolluted (control) site

Dist Km	Chemical component mg g^{-1}								μg g^{-1}		
	N	P	S	K	Ca	Mg	Mn	Fe	Zn	Cu	Pb
2.5	3.78	0.26	0.99	1.43	5.23	0.47	0.79	0.38	0.25	0.100	311
3	3.73	0.24	0.73	1.01	5.70	0.53	0.83	0.36	0.19	0.068	191
7	3.25	0.19	0.49	0.70	6.11	0.46	1.26	0.14	0.11	0.019	44
9	3.71	0.26	0.50	1.08	4.65	0.56	1.10	0.27	0.11	0.012	34
13	3.66	0.25	0.53	1.23	5.65	0.66	1.43	0.12	0.08	0.009	22
30	4.40	0.22	0.51	0.98	5.70	0.67	1.21	0.11	0.07	0.006	12
Control	4.80	0.35	0.41	1.20	5.26	0.49	1.35	0.06	0.05	0.002	1

Concentrations of Na, Al, B, Ni, Mo, Sr, and Cd did not vary in this gradient. (Berg et al. 1991b)
Dist Distance from smelter

Berg et al. (1991b) studied this by collecting fresh Scots pine needle litter along a gradient of increasing distance from a smelter in northern Sweden. The chemical composition of needle litter collected at each site at abscission varied with the distance from the smelter (Table 4.13). A significant positive relationship ($p < 0.05$) was found between the distances from the smelter and Mg concentrations in the fresh litter. The same tendency was also observed for Mn, meaning that these concentrations increase with the distance from the smelter. Of the pollutants, Pb and Zn concentrations showed strong decreases with distance ($p < 0.01$). The same trend was noted for Fe and Cu ($p < 0.05$) and, although less marked, for S and Cd ($p < 0.1$). The concentrations of organic compounds, on the other hand, seemed largely unaffected. The completely unpolluted litter had somewhat lower lignin and higher N and P concentrations than the locally collected needles as well as very low concentrations of heavy metals.

Chapter 5
Changes in Substrate Composition during Decomposition

5.1 Introductory Comments

There are two principal approaches to studies of the chemical changes in litter during decomposition, namely to follow the changes in: (1) organic-chemical composition and (2) inorganic nutrient composition. We will discuss both.

The decomposition of litter organic components by microbes appears to be selective (Chap. 2). Thus, there is a pattern in litter chemical changes over the course of decomposition. This common basic pattern may be modified as a result of the initial chemical composition of a given litter type. The pattern discussed here is based on boreal coniferous forest systems, but probably has a wider generality. For example, even in such a different system as a chaparral (Schlesinger and Hasey 1981), decomposition follows a pattern similar to that in a boreal forest (Berg et al. 1982a). New analytical techniques may change such a pattern and we are aware of that analyses of organic compounds using ^{13}C-NMR is likely to give a somewhat different pattern as compared to that using traditional techniques.

Studies of changes in the chemical components of decomposing litter are uneven, with AUR/lignin having received much of the attention. Still, for Scots pine needle litter, more detailed descriptions have been made, including hemicelluloses, and different fractions of solubles (Berg et al. 1982a). There are also studies on Scots pine needle litter covering the decomposition process from litter fall to a close-to-humus stage. In this chapter, we describe detailed chemical changes for Scots pine litter as a case study. We also present data from other, mainly boreal species. For Mn, N, and AUR/lignin, specific syntheses have been published and these studies are reviewed.

A new concept has developed and come into use in litter decomposition studies as the ^{13}C-NMR technique has developed. Some basic papers are those by Preston et al. (1997, 2006, 2009ab) giving a detailed comparison of proximate analysis and their comparison of the same litter using the ^{13}C-NMR technique is very useful. The papers by Ono et al. (2009, 2011) give a direct application of NMR analysis on decomposing litter. We intend to present results of the traditional analysis as

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well as ones using NMR technique. There will, however, be an emphasis for gravimetric lignin (AUR) (see Appendix III for a background).

The dynamics of nutrients in litter decomposition has been studied often due to its relationship to nutrient cycling in ecosystems (O'Neill et al. 1975; Anderson and Macfadyen 1976). Several such studies on nutrient dynamics also deal with chemical composition changes during decomposition (Dwyer and Merriam 1983; Berg et al. 1987; Dziadowiec 1987), and the dynamics of the major plant nutrients (Berg and Staaf 1980a, b; 1987; Blair 1988a, b; Rashid and Schaefer 1988). There are few studies, though, that describe nutrient dynamics covering the whole process from newly shed decomposing litter until the humus stage.

The limit between the concepts 'nutrients' and 'heavy metals' is not clear in the literature. The general view is that nutrients are inorganic elements that are essential for life processes, whereas heavy metals are inorganic elements that, in sufficiently high concentrations, can be damaging to life processes. Although heavy metals can be anthropogenic pollutants, they also occur naturally. In this chapter, we discuss heavy metals in basically unpolluted systems and discuss their dynamics in a fundamental, natural stage.

5.2 Organic-Chemical Changes during Litter Decomposition

5.2.1 Traditional Analytical Fractions

5.2.1.1 Cellulose

We showed (Chap. 2) that in the early stage of decomposition, the insoluble components cellulose, hemicelluloses, and AUR were degraded at different rates. Somewhat later in the decay process, the degradation rates of these components became similar (Fig. 2.5). The initially different decay rates mean that the concentrations of these components also change at different rates. Thus, after an increase the concentration of cellulose decreases slowly (Fig. 5.1) and at about 70 % accumulated mass loss, it was similar to the initial value (Berg et al. 1982a).

In the late stage of decay when degradation of lignin/AUR dominates the decomposition of litter (Fig. 2.2), the degradation rates of the insoluble components decrease and become similar. During this late stage, the concentration of cellulose decreased slowly (Fig. 5.1).

5.2.1.2 Hemicelluloses

The most common hemicelluloses decompose in a similar fashion in litter. For the most part, they behave like cellulose, although they may have different positions in the decomposing fibers. The concentrations of, for example, xylans, mannans,

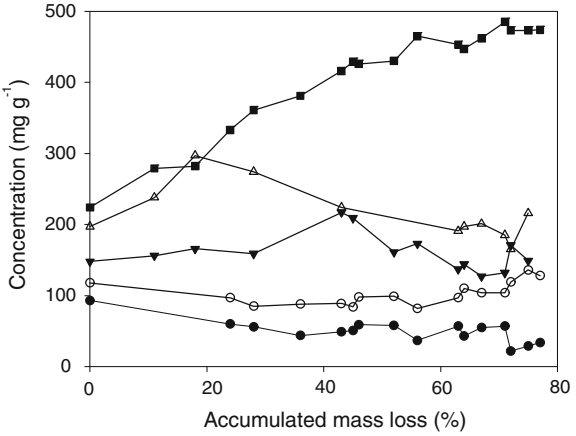

Fig. 5.1 Changes in concentrations of water solubles (●), ethanol solubles (○), cellulose (△), combined hemicelluloses (▼), and AUR (■) in decomposing Scots pine needle litter. (B. Berg unpubl.)

arabinans, and galactans are about constant in the early stage. Their concentrations in the late, lignin-regulated, stage of decomposition become about constant when compared to each other. Considering the structure and complexity of the hemicelluloses, we may simplify our discussion and regard them as a group. When considered together, we may see that their concentration at 70 % accumulated mass loss is about the same as at the start of the incubation (Fig. 5.1).

5.2.1.3 'Lignin' is Often Determined as Acid Unhydrolyzable Residue

Lignin is not a very clear concept either in fresh or decomposing litter. Lignin is often defined on the basis of proximate analytical methods rather than purely chemical criteria (see also Appendix III). When applied to freshly fallen litter or undecomposed plant materials, some proximate methods yield results close to what would be chemically defined as lignin. However, in decomposing plant litter, the lignin is modified by the humification processes, including condensation reactions, and by partial degradation by microorganisms. The formation of these decay products, which are included in the AUR/lignin fraction, may raise arguments about the extent to which true lignin is measured in decomposing litter. In addition, the 'lignin' determined by gravimetric methods will contain, among other things, cutin, waxes, tannins as well as chitin from fungal mycelium, and an inorganic fraction (ash) that can be of a considerable magnitude. Although the latter fraction for Scots pine litter is about 1 % of the total litter mass, it may amount to some percent in the gravimetric lignin analysis. The ash content of newly shed deciduous litter can be much higher, going above 10 % in some cases. Furthermore, ash concentrations may increase during decay. This ash fraction should be considered when reporting AUR contents of decomposing litter.

We contend that although what is determined is not true lignin, it is a mixed chemical fraction with compounds, some of which have similarities to true lignin. It is important to note that even native lignin is highly variable among and even within

species. Thus, even native lignin cannot be described with the same chemical precision as cellulose or many other plant polymers. Lignin is not a well-defined compound when it is produced, and it remains a poorly defined compound as it is decomposing. The nomenclature for lignin that has been modified during decomposition is still in question. A term like 'lignins' is sometimes used and even the misleading term 'acid-insoluble substance' is seen in the literature. A recent suggestion is 'non-hydrolyzed remains' (NHR, Faituri 2002). A more recent suggestion is Acid Unhydrolyzable Residue' (AUR) (Preston et al. 2009b), which has won acceptance.

It should be pointed out that although the terminology sometimes is misleading, the gravimetric lignin or AUR fraction that contains recalcitrant, 'non-hydrolyzable residue' is today an important concept to litter decomposition although we also need methods to identify native lignin as well as to identify the compounds of AUR.

In the course of decomposition, when the more easily degradable compounds are decomposed, AUR remains relatively intact for a long time. This means that the litter becomes enriched in AUR and its concentration increases (Figs. 5.1 and 5.2). A number of studies have shown that the concentration may reach even above 50 % (Table 5.1). At a certain stage when the open structures of the more available holocellulose are decomposed, the remaining fiber will have AUR/lignin and its modified products as a protective barrier, and when holocellulose and lignin are degraded at similar rates the relative proportions of both holocellulose and AUR remain nearly constant.

The AUR analysis gives normally a clear increase in concentration and is a useful index for litter recalcitrance. However, in decomposing litter, AUR integrates the most hydrolysis-resistant organic structures and is an operational fraction derived from lignin, condensed tannins, cutins, and waxes (Preston et al. 2009b). As an index of litter recalcitrance and age, it may be very useful. However, we must call it an empirical index.

5.2.1.4 Repeatability and AUR Concentration Increase Rate (AURCIR)

Repeatability of AUR concentration changes. AUR concentration changes versus time may be related to duration of decay, which often can be described by an asymptotic curve. The AUR concentration may, on the other hand, be related to accumulated litter mass loss, resulting in a linear increase (Fig. 5.2). Such a pattern in AUR concentration has been found for Scots pine, lodgepole pine, and Norway spruce. Deciduous litter like birch leaves give linear relationships too, but much mass is lost initially, resulting in a quick increase followed by more constant values (Berg et al. 1984). For Scots pine, the AUR concentration increases from the initial value up to c. 50 % and above (Fig. 5.2) for reasons discussed earlier (Chap. 2), and in this interval, the linear relationship is highly significant (Fig. 5.3).

This linear increase rate appears to be repeatable within a given stand. Native Scots pine needle litter was incubated annually for 14 consecutive years, and the increase rate values for the 14 sets of decomposing needle litter were compared

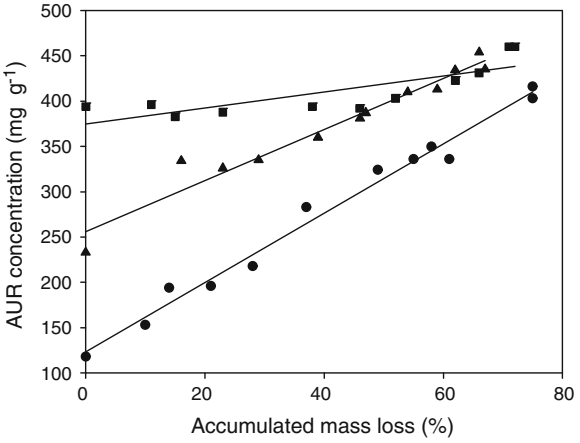

Fig. 5.2 Changes in AUR concentrations during decomposition of needle litter of Scots pine (▲), lodgepole pine (■), and Sugar maple (●) with different initial AUR concentrations. AUR concentration is plotted versus litter accumulated mass loss. From Berg et al. (1997)

(Table 5.2). The difference between years was the between-year variation in initial chemical composition (Berg et al. 1993e; Johansson et al. 1995; Table 4.5) and the annual variation in climate. Comparing the linear equations for AUR concentration increase among the 14 sets, the differences were found in the intercepts rather than in the slopes, the intercepts reflecting the initial lignin concentration. The average slope for one site was 3.08 for $n = 14$. The slope when using all Scots pine values in one linear regression was 2.92 with an R^2_{adj} of 0.894 (Fig. 5.3).

Two further boreal coniferous litter species were investigated (Berg et al. 1997), namely those of lodgepole pine and Norway spruce. These also showed repeatable increase rates in AUR concentration (AUR Concentration Increase Rate: AURCIR). For lodgepole pine, incubations at the same main site showed a low variation among slopes (average value was 1.21; $n = 5$), while the slope when all the five data sets were combined became 1.24; $R^2_{adj} = 0.610$; $n = 55$; Table 5.3), thus, less than half the slope for Scots pine litter. For local Norway spruce litter, using 7 sets of data for incubated litter at one site gave a slope of 2.95 ($R^2_{adj} = 0.841; n = 56$).

The influence of initial AUR concentration. Different litter types have different behaviors with respect to AUR disappearance. For litters rich in AUR, for example, lodgepole pine and Norway spruce needle litter, AUR disappearance begins at or soon after litter decomposition has started (Berg and Lundmark 1987; Berg and Tamm 1991). Even in these cases, the concentrations of AUR increase as decomposition proceeds. There is, however, variation between AURCIR values for different litter species collected at and incubated in their own ecosystem. At a site with monocultures of lodgepole pine and Scots pine, the litter of lodgepole pine had an AUR concentration of about 350 mg g^{-1} and Scots pine about 290 mg g^{-1}. Both litter types had significant linear relationships between accumulated mass loss and the increase in AUR concentration, with the slopes (AURCIR) being 1.24 and 2.55, respectively. The litter with initially higher AUR concentrations (lodgepole pine) had significantly lower slopes (see also Table 5.2).

Table 5.1 Long-term organic-chemical changes in some different decomposing litter types expressed as initial concentrations and as the concentrations when the given level for accumulated mass loss was reached

Species	Wsol (mg g^{-1})		Esol (mg g^{-1})		Holocell (mg g^{-1})		AUR (mg g^{-1})		Final m.l. (%)
	init	fin	init	fin	init	fin	init	fin	
Needle litter									
Scots pine[a]	92	34	120	126	347	92	223	472	77.1
Lodgepole pine[b]	109	44	42	53			366	482	75.3
Norway spruce[c]	114	38	60	31			344	516	51.3
Can. hemlock[d]	181	53	177	36	396	234	206	226	45.1
White pine[d]	162	18	166	46	447	219	225	185	53.2
Leaf litter									
Silver birch[b]	321	40	57	43			263	506	65.4
Gray alder[b,c]	264	33	39	36			264	475	55.5
Red oak[d]	210	55	90	15	452	171	248	213	54.6
Sugar maple[d]	336	41	112	12	431	94	121	99	75.4

Wsol Water solubles, *Esol* ethanol soluble, *Holocell* holocellulose, *fin* final, *init* initial, *m.l.* mass loss

[a] Berg et al. (1982a)
[b] Berg and Ekbohm (1991)
[c] Berg et al. (1991a)
[d] Aber et al. (1984)

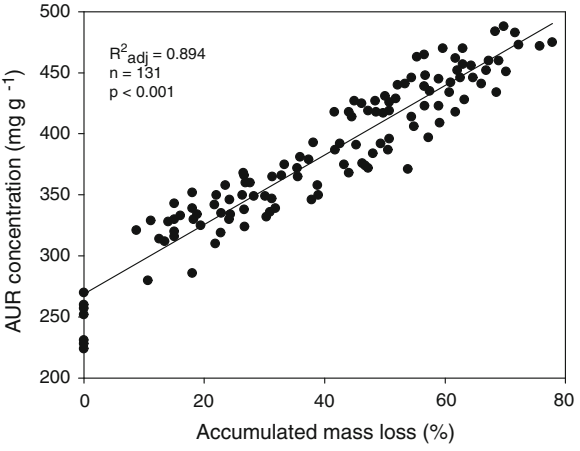

Fig. 5.3 The relationship between the increase in AUR concentration and accumulated mass loss for 14 different incubations of local Scots pine needle litter at a site with Scots pine forest on nutrient-poor soil (central Sweden). All measurement points are shown together with the common linear regression line. From Berg et al. (1997)

In a comparison of five different data sets each for lodgepole pine and Scots pine, Berg et al. (1997) found a highly significant negative relationship between AUR increase rate and initial AUR concentrations, with an R^2_{adj} value of 0.938 indicating that the higher the initial AUR concentration, the lower the rate of increase. This is probably due to an apparent upper (empirical) limit for AUR concentration of about 50 % (cf Fig. 5.2). It appears that there is also a more

Table 5.2 Linear regressions of AUR concentration in decomposing litter versus accumulated mass loss for needle litter of three species incubated at their own stands. The slope of the linear relationship *AUR concentration increase rate* is abbreviated AURCIR. Comparisons of AURCIR are made both by combining all values from different litter incubations into a single regression and by taking the average slopes for individual studies. From Berg et al. (1997)

Species	Intercept (SE)	AURCIR (SE)	R^2_{adj}	*N*	*p*<
Scots pine					
All values	262.0 (20.8)	2.924 (0.089)	0.894	131	0.001
Avg. of 14 slopes		3.08 (0.091)		14	
Lodgepole pine					
All values	370.6 (25.6)	1.24 (0.134)	0.610	55	0.001
Avg of 5 slopes		1.21 (0.118)		5	
Norway spruce					
All values	362.7 (18.7)	2.95 (0.174)	0.839	56	0.001
Avg of 4 slopes		2.92		4	

SE Standard error, *n* number of data points, *Avg.* average

general relationship between initial AUR concentration and AUR increase rate. Berg et al. (1997) investigated a larger data set and examined the influence of both climate and initial AUR on the AURCIR (below).

For Norway spruce, they investigated the relationship between initial AUR concentration and AURCIR using data from an intensively studied site (Berg and Tamm 1991). The negative relationship obtained between initial AUR concentrations and AURCIR was again significant. The relationship between a higher initial AUR concentration and a lower slope thus also holds for spruce. The relationship between AURCIR and initial AUR concentration still held when they combined all data from coniferous litters ($p < 0.001$) and gave an R^2_{adj} value of 0.313 with $n = 94$.

Variation in AUR concentration increase rate with climate. For Scots pine, clear differences have been found in the magnitude of the AUR concentration increase rate between northern and southern sites in Scandinavia. In their studies, Berg et al. (1997) used a unified litter preparation over a gradient ranging over most of Sweden and into northern Germany. The resulting increase rate values were then related to climate (Berg et al. 1997) using the climate index actual evapotranspiration (AET) (Meentemeyer 1978). The increase rates for Scots pine gave a highly significant positive relationship with AET with $R^2_{adj} = 0.545$, and $p < 0.001$ for $n = 30$.

5.2.2 Relationships between Holocellulose and AUR

Attempts have been made to describe how the concentrations of cellulose and hemicellulose change during decomposition as compared to AUR. The concentration of holocellulose decreases and that of AUR increases until a level is

Table 5.3 Lignocellulose index (*LCI*) values from forest soils in northeastern United States. Modified from Melillo et al. (1989)

Species/location	Horizon	LCI
White pine stand/New Hampshire (USA)[a]	Oi	0.50
	Oe	0.66
	Oa	0.73
	A	0.78
	B	0.76
Spruce/Maine (USA)[a]	Oi	0.52
	Oe	0.73
Hardwood-spruce mix/Maine (USA)[b]	Oi	0.45
	Oe	0.63
	Oa	0.78

[a] Waksman et al. (1928)
[b] Waksman and Reuszer (1932)

reached at which the proportions remain constant. Two such quotients are as follows:

$$\text{HLQ} = \text{holocellulose}/(\text{lignin} + \text{holocellulose}) \quad \text{Berg et al. (1984)}$$

and

$$\text{LCI} = \text{lignin}/(\text{lignin} + \text{holocellulose}) \quad \text{Melillo et al. (1989)}$$

The former quotient approaches asymptotically a minimum value, which may be different for different litter types. For example, Berg et al. (1984) found a clear difference between the HLQ values for Scots pine and silver birch.

In an attempt to give a more general view on the concept of LCI, Melillo et al. (1989) introduced the concept 'biological filter,' and compared the development of the LCI quotient during decomposition, to the quotients found in different humus types (Table 5.3). In their study, the quotients for decomposing Red pine needle litter ended at 0.67, and the values for the corresponding humus were 0.72 in the forest floor and 0.73 in the mineral soil.

5.2.3 ^{13}C-NMR Technique

5.2.3.1 Cellulose and Hemicellulose

As we mentioned earlier, in ^{13}C-NMR analysis one or more specific bonds may represent a compound. More specifically, we may say that this method indicates specific bonds that may appear in one or several chemical compounds. For cellulose, the O-alkyl-C, which is represented by, for example, carbon 2, 3, and 6 (Fig. AIII.1), may be followed and represent those sugars (hexoses) in cellulose

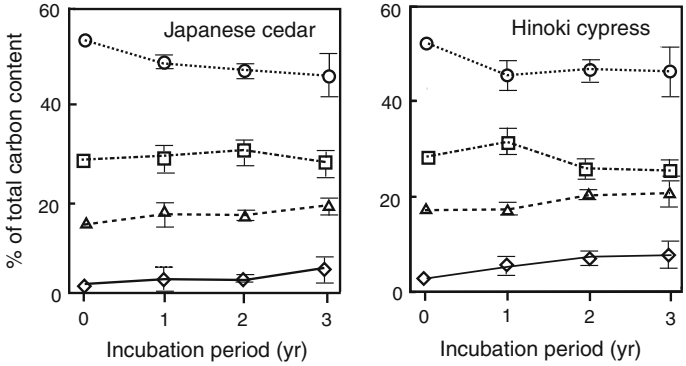

Fig. 5.4 Changes in concentration of the O-alkyl-C bond in hexose-based carbohydrates (–O–), the aromatic-C bond (–Δ–) for carbons 1 through 6 in the aromatic lignin ring and in condensed tannins (see also Table AIII:I), the aliphatic C bond (alkyl-C) (–□–), in, for example, long chains and in the acetate of some hemicelluloses and the carboxyl-C (–◇–) in, for example, carboxylic acids, amides, and esters. Foliar litter of Japanese cedar and Hinoki cypress were used as substrate. We may see a faster decrease in concentration (O-alkyl bond) in the first year, possibly relating to unshielded carbohydrates. The aromatic bonds appear to increase in concentration. From Ono et al. (2011)

and hemicellulose molecules that have 6 carbon atoms, for example, glucose (cellulose and starch), mannose (mannan), and galactose (galactan). That means that some hemicelluloses built by sugars with 5 carbon atoms are not included, for example, arabinan based on arabinose and xylan based on xylose. A problem is that the carbon β on the aliphatic side chain in lignin (Fig. A.III.2b also gives a response, which may need to be compensated for.

An alternative is to follow the di–O–alkyl–C (the O–CH_2–O bond) in cellulose and hemicelluloses, for example, carbon 1 in cellulose (Fig. A.III.1), which includes the hemicelluloses.

The development of these bonds has been followed over time in some decomposition studies. Thus followed Ono et al. (2011) the O–alkyl–C bond in decomposing litter of Japanese cedar and Hanoki cypress over 3 years (Fig. 5.4) and recorded a decrease in concentration. That pattern was found also for Japanese beech and an oak species (Ono 2009). Preston et al. (2009b) found a decrease in concentration of the O–alkyl–C bond and of 8 foliar litter species at least 6 followed that pattern of a decrease. They also found that to be the pattern, for the average values for 10 foliar litter species, when litter decomposition was followed for 6 years.

The di–O–alkyl–C bonds showed smaller changes (Preston et al. 2009b) than did the O–alkyl–C bond, and the variation was larger.

An interpretation of bonds to traditional chemical compounds has not yet been done. Possibly, we may use terms like ‘O–alkyl–C bonds in lignified tissue’ or ‘unshielded O–alkyl–C bonds for components in the late and early stages’, respectively. The O–alkyl–C bonds in Fig. 5.4 show a fast decrease in

concentration in the first year of decomposition. This may correspond to a fast decomposition of carbohydrates, resulting in a decrease in concentration in the early phase. In the late phase with lignified tissue, there would be less of a change in concentration (Chap. 2).

5.2.3.2 Lignin and a Group of Newly Synthesized Compounds

We may see four types of bonds that represent lignin, namely alkyl–C, aromatic–C, phenyl–C, and methoxy–C (Table AIII.1). In their study, Preston et al. (2009b) using 10 foliar litters found a general increase in concentration for all four. Ono et al. (Fig. 5.4) measured aromatic–C and noted an increase as well. Although these increases are clear, they do not necessarily mean an increase in a specific resistant compound. Preston et al. (2009b) give an example using methoxy–C. That signal may come from methoxy–C of lignin but may also arise from carbon in amino acids and proteins and may be an effect of the development of the substrate.

It appears, however, that at least part of the native lignin does not decompose any more slowly than other major components (Johansson et al. 1986; Grandy et al. 2007; Klotzbücher et al. 2011). Thus although Preston et al. (2009b) found that the average values for the three bond types increase, this does not mean that the concentration of a compound like lignin increases.

5.2.3.3 Some Suggested Indices

Some authors have suggested different indices for the aging litter. Ono et al. (2011) and Preston et al. (2009b) used alkyl–C-to-O–alkyl–C as a measure of decomposition level or 'humification.' That index means the ratio between the fraction of aliphatic-chain C and the fraction of carbon 2,3, and 6 in hexose-based carbohydrates (e.g., cellulose). This index increases with accumulated mass loss. Some further indices were suggested by De Marco et al. (2012) namely methoxy–C-to-phenol–C and a hydrophobicity index, namely (aryl–C + phenol–C + alkyl–C)-to-(carboxyl–C + O–alkyl–C). Both increase with accumulated mass loss.

5.3 Nutrient and Heavy Metal Concentrations during Decay

5.3.1 Changes in Concentrations of Elements in Decomposing Litter

Three principal patterns of nutrient concentrations have been observed in litter during decay, based on the release and accumulation of nutrients. Some nutrients

are released from the litter at a rate that is low and proportional to accumulated mass loss, resulting in a linear concentration increase with cumulative mass loss. Other nutrients may be readily leached from the litter and disappear faster than the litter mass as a whole, resulting in linear or curved negative relationships to accumulated mass loss. Finally, some nutrients are strongly retained within or even imported into the litter-microbe complex, resulting in an exponential increase in concentration versus litter mass loss. These latter nutrients can increase in both concentration and amount during decay.

5.3.1.1 Scots Pine Litter

The leaching of most nutrients from Scots pine litter is generally low which means that their loss from the litter is more closely related to microbial decomposition processes than to initial leaching. The relationships presented here thus may be representative for pine litter in a common boreal forest type. There appears to be too few studies to suggest any generality. To obtain a standard for comparing nutrient dynamics among litter types independently of decay rates, we have plotted nutrient concentrations relative to cumulative litter mass loss rather than relative to time (eg. Figs. 5.5 and 5.6).

Nitrogen. The concentration of N in litter increases during decomposition. This increase may be described versus time since the start of the incubation, or as a function of litter mass loss, in which case we regard the decomposition process of

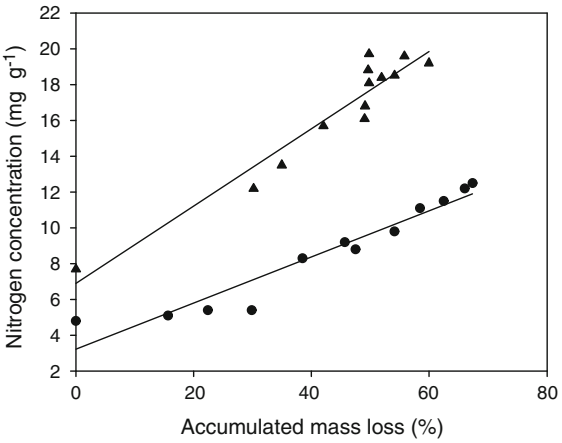

Fig. 5.5 The increase in N concentration in decomposing litter, as compared to litter accumulated mass loss. The linear relationship, which is empirical, appears to have a generality. Still, the relationship is dependent on the sampling intensity. The Scots pine needle litter (●) having an initially slower decomposition than silver birch leaf litter (▲) gives a clearer linear relationship. Note the large mass loss for birch litter in the first sampling, indicating heavy leaching, alternatively a fast decomposition of, for example, solubles (B. Berg unpubl.)

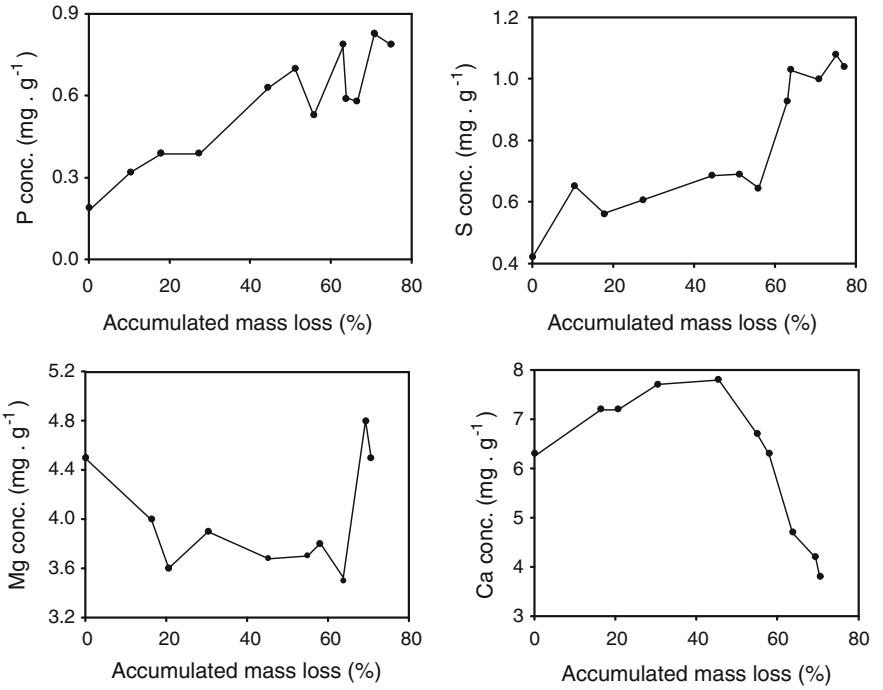

Fig. 5.6 Changes in concentration of phosphorus, sulfur, calcium, and magnesium in decomposing Scots pine needle litter (B. Berg unpubl.)

litter as a driving force for the change in N concentration. In this latter case, a positive linear relationship results (Fig. 5.5), allowing comparisons between studies, sites, and experimental treatments. This kind of linear relationship normally has R^2 values well above 0.9, is empirical, and has not been explained.

For boreal Scots pine litter, the N concentration may increase about 3-fold during decomposition, starting with c. 4 mg g^{-1} and increasing up to c. 12 mg g^{-1} (see the special study below).

Phosphorus. The concentration of P in litter increases during decomposition, in a manner very similar to that of N. Like for N, this relationship can be described as a positive linear function of accumulated mass loss (Fig. 5.6). In addition, for P, the linear relationship is empirical. For Scots pine, a 4-fold increase from c. 0.2 to 0.8 mg g^{-1} has been recorded (Staaf and Berg 1982).

Sulfur. As was the case for N and P, the concentration of S in litter increases mainly linearly during decomposition with respect to accumulated litter mass loss. Also, in this case, the positive linear relationship is empirical (Fig. 5.6), and for Scots pine, an increase from 0.4 to 1.0 mg g^{-1} has been recorded (Staaf and Berg 1982).

Calcium. A characteristic of the Ca concentration dynamics during decomposition is a peak in concentration followed by a decrease. The turning point corresponds closely to the point in decay at which a net AUR degradation begins (B. Berg and C. McClaugherty unpubl.; Fig. 5.6).

Potassium. As K is highly soluble, a proportion of the total is leached very soon after the litter has fallen. Normally by the first sampling in decomposition studies, a large reduction in concentration to a minimum is seen, after which the concentration starts to increase again (Fig. 5.7). Due to the high mobility, rather rapid and large changes in K concentration may take place thereby often creating uneven concentration graphs that may change considerably among studies. As regards concentration, we may divide the decomposition process into stages (see Fig. 5.7).

Magnesium. The concentration of Mg decreases slowly without the fast leaching that was seen for K. However, as for K, the decrease is interrupted and an increase is observed. As a simplification, the graph may be described as a positive X^2 graph (Fig. 5.6).

Other nutrients/heavy metals. There appear to be too few studies on heavy metals to allow us to suggest that the graphs presented below are generally applicable. Still, a group of them have similar patterns with clear trends. The few available studies indicate that the concentrations of most heavy metals increase as the litter decomposes, even up to around 80 % mass loss. The nutrients/heavy metals Cu, Pb, Fe, Zn (Fig. 5.8) as well as Ba, Sr, and Al all have a pattern of increasing concentrations during litter decomposition, essentially following an exponential graph. In all cases, their concentrations increase faster than just a conservation of the existing amount would suggest. Thus, it is likely that an import

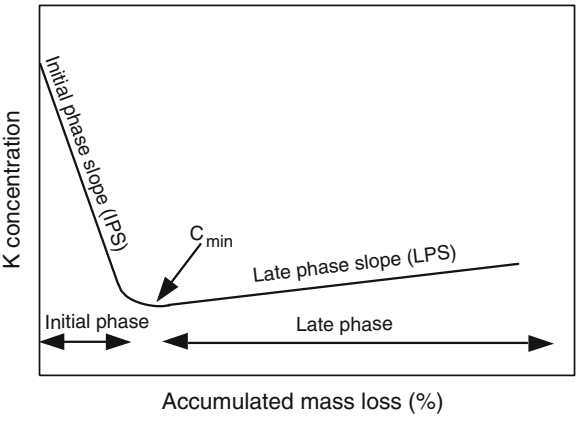

Fig. 5.7 Overview graphs for changes in K concentration with accumulated mass loss. Two phases in K concentration changes are identified: (1) The 'initial phase' has a rapid release of K; (2) The 'late phase' is the consecutive, equally clearly distinguished phase with much slower concentration changes. Slopes of concentration changes in the initial phase (IPS) and in the late phase (LPS). The minimum concentration for K reached during its release has been called C_{min}. From Laskowski et al. (1995)

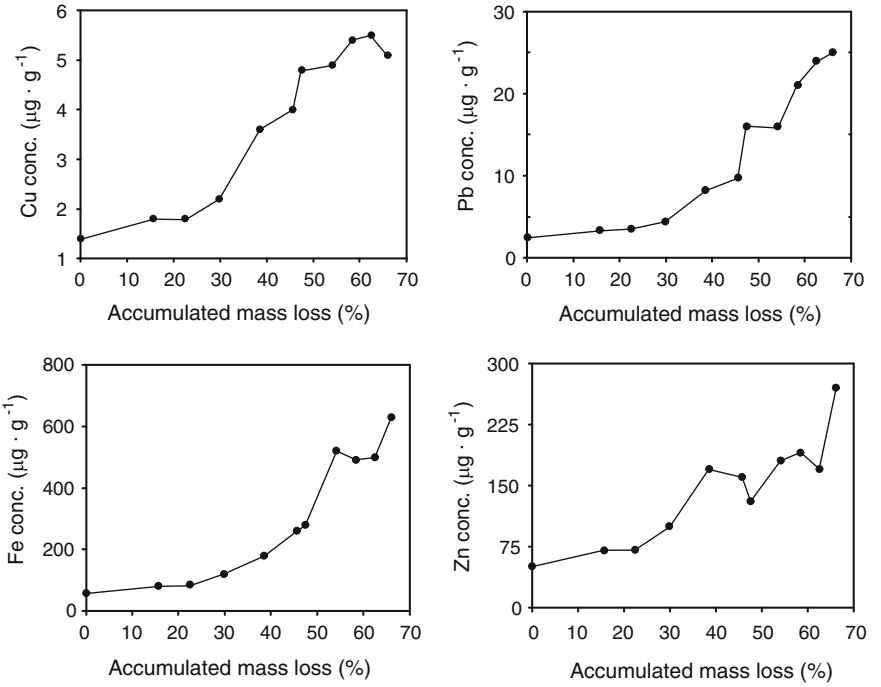

Fig. 5.8 Changes in concentrations of the heavy metals copper, lead, iron, and zinc with accumulated mass loss in decomposing Scots pine needle litter (B. Berg unpubl.)

takes place. Iron and Pb are known to be relatively immobile over a wide range of soil acidity (Bergkvist 1986) and are characterized by high, exponential concentration increases. In a case study for Al, the increase was from initially 280 µg g^{-1} to c. 900 at approximately 65 % mass loss. For Pb, the corresponding figures were 2.5 and 25 µg g^{-1}, for Cu 1.4 and 5, for Fe 55 and 600 µg g^{-1}, for Ba 4 and 28 µg g^{-1}, and for Sr, there was an increase from c. 5 to c. 10 µg g^{-1}. The concentration of Cd increased from c. 0.1 µg g^{-1} to c. 0.4 at 65 % mass loss.

At least two of the nutrients/heavy metals, Mn and Cd, show an increasing solubility and mobility with decreasing pH. They are thus often leached from litter. However, such a property is not independent of the microbial population, and at low concentrations when the metals are not in excess, a low pH does not necessarily mean a high net mobility. The microbial population could retain or import nutrients in the decomposing litter-microbe complex. Nevertheless, for Scots pine, the typical pattern for Mn was a concentration decrease and at a rate that was in proportion to litter accumulated mass loss (below).

5.4 Special Studies on Mn and N Dynamics

5.4.1 Mn Dynamics

5.4.1.1 Concentration Changes with Accumulated Mass Loss

In a paper on Mn dynamics in litter, Berg et al. (201Xb) investigated available data from decomposition studies, originating from 10 litter species, mainly from boreal and temperate forests. They used data for pine spp., Norway spruce, and a combined group of deciduous species and used decomposition studies in which Mn was analyzed in each litter sampling. They thus related concentrations and remaining amounts of Mn in litter to accumulated mass loss. For Scots pine litter, the pattern for Mn concentration with accumulated mass loss varied among studies. The variation may depend on initial concentration, ranging from an increase at low initial concentrations to a decrease at high initial levels. The dynamics of Mn in decomposing litter is so far little studied, and we have not been able to find any good review.

The changes in Mn concentration with litter mass loss appeared not to follow any regular pattern across species and genera (Fig. 5.9a, b, c). Even within a species (Scots pine), the pattern varied (Berg et al. (201Xb). Three groups of litter were compared using available data: (1) pine spp., (2) Norway spruce, and (3) deciduous litter. Mainly, it appeared that the concentration decreased, and at c. 15–20 % accumulated mass loss, Mn concentrations reached a minimum at which all three groups had similar Mn levels, after which the three groups showed different patterns with increasing Mn concentrations following accumulated litter mass loss. Very contrasting behavior was seen for pine spp. and Norway spruce.

Pine spp litter. For pine litter, a high initial Mn concentration resulted in a decrease in concentration as decomposition proceeded. We may see that for the litter with a high initial level (mainly lodgepole pine), concentrations decreased with accumulated mass loss, whereas that with a very low level (Aleppo pine) had an increase. Manganese in litter with a medium initial concentration decreased to a minimum level after which an increase followed.

Combining all pine data (Fig. 5.9a) gave a not very clear pattern for changes in concentration, and at 60–70 % accumulated mass loss, the range in concentrations was about as wide as for the newly shed litter. A quadratic function was significant ($R^2 = 0.070$; $n = 330$; $p < 0.001$) but indicated a very low increase in concentration (Fig. 5.9a), significantly lower than for the group of Norway spruce litter.

Norway spruce litter. In contrast to concentrations for pine spp, the Mn concentration for spruce litter varied but mainly increased (Fig. 5.9b). For Norway spruce litter, the concentration change with accumulated litter mass loss showed a larger variation than for pine litter although the main part of the studies had a similar pattern with a minimum followed by an increase.

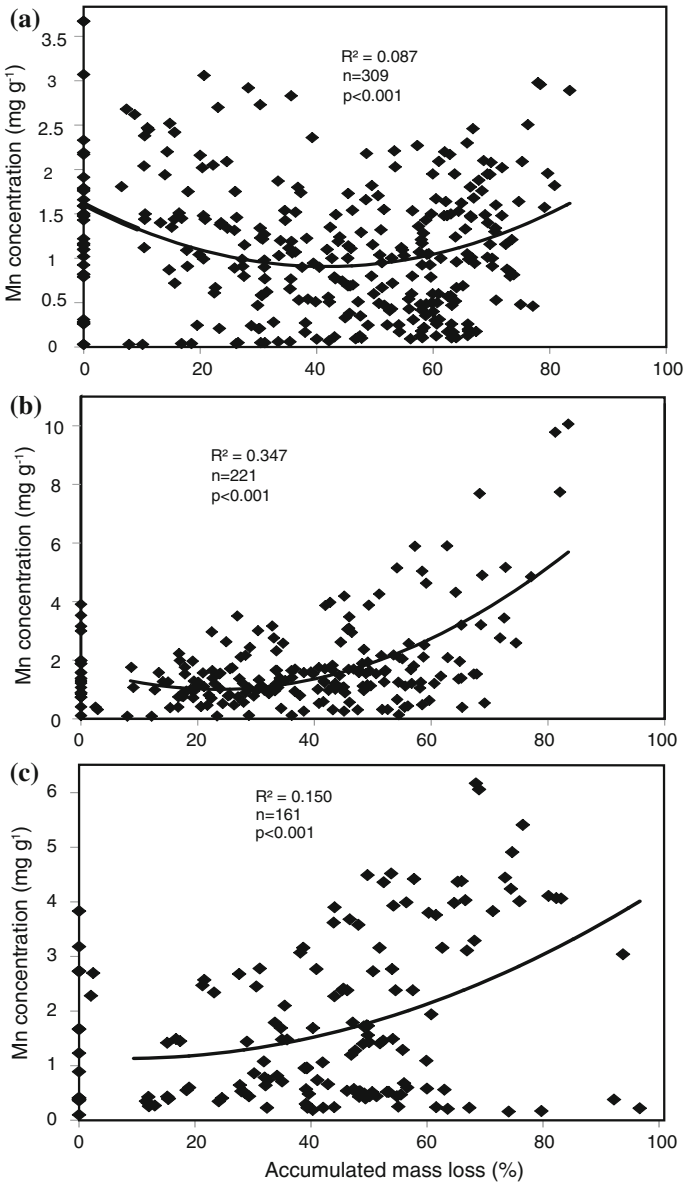

Fig. 5.9 Changes in concentration of Mn relative to accumulated litter mass loss for some deciduous and coniferous foliar litter species. **a** needle litter of Scots pine, lodgepole pine, and Aleppo pine, 37 decomposition studies, **b** needle litter of Norway spruce, 26 decomposition studies. **c** Leaf litter from available studies on silver birch, common beech, common oak and gray alder, in all 21 decomposition studies. Please note—different scaling on the Y axes. Data from Berg et al. (201Xb)

Spruce litter had a clearly higher increase in Mn concentration with accumulated mass loss than both pine litter and that of deciduous species, following a quadratic function ($R^2 = 0.347$; $n = 309$; $p < 0.001$) (Fig. 5.9b).

Scots pine and Norway spruce in paired stands. In their synthesis, Berg et al. (201X) also investigated paired stands, namely 8 ones with Norway spruce and Scots pine on the same soil and the same climate. Each group of litter followed a significant positive quadratic function ($X^2 - X$). Both groups had similar behavior as in the comparison using all available data for pine spp. and Norway spruce (Fig. 5.9) and the two functions were significantly different at 80 % accumulated mass loss ($p < 0.001$). The average Mn concentration at 80 % accumulated mass loss was 6.26 mg g^{-1} for Norway spruce litter and 1.47 mg g^{-1} for that of Scots pine. The quotient at 80 % mass loss for Norway spruce and Scots pine was 4.3, thus more emphasized for paired stands than for all available data.

Deciduous litter. Also for the combined deciduous species, there was a clear increase in Mn concentration, and at 80 % accumulated mass loss, there was a wider span in Mn concentration than at litter fall (Fig. 5.9c).

5.4.1.2 Manganese Release Patterns during Decomposition

We may see that Mn release was proportional to accumulated mass loss (Fig. 5.10). This was observed when comparing the Mn release rates for some litters with different initial concentrations. It appears that Mn release is about linear to accumulated mass loss (Fig. 5.10). Berg et al. (201Xb) investigated this for 84 decomposition studies encompassing Scots pine, lodgepole pine, Aleppo pine, Norway spruce, common beech, silver fir, gray alder and sitka alder and

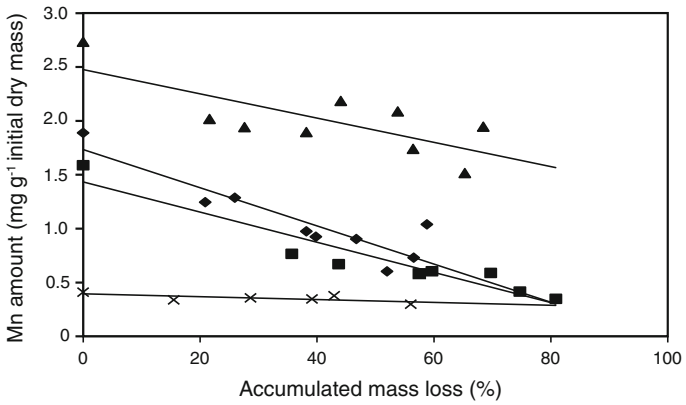

Fig. 5.10 The release of Mn from decomposing litter could be approximated to follow a linear function versus accumulated litter mass loss. We may note that the slope is more pronounced at higher initial concentrations. Figure shows litter from Scots pine, lodgepole pine, and Aleppo pine. Data from Berg et al. (201Xb)

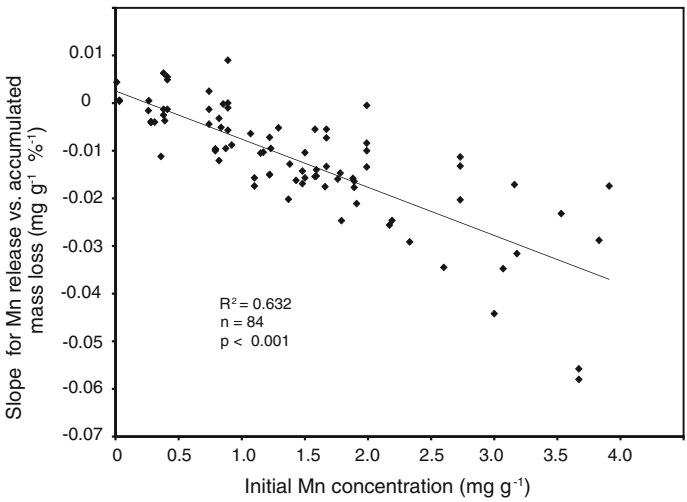

Fig. 5.11 Net release/uptake of Mn in foliar litter of pine spp. ($n = 37$), Norway spruce spp. ($n = 26$), and deciduous species ($n = 21$). With a linear Mn release versus accumulated mass loss, the slope has been related to initial Mn concentration in the litter. The main part of the data originates from boreal and temperate forests. From Berg et al. (201Xb)

found a linear release for the individual studies (cf Fig. 5.10). As the slope of such a linear relationship gives the release rate, the slopes were related to initial concentrations of Mn. In a development, they estimated the slope for 84 such relationships. The slope (the release rate) was related to litter initial Mn concentration. It appeared that the release rate was in proportion to the litters' initial concentration of Mn, and this relationship seemed not to be dependent on species (Fig. 5.11).

5.4.2 Nitrogen Concentration Dynamics over a Climatic Gradient

Nitrogen concentration increase. That N concentrations increase in decomposing litter is widely known. When the increase in N concentration is related to time since incubation, the result is a curve with an asymptotic appearance. We have related the increasing N concentrations to litter accumulated mass loss (cf. above) for several litter types, resulting in a linear increase, possibly until the limit value for decomposition is reached (Aber and Melillo 1982; Berg et al. 1997; Fig. 5.5). Such a linear increase has been found for many species including foliar litter of Scots pine and Norway spruce. Some deciduous litter species, such as silver birch, also give linear relationships, but much mass is lost initially, resulting in a fast increase in N relative to mass loss (Fig. 5.5). For Scots pine, the increase in

concentration is linear from an initial 4 mg g^{-1} up to 12–13 mg g^{-1} N at about 75 % accumulated mass loss (Fig. 5.12). Still, the reasons for the straight-line relationships are far from clear, given the simultaneous in- and outflows of N during the decomposition process (Berg 1988). This linear relationship is an empirical finding and for systems such as coniferous foliar litter, the relationship appears to be highly significant (Fig. 5.12a).

Berg et al. (1997) compared the linear relationship for accumulated mass loss versus N concentrations among several sets of decomposing Scots pine needle litter in one system (Fig. 5.12b). They called the slope of the relationship the Nitrogen concentration increase rate (NCIR). The litter was naturally produced from a Scots pine monocultural system, and the variation in initial N concentration was the observed annual variation. For one site, the relative increase rates in N concentration showed significant linear relationships to litter mass loss for individual sets of litter, as well as for the average combined from all 14 sets of litter. The NCIR values in this comparison had an average of 0.1109, and the slopes ranged between 0.055 and 0.129 (SE = 0.0047) indicating that for a given litter type and system, the variation in NCIR was somewhat limited (Table 5.4).

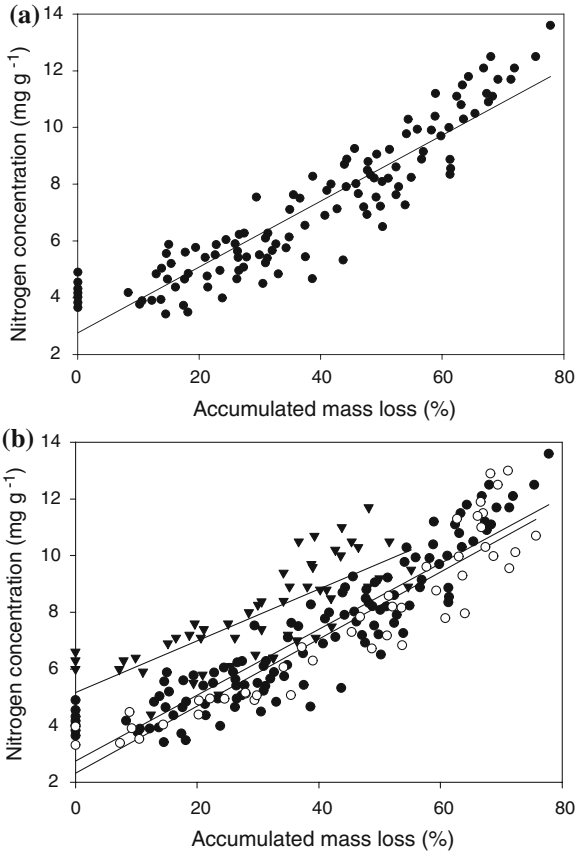

Fig. 5.12 **a** Overall relationship between increasing concentrations of N and accumulated mass loss for decomposing Scots pine needle litter. Incubations were made at one site, a nutrient-poor Scots pine forest. Data are pooled from 14 sets, each representing an incubation of local litter from a different year. **b** Litter N concentration as a function of accumulated mass loss for decaying coniferous litters (●) Scots pine—14 sets, (○) lodgepole pine—five sets, and (▼) Norway spruce—four sets. Coefficients of determination (R^2) are 0.845 ($n = 131$), 0.851 ($n = 54$), and 0.638 ($n = 56$), respectively. From Berg et al. (1997)

Table 5.4 Overall *Nitrogen concentration increase rates* (NCIR) for local needle litter of three coniferous tree species incubated at three sites. Comparisons are made both by calculating regressions over the combined data set, and by taking the average slopes of individual data sets. Nitrogen concentrations were regressed *versus* litter mass loss. From Berg et al. (1997)

Site—species	Intercept (SE)	Slope (NCIR) (SE)	R^2_{adj}	R	n	P
Jädraås—Scots pine						
All values combined	2.941 (0.985)	0.1107 (0.0042)	0.843	0.919	131	<0.001
Malung—Lodgepole pine						
All values combined	2.762 (1.128)	0.1171 (0.0065)	0.862	0.928	54	<0.001
Stråsan—Norway spruce						
All values combined	4.769 (1.124)	0.1019 (0.0105)	0.638	0.799	56	<0.001

SE standard error, *n* number of data sets

In a comparison of NCIR values for lodgepole pine needle litter, the slopes of five lodgepole pine data sets gave similar results with an average slope of 0.1151 and a standard error of 0.0060 (Table 5.4). For needle litter of Norway spruce, the average slope was similar to that of the pine litters and reasonably consistent among four sets of litter (Table 5.4). The conclusion may be that although the increase in N concentration during decomposition is empirical, it is consistently observed. When the three different studies are compared, we see that the two pine species, having similar N levels, increase in parallel (Table 5.4), whereas the Norway spruce litters, as a result of initially higher N concentrations, form a group above the pine litter, while having similar slopes (Fig. 5.12b).

The influence of initial litter N concentrations. Scots pine green needles with a higher initial N concentration had a much larger NCIR than brown needles, meaning that the increase rate was larger. A similar trend was observed for decomposing Norway spruce needles. Both green needles and N-enriched needles, collected from N-fertilized plots, had higher NCIR values than the more N-poor regular brown needles. However, the difference between natural and fertilized needles was not significant (Berg et al. 1997). This property of NCIR, to increase with increasing initial N concentration, appeared to be in common for different species. Thus, natural needle litter of lodgepole pine and Scots pine had similar initial N concentrations and the two species also had similar average NCIR values.

Significant relationships between initial litter N concentrations and NCIR values were found within the Scots pine species (Fig. 5.13), whereas for Norway spruce needles alone, Berg et al. (1997) found no such relationship. In an attempt to find a global relationship, they considered all available data both from coniferous and deciduous litter and found a significant relationship, which seems to hinge on the relatively few extreme points corresponding to green and deciduous

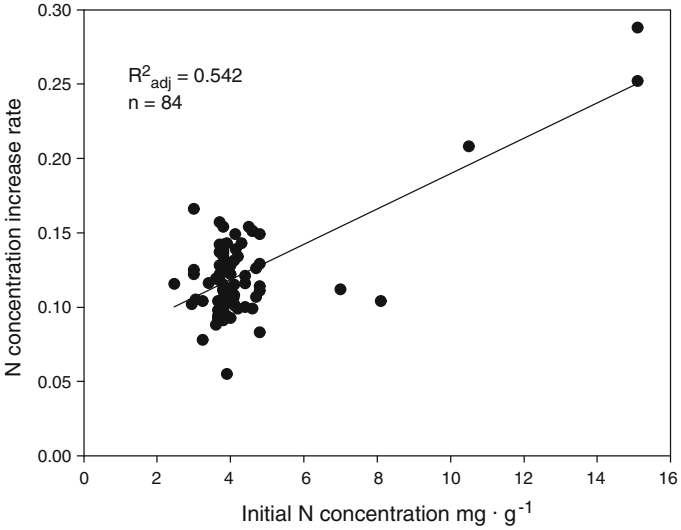

Fig. 5.13 Linear relationship between initial concentration of N in decomposing Scots pine needle litter and the slope of N concentration versus accumulated mass loss (Nitrogen concentration increase rate or NCIR). Many individual points are obscured due to overlap. From Berg et al. (1997)

litters (Fig. 5.13). Thus, on that scale, NCIR is only weakly influenced by initial N concentrations, except when considering extreme cases. However, to the extent that a relationship does occur, it is a positive one. This means that N concentrations increase to a somewhat greater extent with accumulated mass loss when initial N concentration is higher. Berg and Cortina (1995) also saw this when comparing NCIR for seven very different litter types incubated in one system (Fig. 5.14).

One mechanism for conserving N in decomposing litter could be via covalent bonding to macromolecules during the humification process. An example of this is the ammonia/ammonium fixation described by Nömmik and Vahtras (1982). Two recent papers give further compounds, for example, the one by Knicker (2004; Fig. 2.4) and one by Thorn and Mikita (1992). Thus, if the initial amount of N in the litter was higher, there would be more available for fixation, giving a higher NCIR. Such a conclusion is reasonable since Axelsson and Berg (1988) found that the N availability is limiting the rate of the process.

Influence of climate—Scots pine systems. For local natural Scots pine needle litter and a unified Scots pine needle litter preparation, the relationship between NCIR and AET was investigated across a climatic gradient in Sweden, with AET ranging from 380 to 520 mm. There was a highly significant relationship for Scots pine ($R^2_{\text{adj}} = 0.640, n = 31, p < 0.001$) indicating that the N concentration will increase faster (relative to accumulated mass loss) under a warmer and wetter climate. This correlation was significant when both local and unified needle litter

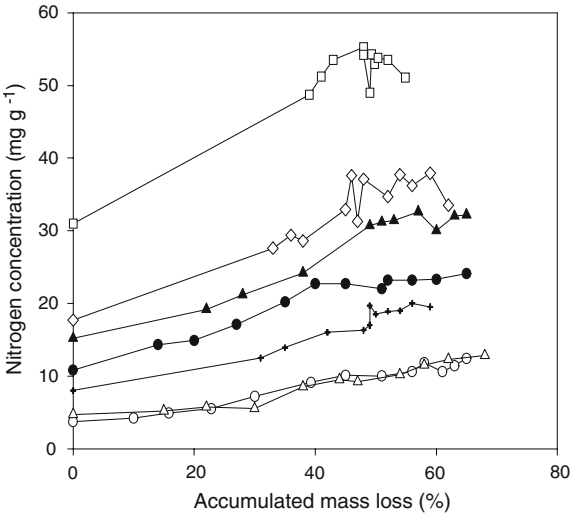

Fig. 5.14 Changes in N concentration as related to accumulated litter mass loss for seven litter types incubated in a 130-year-old Scots pine forest. Brown Scots pine needle litter (△), green Scots pine needles (▲), brown needles of lodgepole pine (○), green needles of lodgepole pine (●), brown leaf litter of silver birch (◆), green leaves of silver birch (◇), green leaves of gray alder(□) From Berg and Cortina (1995)

was used and also when using only local needle litter ($R^2_{adj} = 0.517$, $n = 18, p < 0.001$).

Influence of climate—Norway spruce systems. Norway spruce litter was investigated separately (Berg et al. 1997). In a climatic gradient in Sweden, the NCIR values increased with increasing AET values and the relationship was highly significant ($R^2_{adj} = 0.534, n = 14, p < 0.01$).

Influence of climate—a general relationship? Berg et al. (1997) found that for Norway spruce, NCIR increases slightly more with increasing AET than for Scots pine litter (slopes of 0.00055 and 0.00038, respectively; Fig. 5.15), but the difference was not significant. In the comparison between NCIR and initial N concentration, there were differences between the Norway spruce litter and that of

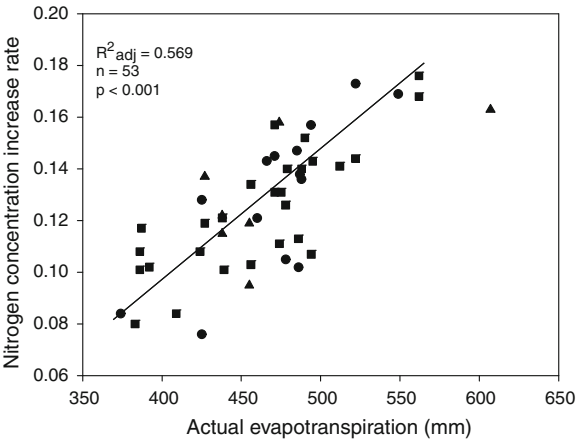

Fig. 5.15 A linear relationship between the climatic index actual evapotranspiration (AET) and Nitrogen concentration increase rate (NCIR) in decomposing needle litter of (●) Scots pine, (■) Norway spruce, and (▲) other pines lodgepole pine and white pine. From Berg et al. (1997)

pine. Berg et al. (1997) concluded that in the analysis versus climate, the relationships for Norway spruce and Scots pine were sufficiently similar to allow a stepwise combining of the data. First, the values for Scots pine and Norway spruce were combined, resulting in a highly significant relationship with a low standard error ($R^2_{adj} = 0.604, n = 45, p < 0.001$). This means that for both Scots pine and Norway spruce, the climatic factor was more important for the increasing concentration of N in litter than was the species or the initial N concentration.

In a second step, they combined all brown coniferous litter and obtained a highly significant linear relationship with $R^2_{adj} = 0.569, n = 53, p < 0.001$). It may be worth pointing out that the white pine needle litter data came from a more southern site with a relatively high AET but did not deviate from the general relationship.

Finally, in an analysis combining coniferous and deciduous litters, the relationship was still highly significant ($R^2_{adj} = 0.628, n = 59, p < 0.001$). Deciduous litters departed from the pattern exhibited by coniferous litters, but the overall relationship remained significant. Thus, climate, as indexed by AET, is a significant factor in affecting the rate of N concentration increase in decomposing leaf litter. As these increases were calculated on the basis of accumulated mass loss rather than time, the results mean that, after a certain mass loss, a particular litter decaying in an area with higher AET will contain more N than the same litter decaying in an area with lower AET.

Chapter 6
Chemical Constituents as Rate Regulating: Initial Variation and Changes during Decomposition. New and Traditional Analytical Techniques

6.1 Introduction

In Chap. 5, we reviewed the patterns of litter chemical composition and their changes that occur during decay. This chapter focuses on the influence of that changing litter quality on the decay processes and will show that the influences of selected litter chemical components change dramatically during decay, sometimes even reversing the direction of their effect. For this purpose, the three-phase model and its development were introduced (Chap. 2) to organize our explanation of the effects of chemical variation, changes in mass-loss rates and decomposition patterns.

In the last decades, clear progress has been made as regards both decomposition data and analytical techniques for organic compounds, in part revealing new relationships and providing new information. We thus not only have a larger set of data and decomposition patterns, based on conventional chemistry but also have an increasing amount of data based on the new and more specific ^{13}C NMR technique.

Combining new and traditional technique so far has not given information, which leads to a unified picture, although a main part of the patterns are in common. We therefore have presented patterns and models based on both traditional and new techniques.

Chemically distinct litter species or litter that has been chemically modified as a result of for example fertilization or pollution will follow different patterns during the decomposition process. Higher concentrations of the main nutrients N, P, and S may increase the initial decomposition rate and in later stages change the decomposition pattern. The case study litter (Chap. 2) showed a basic pattern, and in this chapter, we will describe the effects of variations in the concentrations of the main nutrients as they appear in different species. Nutrients other than the principal ones may be important in some litters. For some foliar litter species, notably Norway spruce and common oak, the patterns differ completely and initial rates may be related to concentration of Mn. These litter species have been the basis for suggesting a flexible early stage in the three-phase model. A recent paper on effects of Na being the nutrient limiting decomposition rate (Kaspari et al. 2009) we just report.

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7_6,

The decomposition process normally reaches a stage at which decomposition almost stops or proceeds so slowly that the stage may be approximately described mathematically by an asymptote, or as a limit value for the decomposition process (Chap. 2). For foliar litter, the limit value is normally in a range between 50 and 100 % accumulated mass loss. Using available data, the limit value has been negatively related to initial litter N concentrations, which means that the more N rich (and generally more nutrient rich) the litter is, the sooner the limit value is reached and the less the litter will decompose under comparable environmental conditions. The concept limit value, which has been generalized for foliar litter types, is developed in this chapter. Using the litter genus *Pinus*, the limit value has been positively related to initial litter Mn concentration (Berg et al. 2010). There is a general positive relationship between the concentration of Mn and the degradation of lignin and modified lignin as well as litter decomposition. This relationship is not explained experimentally, but Mn is known as a cofactor in a lignin-degrading enzyme, namely Mn peroxidase (Perez and Jeffries 1992; Hatakka 2001).

Generally raised N concentrations in litter support the process of leaching of C compounds from that litter (Fog 1988). This leaching may begin in the early phase and continue through the remaining phases to humus-near stages. There are extreme cases reported, such as an actual disintegration of very N-rich humus that was due to a change in the microflora. This resulted in a very rapid degradation accompanied by a leaching of N-containing compounds (Guggenberger 1994).

The intention of this chapter is to demonstrate and systemize the changing effects of several chemical components on rates and patterns of litter decomposition. We use several litter species and intend to generalize the model presented in Chap. 2.

Recent studies have created a new development of the whole model concept. The findings about the role of Mn beginning in the initial stages of decomposition for newly shed litter have changed and modified the concept ‘early stage’ or ‘initial stage.’ We therefore have developed the three-stage model, refined the definition, and identified two main cases or patterns of decay, especially for the initial stage.

6.2 New Finding, Possible to Relate to a Phase-Based Model

Although studies in litter decomposition have been ongoing for a long time, there has been a strong development in the last 20–30 years and basic discoveries have been made. The concept of the main nutrients as limiting factors has been a basic one and was used to construct the three-phase model. However, new discoveries may lead to new model concepts, and we have provisionally included the finding of Kaspari et al. (2009) in the model, with Na as a possible limiting factor at inland sites.

In an inland study, they made a set of experiments using leaf litter, supporting that adding or 'fertilizing' with sodium actually increased decomposition rates of whole litter. They recorded a weak loss of AUR/lignin.

The general average level of Na in the litter they studied was c 0.04 %, and during the experiment, Na was taken up to the litter and immobilized. They discussed the relevance of the land's distance from sea as Na may be transported by sea spray. The fact that more than 80 % of the global landmass is located at more than 100 km inland may mean that Na could have a role of limiting nutrient over potentially large areas.

We believe that this finding may lead to a new way of thinking as regards limiting factors for litter decomposition. That Kaspari et al. (2009) found Na to be limiting for decomposition may open up for further discoveries as regards limiting factors for litter decay.

6.3 A Three-Phase Model Applied to Different Litter Species of Different Chemical Composition

The decomposition dynamics in most needle and leaf litters investigated to date follow the model presented in Fig. 6.1a. The model appears to be appropriate for needle litter of different pine species, as well as different types of broadleaf litter, and probably also litter from grasses and herbs. The model thus appears to have a relative generality, let be that the early phase, dominated by the decomposition pattern set by polymer carbohydrates, may have very differing extensions. The carbohydrate-dominated early phase may thus reach from close to 0 % of the litter mass to at least 40 % depending on litter species.

The research field of litter decomposition appears to be under strong development, and we may expect further discoveries that may change the concept of the three-phase model, which is just a way to organize present knowledge. So, we may see the presented model as just a development stage in the search after a structure for our knowledge.

Different plant litter types and species have different chemical composition when shed (Chap. 4) and probably the cellulosic fibers are lignified to different extents. Such properties are apparent in the early stage, for example, as regards measurable rate-limiting factors. Some of these properties are also reflected in late stages of decomposition and higher initial concentrations of N and AUR/lignin result in higher concentrations of these components during the whole decomposition process (Chap. 5). To describe this, we have chosen to apply and develop the three-stage model described earlier by Berg and Matzner (1997) and developed from Berg and Staaf (1980). They defined a late stage or 'lignin-dominated' phase in which the degradation of AUR dominated the litter mass loss and the degradation of AUR/lignin in turn may be related to litter Mn or N concentrations (below).

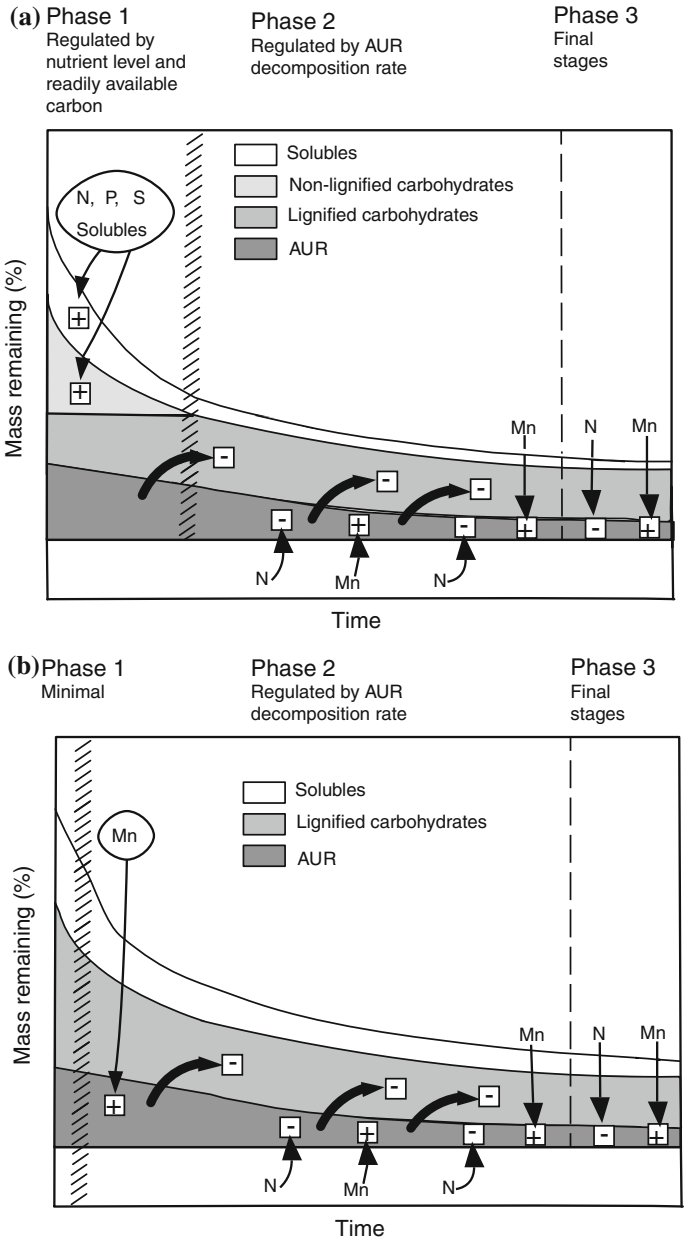
(a) Phase 1
Regulated by nutrient level and readily available carbon
Phase 2
Regulated by AUR decomposition rate
Phase 3
Final stages
Solubles
Non-lignified carbohydrates
Lignified carbohydrates
AUR
N, P, S
Solubles
Mass remaining (%)
Mn
N
Mn
N
Mn
N
Time
(b) Phase 1
Minimal
Phase 2
Regulated by AUR decomposition rate
Phase 3
Final stages
Solubles
Lignified carbohydrates
AUR
Mn
Mass remaining (%)
Mn
N
Mn
N
Mn
N
Time

Fig. 6.1 Model for chemical changes and rate-regulating factors during decomposition, modified from Berg and Matzner (1997). **a** The decomposition of water-soluble substances and unshielded cellulose/hemicellulose is stimulated by high levels of the major nutrients (early stage—phase 1). When all unshielded holocellulose is decomposed, only lignin-encrusted holocellulose and lignin remain. The early phase has been observed to last up to c. 40 % mass loss (Group I; Table 6.1). In the late stage—phase 2, the degradation of lignin dominates the litter decomposition rate. Nitrogen hampers the degradation of lignin and higher N concentrations suppress the decomposition, whereas Mn appears to have a stimulating effect on the degradation of lignin and litter. Finally, in the humus-near stage (phase 3), the AUR/lignin level is nearly constant, often at a level of 50–55 %, the litter decomposition rate is close to zero and the accumulated mass loss reaches its limit value. **b** With the early phase missing or very short, we may see that nutrients influencing lignin degradation dominate (Mn—positively and N—negatively). Lignin/AUR degradation dominates litter mass loss from the start of the incubation, and Mn litter concentration is determining for litter mass loss. These models are modified according to a suggestion of Klotzbücher et al. (2011). They found that there is a loss of lignin from the start of the incubation

Litter species studied so far can be placed provisionally into one of two main groups under this model based on the litters' properties in the early stage and their behavior in the late stage (Table 6.1). We consider these groups as a part of a pattern in development and expect them to change as new information becomes available. There are thus cases with a clear 'early phase' as well as cases in which the 'early phase' is short or not even possible to measure. In the latter case, this means that the decomposition process starts in or very close to the 'late phase' or 'lignin-dominated' phase.

The three-phase model was based on traditional analyses for AUR/lignin and polymer organic compounds ('proximate analysis'). There are few comparisons of proximate analyses and that using ^{13}C NMR (cf. Preston et al. 2009a, b; De Marco et al. 2012). However, we intend to discuss a comparison and have used available NMR data in order to apply these on the three-phase model.

As an initial reference point for early stage decomposition on which to base further discussion, we consider the decay of Scots pine needle litter (Chap. 2). For newly shed Scots pine litter with different nutrient levels, the decomposition rate was linearly related to concentrations of total N, P (Fig. 6.2), and S, until an accumulated mass loss of between 26 and 36 % was reached (year 1), mainly corresponding to an early phase.

We also discuss the late stage of decomposition and the concept of the limit value with respect to the varying litter chemical composition. The humus-near stages are explained with respect to limit values and their relationship to the chemical composition of litter. Different litter types, however, have somewhat different patterns in relation to the model and that is discussed. We can thus see two main patterns or groups of foliar litter decomposition. We have given each group provisional names: 'Group I,' and 'Group II,' and they are presented in Table 6.1.

Even if we can have a general definition of a reasonably clear border between the early and the late stages of decomposition using the degradation of lignin/AUR, there may be an 'intermediate zone' as discussed for pine litter (Sect. 2.6.2;

Table 6.1 Overview of a possible division of foliar litter types into groups with different properties, organized into the three-stage model (Fig. 6.1). The names of the groups are provisional. We consider that the properties of the early stage determine to what group the litter belongs

Group I (e.g. *Pinus sp*)
Early stage Initial mass-loss rates may be positively related to initial concentrations of N, P, or S and at inland sites, possibly to that of Na. In some broadleaf litter species, mass loss may be fast, due to leaching or a fast decomposition of, for example, remaining starch. Climate has a clear influence on decomposition rates. The extent of the early stage may vary.
Intermediate stage See Sect. 2.6.2. A stage in which there is no positive relationship to, for example, N and P, no positive relationship to Mn or negative to AUR and N.
Late stage Decomposition of AUR/lignin appears to regulate the decomposition of remaining litter mass. The stimulating effect of main nutrients (above) and climate has ceased. Mass loss e.g. annual mass loss may be related positively to Mn or negatively to N or lignin/AUR, possibly to all three factors.
Limit value (humus-near) stage Identified by an estimated limit value. The level of the limit value may be related to litter Mn concentration.
Group II (e.g., Norway spruce, common oak)
Early stage In this group, an early stage is missing or so short that it possibly is not measurable. Initial mass loss may be related to litter Mn concentration.
Late stage Lignin decomposition appears to dominate decomposition of remaining litter. Annual mass loss has been related to concentrations of Mn and AUR/lignin (just two litter species investigated). Influence of site climate is probably very small or negligible.
Limit value stage Related to litter Ca concentration for common oak. Information sources are limited.

Fig. 2.7). The humus-near stage may be defined as the size of the stable fraction using the limit value.

When litter has reached the humus-near stage, we may start discussing the stability of the humus as such, let be that humus may be defined by the limit value. When considering a humus layer, it is of course difficult to distinguish between newly formed ‘stable humus’ and older, formed earlier. We therefore have added a short section called ‘humus stability.’ Several functional properties, such as the effect of N on decomposition, appear to be common to different stages. Thus, properties of the humus-near stage may persist into the humus stage.

6.3.1 Early Decomposition Stage: Dominated by Cellulose and Hemicelluloses

6.3.1.1 Extent of the Early Phase: What is Decomposed?

The size of the early, carbohydrate-dominated stage appears to vary with litter species, and two main patterns have been reported. The so far most common case is one observed and discussed for Scots pine and *Pinus sp* (Chap. 2). At least some pine species have a clear initial stage in which N, P, or S are rate determining for

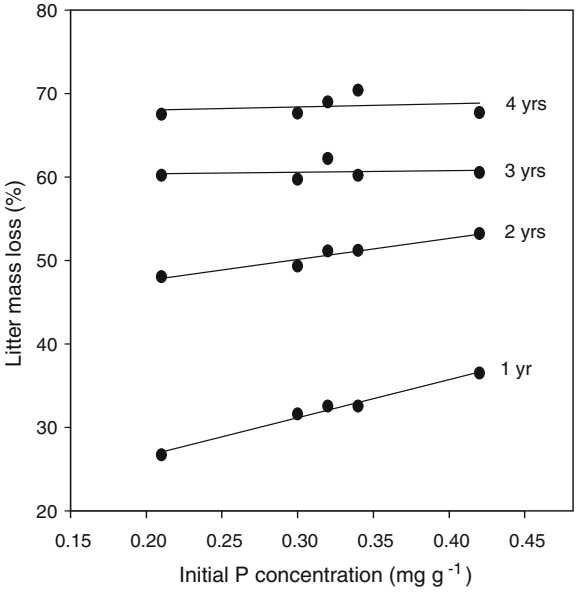

Fig. 6.2 Relationships between initial concentrations of P and increasing mass loss of Scots pine needles. A set of five collections of Scots pine needle litter from N-fertilized plots was used. Annual mass loss was calculated for the 1st, 2nd, 3rd, and 4th year. The values for mass loss were related to concentrations of nutrients and AUR at the start of each year. The slope decreases as the rate-stimulating effect of P decreases and that of another factor takes over. Initial concentrations of N showed a very similar pattern (B. Berg unpubl.; data from Berg and Staaf 1980). The ranges for accumulated mass loss within each year were as follows: year 1, 0–36.3 %, year 2, 26.5–53 %, year 3, 48.1–60.4 %, year 4, 59.4–70.4 %

the degradation of water-soluble substances, as well as unshielded cellulose and hemicellulose. Such a carbohydrate-regulated phase appears represented also among broadleaf species, sometimes with a high leaching of easily degradable compounds, possibly including remaining starch (Group I; Table 6.1).

For Scots pine needle litter, it was estimated that the shift in phases took place at a mass loss of between 26 and 36 %. In a separate study on Scots pine needle litter, Couteaux et al. (1998) determined the change in phases to take place at about 27 % accumulated mass loss. For lodgepole pine litter, the early phase was seen to be shorter and end at around 20 % or lower (B. Berg, unpubl.).

Leaf litter of, for example silver birch and gray alder, appears to have an initially high decomposition rate followed by an abrupt shift from the early to the late stage at c. 40–45 % mass loss. Such a high mass loss may take place in just a few months and may be due to the properties of the carbohydrate fraction. We may speculate that for some broadleaf litter, a high content of, for example, remaining starch may result in a faster decomposition as compared to holocellulose, although such a fast mass loss would not be due to leaching. Still, a mass loss of 40 % may take place in a few months. For litters that leach C compounds initially, for

example several deciduous foliar litter types, mass-loss rates are the result of a combination of microbial decomposition and leaching (see Glossary). The loss of organic matter from newly shed litter through soaking the litter in water may reach rather high values, although this initial leaching can be limited in some litter types. For example, Scots pine needle litter may lose just a few percent from leaching (Bogatyrev et al. 1983), while some deciduous litters may leach considerably more, in part because they have a higher concentration of water-soluble substances (Table 4.1).

The loss of soluble material is not all due to leaching. In a study of sugar maple leaves, McClaugherty (1983) determined that most of the soluble carbohydrates and soluble phenols lost during the first year were either consumed by microorganisms or converted to insoluble compounds. After 1 year, only 21 % of the initial soluble carbohydrates remained in the leaf litter, 15 % had been leached, and 64 % had been respired or converted. For soluble phenols, the figures had a similar pattern: 29 % leached, 4 % remaining, and 67 % consumed or converted. Freeze–thaw cycles increase the leachable amount both of C compounds and of nutrients. Initial leaching is possibly influenced mainly by the litter type (e.g. coniferous *vs.* deciduous), or litter species, freeze–thaw cycles, and concentration of solubles.

A recent report (Klotzbücher et al. 2012) indicates that there is a degradable fraction of native lignin in the early stage. They investigated five litter species (Scots pine, Norway spruce, mountain ash, common beech, and sycamore maple) decomposing for 27 months. Using the CuO analysis, they found that for all five litter species native lignin was degraded from the very start, with the first sampling after 3 months. It is reasonable to assume that although part of the lignin was degraded, it may not have been dense enough to dominate the decomposition process.

We may distinguish a second group of foliar litter (Group II; Table 6.1), which appears to be one in which no real initial phase can be found and the litter behaves as with lignin/AUR being rate regulating and degraded already initially, which means that the decomposition starts in a late phase, dominated by the degradation of lignin/AUR. In this latter case, N, P, and S seem to have no stimulating effect on decomposition rate. Rather we may expect an effect of varying Mn concentrations and/or lignin (AUR). This has been reported for Norway spruce and for common oak.

Considering the development in litter decomposition science, we need to develop the terminology for the early and late phases (see Glossary in App I). We may relate it to the polymers that are degraded initially and the factors regulating the decomposition. The ‘early phase’ thus refers to loss of solubles and unshielded polymer carbohydrates as well as to effects of climate and concentrations of the main nutrients (N, P, S). The ‘late phase’ which was originally defined as the one in which lignin/AUR degradation dominated the litter mass loss may be considered as a phase, which is dominated by the degradation of lignin/AUR, which in its turn is related to factors regulating the degradation of AUR/lignin. A more rational term may be ‘lignin-dominated phase.’

6.3.1.2 Early Stage Mass Loss: How can Initial Rates be Described?

There are different ways of expressing the decomposition rate in the early stage. A common way to measure and compare decomposition rates is to use mass loss for a given period, often one year or to calculate a rate constant over a period (e.g. Eq. 9.2), both just integrating mass loss over time. However, certain drawbacks with this approach have become recognized as more data started to appear. Thus, a short early stage, either with a low mass loss or one with a high initial mass loss, both followed by a late stage may be difficult to relate to limiting nutrients if the sampling period is too long or a rate constant is determined over a longer period. For example, a first sampling after several months or one year may mean that the litter is well into the late phase and the resolution simply becomes too low to identify limiting nutrients. A very short early stage at a site with high decomposition rate may thus lead to that an early, carbohydrate-dominated phase is not recorded.

The majority of studies on litter decomposition found in the literature appear to present results from the early decay stage. These studies often show positive relationships between initial decay rates or CO_2 release from litter and concentrations of either the group of major nutrients (N, P, S) or the concentration of water-soluble substances. There are also reported relationships between initial mass-loss rates and concentration of Mn (Group II; Table 6.1).

A further way to determine the initial rate of decomposition is to use the mass-loss data from a whole study (Fig. 6.3), ranging from the first sampling of litter bags to the very last one, perhaps after several years. Equation 6.1 gives the initial rate (k_{init}) at time zero and the limit value (m). The values inserted into the function are accumulated litter mass loss ($m.l.$) and time (t). The equation is presented in detail in Chap. 9.

$$m.l. = m\left(1 - e^{-kt/m}\right) \tag{6.1}$$

One advantage of using this equation is that a higher number of measurements are used, and another that the initial rate estimated is the rate at time zero. It is not directly dependent on time for sampling but the calculation considers all samplings. K_{init} gives the rate as the derivative at time zero and thus has a better potential to identify initial mass-loss rates.

6.3.1.3 Initial Chemical Composition and Different Indices Related to Early Phase Decomposition Rates

A clear early phase dominated by degradation of carbohydrates and solubles. Different approaches have been undertaken to identify a chemical index for the initial decay rate. One is simply the concentration of a given nutrient, such as N or P. A positive relationship between a nutrient and initial decomposition rate is a crude measure of its rate-regulating function. A discussion about which of these

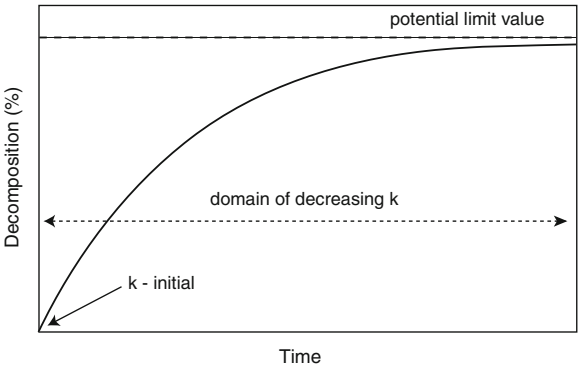

Fig. 6.3 Mass-loss rates for decomposing litter gradually decrease and the accumulated mass loss may approach an asymptote, a limit value. The process may be described using Eq. 6.1 (see also Chap. 9). The function may be used to estimate the decomposition rate at any point in time. The initial decomposition rate (*k-initial*) gives the rate at time 0

main nutrients that is rate regulating is not always meaningful, as other factors (e.g., climate) can be more dominant. We can see (Table 6.2) that for decomposing Scots pine needle litter, the main nutrients P and S show significant correlations to first-year mass loss. That the relationships to N are weaker does not mean that N is without effect. The different R values for N, P, and S probably reflect differences in availability of the respective elements relative to the requirements of decomposer microorganisms.

Part of these interactions are being studied (e.g., Güsewell and Verhoeven (2006)) in order to determine the optimum proportions between N and P and thus determine which of the two that is limiting. However, Güsewell and Gessner (2008) conclude that the ratio between N and P is critical for decomposition rate but that there is no fixed ratio between the two nutrients across litter species and environmental conditions.

In contrast to the three nutrients, N, P, and S are the highly mobile ones, such as K, that are very leachable. Potassium and Mg are neglected here as rate-limiting components, since their concentrations drop heavily immediately after incubation, and so far there has been no indication that they act as limiting nutrients. Different initial concentrations of such mobile nutrients appear not to influence the litter decomposition rate. The finding of Kaspari et al. (2009) that Na may be limiting at inland sites may, however, open new views on limiting factors.

The lower R value for the relationship to initial N (Table 6.2) could reflect the fact that part of N is stored in litter in forms that are less available to the microorganisms that first invade the litter. All the three main nutrients (N, P, S) are found in compounds in which they are bound by covalent bonds, and it appears that with part of N bound to aromatic polymers and newly formed products (Fig. 2.4) that part of the N fraction may be less available. Aber et al. (1984) measured the amount of N associated with solubles, holocellulose and AUR fractions of six foliar litter species (Table 6.3). They found that between 26 and 38 % of the total N was associated with the AUR fraction. In a similar investigation, Berg and Theander (1984) estimated that c 1/3 of the litter N was associated with AUR. This means that while a value for total N may be used as an index, it will over-estimate

Table 6.2 Correlation coefficients (R) for linear relationships between first-year mass loss and initial concentrations of some main nutrients, water-soluble substances, and AUR as well as the AUR-to-N ratio. Significance levels are given under the R values

	Scots pine[a]	Norway spruce[b]	Norway spruce[c]	Common oak[d]	Multiple species[e]
N	0.446	0.305	0.045	0.467	0.706
	ns	ns	ns	<0.05	<0.01
P	0.904	0.556	0.063	0.378	0.761
	<0.001	ns	ns	ns	<0.001
S	0.780	nd	nd	nd	0.508
	<0.01				<0.05
K	0.899	0.511	0.126	nd	0.649
	<0.001	ns	ns		<0.01
Ca	0.148	−0.693	0.032	0.446	0.161
	ns	<0.05	ns	<0.05	ns
Mg	0.520	0.326	0.195	nd	0.750
	ns	ns	ns		<0.001
Mn	nd	−0.226	0.570	0.581	nd
		ns	<0.05	<0.01	
Wsol	0.217	0.888	0.265	nd	0.792
	ns	<0.01	ns		<0.001
AUR	−0.145	−0.663	0.122	−0.480	−0.118
	ns	<0.1	ns	<0.05	ns
AUR:N	−0.650	−0.593	0.055	nd	−0.773
	<0.05	ns	ns		<0.001
N	11	9	14	20	18

n Number of samples, *nd* not determined, *ns* nonsignificant, *Wsol* water soluble

[a] Experimental Scots pine needle litter mainly originating from fertilized plots and with increased nutrient levels incubated in a Scots pine forest (site Jädraås, Sweden). Data from Berg and Staaf (1980)

[b] Experimental Norway spruce needle litter originating from fertilized plots and with increased nutrient levels, incubated at the same plot. Data from Berg and Tamm (1991)

[c] Norway spruce needle litter incubated at 14 sites along Sweden with AET ranging from 371 to 545 mm. In that case, no climatic influence could be traced. Data from Berg et al. (2000)

[d] Common oak leaf litter collected from 20 different stands and incubated in one site. Data from Davey et al. (2007). Rate calculated using Eq. (9.5)

[e] Experimental Scots pine litter (above) as well as brown and green leaf litter from Scots pine, lodgepole pine, silver birch, gray alder as well as trembling aspen. Data from Berg and Ekbohm (1991), Berg and Staaf (1980), Berg et al. (2003)

the amount of available N. As we may see (Table 6.2), a consequence is that this index may not be very reliable between species with different levels of available N . Considering ^{13}C NMR, we have not yet found any investigation that has quantified the amount of N bound in, for example, newly formed lignin-like compounds.

According to the literature, P and S do not appear to be bound like N, and as a result may be more available to leaching or microbial uptake (Stevenson 1982).

Table 6.3 Initial N associated with extractable, acid hydrolyzable, and AUR/lignin fractions of six foliage litter species collected at Black Hawk Island, Wisconsin, USA. (Aber et al. 1984)

Litter	Extractable [mg g^{-1} OM]	Acid hydrolyzable	AUR
Bigtooth aspen leaves	4.0	1.5	2.8
Canadian hemlock needles	4.5	1.5	2.3
Red oak leaves	4.1	1.7	2.4
Sugar maple leaves	5.5	0.5	2.3
White oak leaves	4.7	0.7	3.0
White pine needles	2.2	0.0	2.2

OM organic matter

The C–to–N ratio is another index which conceptually expresses N concentration in the organic matter and may give a good relationship to mass loss for the early stage. The concept of C–to–N as an index was originally developed to be a rule-of-thumb for digestibility of fodder (e.g., fresh hay) but is today in use for soils as a means of predicting N dynamics. For most investigated species of newly shed litter, a low C–to–N ratio usually suggests an initially high decomposition rate. One advantage of this index is that the ash component (Sect. 2.3) is accounted for.

A further index is the AUR-to-N-ratio (Melillo et al. 1982). This ratio was based on the hypothesis that N and lignin/AUR had opposite effects on the decomposition rate, where N is a rate-stimulating and lignin/AUR a rate-retarding factor. The ratio is generally a good predictor of mass loss during initial stages of decay, particularly for litters of the same types for which it was derived (cf. Table 6.2). The correlation between the AUR-to-N ratio and first-year mass loss may be significant even if the correlation between AUR and N taken individually with first-year mass loss is not significant. Thus, for Scots pine litter, the AUR-to-N ratio was significant, although neither N nor AUR concentrations showed significance when taken alone.

For late stages (see below; Chap. 2), the AUR-to-N index is of little value, since N for the late stages rather has a rate-retarding effect. The value of this index as a predictor of decay rate thus decreases as the decay process develops, see also Norway spruce and common oak (below). When combining several litter types, levels of N, P, S and water-soluble substances all had significant predictive capacity.

Two confirming studies adding N to decomposing foliar litter. The effects of N, namely stimulating in the early stage and suppressing in the late one, have been confirmed experimentally in two studies. Using green leaves and leaf litter of pin oak with different initial concentrations of N, Hobbie et al. (2012) added inorganic N and organic N as well as a mix of nutrients (P, K, Ca, Mg, and Fe). They also incubated litter in a stand with long-term N additions. Calculating k_{init} (k_A) using an asymptotic function adapted for remaining amount, they obtained a significant increase in accumulated mass loss (Fig. 6.4). We may see that decomposition of

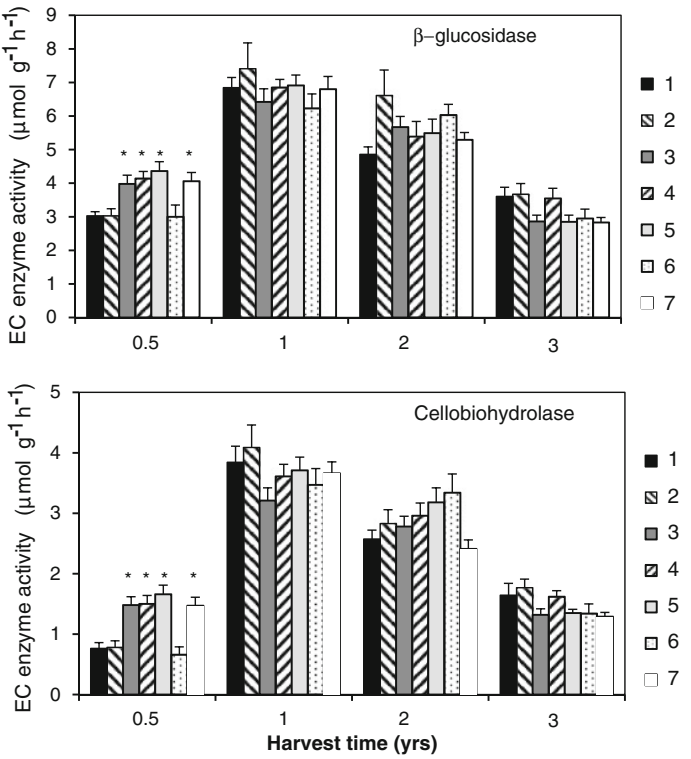

Fig. 6.4 Hydrolytic enzyme activity (β-glucosidase and cellobiohydrolase) on litter substrates harvested during the first three years of the experiment by treatment (averaged over sites and substrates). An *asterisk* indicates that a particular treatment differed significantly from the control treatment at a particular harvest time. Values are means with standard error bars. Overall model R^2 values from 3-way analysis of variance (ANOVA) including treatment, site, and substrate as main effects and done separately for each harvest date ranged from 0.25 to 0.58 for β-glucosidase, 0.24–0.69 for cellobiohydrolase. (1) Control, (2) carbon addition (25.5 g C m^{-2} y^{-1}) as glucose, (3) addition of inorganic N (10 g N m^{-2} y^{-1} as NH_4NO_3), (4) addition of 25.5 g C m^{-2} y^{-1} as glucose and inorganic N (10 N m^{-2} y^{-1} as NH_4NO_3), (5) long-term N additions (10 g N m^{-2} y^{-1} as NH_4NO_3 since 1999), (6) addition of non-N nutrients (P, K, Ca, Mg, S, Fe), and (7) addition of organic N (10 g N m^{-2} y^{-1} as amino acids). From Hobbie et al. (2012)

litter that had received N additions was stimulated and significantly faster. Additions were of different kinds: (1) direct ones using organic N and (2) incubation in stands with long-term N additions. Effects of an addition of inorganic N were not quite significant.

Perakis et al. (2012) using Douglas-fir needle litter with different concentrations of N confirmed that N is a limiting nutrient in the early stage. By adding N fertilizer (ammonium nitrate and urea), they found that the mass loss in the first 8 months increased as compared to the unfertilized litter. They obtained a significant relationship between mass loss and initial litter Mn concentration in

fertilized plots but not in unfertilized. This may mean that there was a lack of available N for decomposition of an available C source. The initial P concentrations were similar among their 8 litter preparations and appear not to have been limiting.

Both studies reported that in the late stage, a clearly decreased accumulated litter mass loss was found when additional N was given, which suggests a suppression caused by the added N (see below).

Decomposition starts with a 'late phase' or 'lignin-dominated' phase. So far, only two litter species have been reported for which decomposition of newly shed litter starts with the 'late,' lignin-dominated phase. The reports show that the initial rate can be best related to litter Mn concentration (Table 6.2). The litter species are common oak (Davey et al. 2007) and a study on Norway spruce needle litter.

Davey et al. (2007) report a decomposition study using leaf litter of common oak collected at 20 stands (Wales, UK). They incubated them in litter bags in one of the stands, thus under an identical climate and followed the mass loss for 2½ years. Using Eq. 6.1, they calculated the initial rates (k_{init}), related them to initial concentrations of nutrients, and found that concentrations of Mn (positive) and AUR (negative) gave the best relationship to initial decomposition rate. Davey et al. (2007) related a high initial decomposition rate (k_{init}) to litter Mn concentration, with a high significance ($R^2 = 0.34$, $p < 0.01$), and the relationship to N was also significant, though less so ($R^2 = 0.22$, $p < 0.05$).

Likewise, Berg et al. (2000) related the first-year mass loss for local Norway spruce needle litter to Mn ($R^2 = 0.325$; $n = 14$; $p < 0.05$). The relationships to N, P, and climate factors were not significant in this gradient with a range in latitude from c. 56 to c. 66°N and a range in MAT from −1.7 to 7.4 °C.

These studies suggest that for some litter species, lignin may be the rate-regulating agent already from the start of the decomposition process. We recalculated the data of Davey et al. (2007) excluding one of their sampled litters from a partly N-polluted area and found that this emphasized the roles of AUR and Mn (Table 6.2) as these relationships became the only significant ones.

That there was no clear carbohydrate-dominated early stage may be explained in part by the fact that both the spruce needles and the oak leaf litter stay as attached dead on the branches for several months. During a prolonged stay, leaching of nutrients may take place, and the decomposition of the litter could start, resulting in increased lignin concentrations and changed concentrations of other nutrients. The implication of this is that the early phase of decomposition may already have passed before the needles are shed and the remaining parts simply are more lignified. Because they remain attached to the twig for extended periods of time after they senesce, significant decomposition can occur while they are still attached to the tree. However, we cannot exclude the possibility of a fiber structure with a high level of lignification for both litter species (cf. Fig. 4.3).

We discuss the effects of the late (lignin-dominated) phase below (Sect. 6.3.2) and that discussion thus is in common for the late stage and the litter of common oak and Norway spruce.

6.3.2 Decomposition in the Late Stage: Lignin-Regulated Phase

6.3.2.1 The Lignin-/AUR-Dominated Decomposition Stage

Often the 'effect of lignin/AUR' on decomposition rate has been illustrated by showing the correspondence between increasing AUR concentrations and decreasing mass-loss rates. A higher concentration of AUR would thus reflect a higher percentage of a compound resistant to decomposition (cf Chap. 5). Examples of such studies are those of Fogel and Cromack (1977), Johansson et al. (1995).

The main reason for defining a late stage or a 'lignin-regulated' phase is that the decomposition in this stage appears to be regulated by the degradation of lignin. A consequence is that factors regulating the litter mass-loss change. In foliar litter, the concentrations of the known influencing nutrients such as N and Mn appear to be high enough to be limiting or regulating and we may ask if concentrations of N can be a better index than AUR concentration. We will discuss the present state of our knowledge below.

6.3.2.2 Some Lignin-Related Decomposition Patterns Across Litter Species

Annual mass loss related to AUR. We previously introduced two main groups of patterns that appear to be characteristic mainly for the decomposition of newly shed litter (Table 6.1). Here, we intend to distinguish and describe the AUR dynamics for different groups of decomposing litter. For a further understanding, we have organized the description of the lignin-dominated (late) stage around the constituents AUR, Mn, and N.

In the studies so far reported, AUR is resistant to degradation and an increasing AUR concentration has been related negatively to decomposition rate of the litter in most foliar litter types. We will present information on the effects of Mn and N on AUR net loss.

The relationship (Fig. 6.5), namely a decreasing rate for one type of litter incubated at its own forest stand, has been observed by several scientists. One basic method to investigate the possible effect of a chemical component on decomposition rate is to incubate the litter over a series of years and regard the litter that changes with decomposition (Chap. 5) as a new substrate at the beginning of each incubation year or period (App II). This is an example of a period mass loss (Glossary, App I). In this case, the litter chemical composition at the beginning of each incubation year is associated with the mass loss during the ensuing year. The AUR concentration at the start of each one-year period is regressed against the mass loss over the corresponding one-year periods and will result in a negative linear relationship for the site and litter species describing the effect of AUR. The relationship between an increasing AUR level in foliar litter and litter decomposition rate is thus easily illustrated (Fig. 6.5).

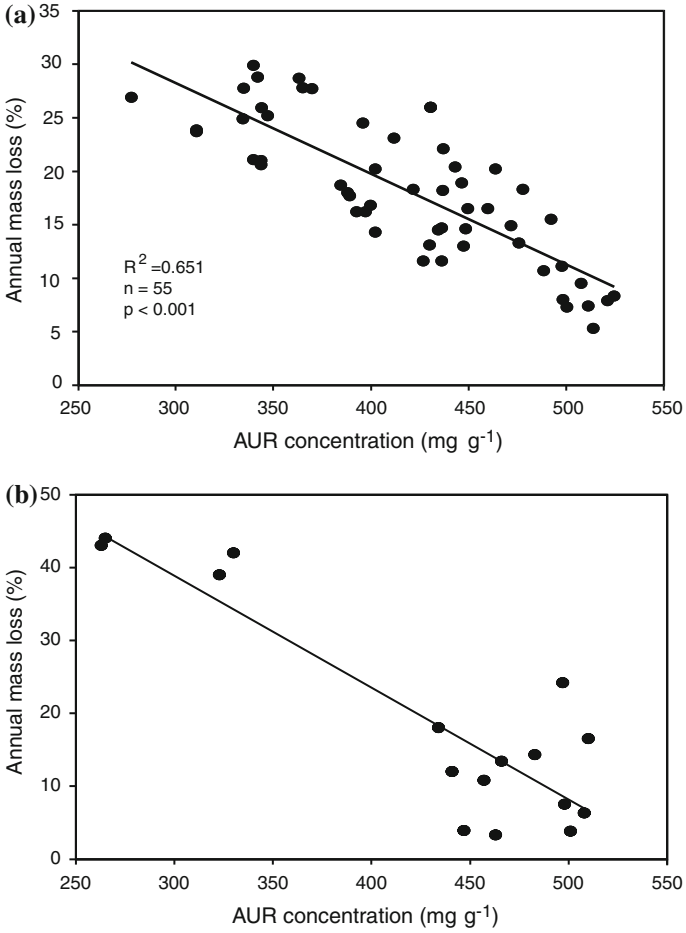

Fig. 6.5 Relationship between AUR concentration at the beginning of one-year decay periods and the mass loss occurring during the following one-year period (annual mass loss). Data include both early and late stages. **a** Scots pine needle litter. **b** Leaf litter of silver birch and gray alder including both early and late stages

6.3.2.3 Reduced Litter Mass-Loss Rate in the Late Stage, Following N Addition

Incubating leaves and leaf litter of pin oak, Hobbie et al. (2012) noted a clear increase in decomposition rates in the early stage (Sect. 6.3.1). Following the incubated litter over time, they found significantly reduced rates for the litter that had received N additions. Hobbie et al. (2012) also followed the development of cellulolytic (Fig. 6.4) and lignolytic enzymes (Fig. 6.6) in the sampled litter and noted a decrease in the lignolytic ones after N additions. Using needle litter of

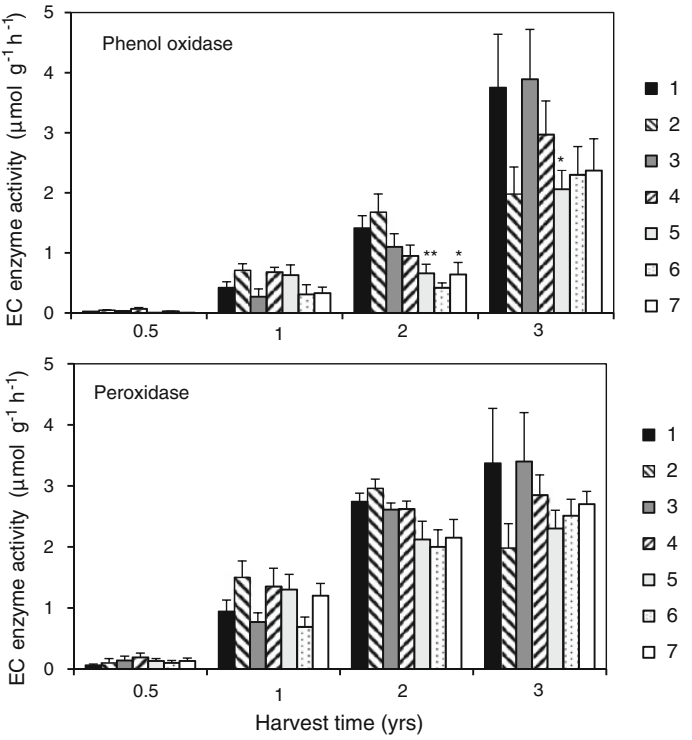

Fig. 6.6 Oxidative enzyme activity on litter substrates harvested during the first three years of decomposition by treatment (averaged over sites and substrates). Statistical comparisons were only done for the 2- and 3-year harvests because of high numbers of zero values in prior harvests. An *asterisk* indicates that a particular treatment differed significantly from the control treatment at a particular harvest time. Values are means with standard error bars. Overall model R^2 values from 3-way analysis of variance (ANOVA) including treatment, site, and substrate as main effects were 0.34 and 0.24 for phenoloxidase and 0.22 and 0.23 after 2 and 3 years of decomposition, respectively. (1) Control, (2) carbon addition (25.5 g C m^{-2} y^{-1} as glucose), (3) addition of inorganic N (10 g N m^{-2} y^{-1} as NH_4NO_3), (4) addition of carbon as glucose (25.5 g C m^{-2} y^{-1}) and inorganic N (10 N m^{-2} y^{-1} as NH_4NO_3), (5) long-term N additions (10 g N m^{-2} y^{-1} as NH_4NO_3 since 1999), (6) addition of non-N nutrients (P, K, Ca, Mg, S, Fe), and (7) addition of organic N (10 g N m^{-2} y^{-1} as amino acids). From Hobbie et al. (2012)

Douglas-fir Perakis et al. (2012) noted a significant decrease in mass-loss rates after additions of ammonium nitrate.

6.3.2.4 Effects of Manganese on Litter Decomposition: Some Case Studies and an Attempt to Synthesis

The effects of Mn on lignin degradation are well established on the level of organisms, such as pure cultures of fungi (Chap. 3). Still, on the level of litter

decomposition, it appears that so far unknown factors may influence what we can measure. In fact, the information available considers rather effects of Mn on litter in a late stage than on lignin/AUR. We have made an attempt to synthesize available data for Scots pine needle litter (Sect. 2.5; Fig. 2.7), and in the present section, we make comparisons between Scots pine litter and that of Norway spruce. However, being aware of (i) rather few studies evaluating the effect of Mn on decomposing litter and (ii) different behaviors in different litter species, we have focused the present section mainly onto a set of case studies for Scots pine and Norway spruce litter.

Manganese appears to have a much wider initial concentration range than N (Chap. 4) and behaves in a very different manner during decomposition. Thus, the initial Mn concentrations over a number of foliar litter species ranged by a factor of almost 400, from 3.9 mg g^{-1} in silver birch (Sweden) to 0.01 mg g^{-1} in Aleppo pine (Libya) (Berg et al. 2010). Whereas it has been possible to see regular patterns in the concentrations of AUR and N, it has not been possible to distinguish any predictable pattern for the variation in Mn concentrations during decomposition (cf Sect. 5.4.1). Even for one litter species decomposing in its own system, the pattern varies among incubated litter sets.

Whereas the effect of Mn in pure fungal cultures is uncontroversial, we may have some alternatives as regards effects on litter decomposition. Thus, is the concentration as such important or the mobility/availability of Mn? Is a net release important or a net uptake, both reflecting mobility? We discussed (Chap. 5) that net Mn release rate was linearly related to its concentration, which allows us just to discuss and speculate.

6.3.2.5 Some Case Studies Relating Litter Mass Loss to Mn Concentration

Scots pine. A recent synthesis (Berg et al. 201Xb) has related annual mass loss for Scots pine litter to Mn concentration using 20 separate decomposition studies. The litter was in a late stage (>30 % accumulated mass loss).

Lodgepole pine litter. A smaller dataset for lodgepole pine needle litter was investigated (Berg et al. 2007). When regressing litter annual mass loss *vs*. AUR concentrations, they obtained a negative linear relationship with $R^2 = 0.424$ and $p < 0.01$, whereas Mn gave an R^2 of 0.281 and $p < 0.05$ (Table 6.4). When AUR and Mn were combined in a linear regression, the R^2 increased to 0.455 ($p < 0.01$). The three stands where the litter was incubated were climatically very similar and had monocultures of pine.

Norway spruce litter. In a climatic gradient (Chap. 7) along Sweden, the mass-loss rates for the first year were related to litter Mn concentration (Table 6.2). Further, for annual mass loss using all available data over 5 years, there was a highly significant positive relationship to litter Mn concentration (Table 6.4). Using data for available nutrients and AUR, Mn concentration appeared to give the best relationship, whereas N and AUR did not give any significance (Table 6.5).

Table 6.4 Comparison of $R^2\left(R^2_{adj}\right)$ for the relationships between annual mass loss and concentration of Mn and AUR in decomposing litter in the late stage. Regressions were made using a stepwise narrower interval in AUR concentrations. From Berg et al. (2007)

[AUR] range	Mn			AUR/lignin			*n*	[Mn] range
(mg/g)	R^2	R^2_{adj}	$p<$	R^2	R^2_{adj}	$p<$		(mg/g)
All available data								
277–509	0.151	0.145	0.001	0.206	0.200	0.001	136	0.04–7.69
>350	0.182	0.175	0.001	0.138	0.130	0.001	115	0.04–7.69
>400	0.215	0.206	0.001	0.059	0.049	00.05	94	0.24–7.69
>450	0.360	0.349	0.001	0.005	–	*ns*	62	0.24–7.69
>475	0.457	0.441	0.001	0.002	–	*ns*	35	0.24–7.69
Norway spruce data only								
>277	0.294	0.284	0.001	0.12o	0.108	0.01	74	0.26–7.69
>475	0.671	0.653	0.001	0.059	0.001	*ns*	20	0.31–7.69
Lodgepole pine data only								
	0.281	0.230	0.05	0.424	0.230	0.01	16	0.71–2.9
Data for Scots pine, lodgepole pine, gray alder, and silver birch								
>475	0.115	0.031	*ns*	0.011	–	*ns*	15	0.24–1.90

ns—not significant

As the AUR concentrations increase with increasing accumulated mass loss, AUR concentrations, in addition to giving the concentration of a substrate also index the decomposition level of the litter

Table 6.5 Linear relationships between all available data for annual mass loss of Norway spruce needle litter and concentrations of some chemical components in the litter. Data from a Norway spruce gradient (Berg et al. 2000) and from an N fertilization site (B. Berg, unpublished). *n*=95

Variable	*R*	R^2	$p<$
Mn	0.597	0.356	0.001
Mg	0.487	0.237	0.001
Wsol	0.454	0.206	0.001
K	0.367	0.135	0.001
Ca	0.254	0.065	0.05
P	0.230	0.053	0.05
All components	0.712	0.507	0.001

Mass losses from the 2nd through the 5th years. Concentrations of N and AUR did not have significant relationships

Several species combined. There appear to be two studies evaluating the effect of Mn in late stages, discussing three litter species. Berg et al. (2007) used a set of decomposition data from Norway spruce, Scots pine, lodgepole pine, Aleppo pine,

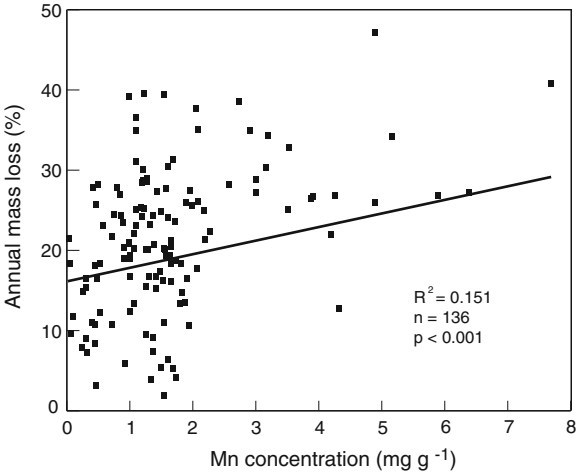

Fig. 6.7 All available data (Norway spruce, lodgepole pine, Scots pine, Aleppo pine, silver birch, gray alder) for annual mass loss of foliar litter in late stages were related to litter Mn concentration at the start of each year. Mass-loss data originate from sites distributed over Sweden plus from two sites in northern Libya. From Berg et al. (2007)

silver birch, and gray alder. All data were taken from litter that clearly was in a late stage of decomposition and an accumulated mass loss above 29 % (lodgepole pine above 24 %), namely data for litter for the 2nd, 3rd, 4th, and 5th years of decomposition. In all, they used 136 values of which 32 were for Scots pine, 75 of Norway spruce, 16 of lodgepole pine, 4 of Aleppo pine, 6 of silver birch, and 3 of gray alder. They related litter mass loss for one-year periods to litter concentrations of Mn and AUR at the start of each one-year period. The concentrations of Mn in litter at the start of such one-year periods ranged from 0.04 to 7.69 mg g^{-1}(the latter in far-decomposed litter) and for AUR from 277 to 509 mg g^{-1}, thus with range factors of 192 and 1.8, respectively.

Most of the litter had Mn concentrations below 2 mg g^{-1} (Fig. 6.7) and included mainly litter of pine species, birch and alder. The main part of the litter with Mn concentrations above 2 mg g^{-1} came from Norway spruce.

In a first step, they regressed all the annual mass loss values to the litter AUR concentration, which resulted in a negative linear relationship ($R^2 = 0.210$; $p < 0.001$). We may thus see that for all litter combined, a negative relationship was found between AUR concentrations and litter mass loss. In a second step, they regressed all annual mass-loss values to litter Mn concentration at the start of each year. All available data ($n = 136$) gave a positive linear relationship ($R^2 = 0.151$; $p < 0.001$; Fig. 6.7; Table 6.4). We may note that the data did not have a natural distribution as the main part had an Mn concentration below of 2.0 mg g^{-1}. A logarithmic transformation gave R^2 values of 0.201 and 0.150, for AUR and Mn concentrations, respectively, both highly significant. When combining Mn and AUR concentrations in a multiple regression, the relationship improved ($R^2 = 0.349$; $p < 0.001$).

By stepwise selecting a narrower interval in AUR concentrations, they progressively obtained a litter substrate that was more decomposed. For all data, with AUR concentrations ranging from 277 to 509 mg g^{-1}, a significant relationship was seen

to litter AUR concentration ($p < 0.001$) as well as to the Mn concentration (Table 6.4). We may see that the narrower the AUR concentration interval was, the more the relationship to Mn improved (R^2_{adj} increased). At an AUR concentration interval of 475–509 mg g^{-1}, the R^2 value for the relationship between litter mass loss and Mn concentrations was 0.457, whereas the relationship for the influence of AUR had become insignificant likely due to the narrow concentration interval (Table 6.4). This reduced dataset ($n = 35$) encompassed 9 values for Scots pine, 1 for lodgepole pine, 20 for Norway spruce, 3 for gray alder, and 2 for silver birch. Berg et al. (2007) divided this dataset ($n = 35$) into two main groups, one for Norway spruce litter (Mn concentration range from 0.31 to 7.69 mg g^{-1}) and one for the other litter types combined with a concentration range from 0.24 to 1.9 mg g^{-1}. For Norway spruce needle litter, the relationship between Mn concentration and annual mass loss became an R^2 of 0.671($R^2_{adj} = 0.653$) with $n = 20$ and for the other, combined litter types 0.115 ($n = 15$; ns). For this whole dataset ($n = 35$) with AUR concentrations >475 mg g^{-1}, all data basically fit to the linear relationship. The main difference between the groups appears to be that the Norway spruce litter had a wider concentration interval with a range factor of 24.8, whereas that for the other litter types was considerably more narrow with a range factor of 7.9.

6.3.2.6 Annual Mass-Loss Rates of Late Stage Litter as Compared to Concentrations of Mn and N

It has been possible to distinguish differences in net loss of AUR and relate them to litter Mn and N concentrations. These estimates of mass-loss rates were based on the measured values for sulfuric acid lignin. It was observed earlier that sulfuric acid lignin in decomposing litter was degraded at very different rates, notably in green N-rich and brown N-poor Scots pine needle litter. The AUR mass-loss rate was lowest for the N-rich litter and highest for the N-poor one (Berg et al. 1982b). Berg and Ekbohm (1991) also fitted a linear model including the N concentration of the litters and found a clear negative relationship between litter N concentration and AUR mass-loss rate (Fig. 6.8). In a more recent approach based on the role of Mn for litter decomposition, Berg et al. (201Xa) related mass loss for AUR (sulfuric acid lignin) to concentrations of Mn using a larger set of decomposition studies mainly on Scots pine ($n = 20$) and lodgepole pine ($n = 5$). They evaluated the relative roles of N and Mn on litter decomposition in the late stage and concluded that their influences were simultaneous. As regards the relative roles of Mn and N on the net disappearance of AUR have not yet been evaluated in relation to their changing concentrations with litter mass loss. However, a recent paper (Berg et al. 201Xa), using initial concentrations of N and Mn related to AUR net loss, has indicated that for Scots pine litter, both nutrients appear to exert their influence simultaneously.

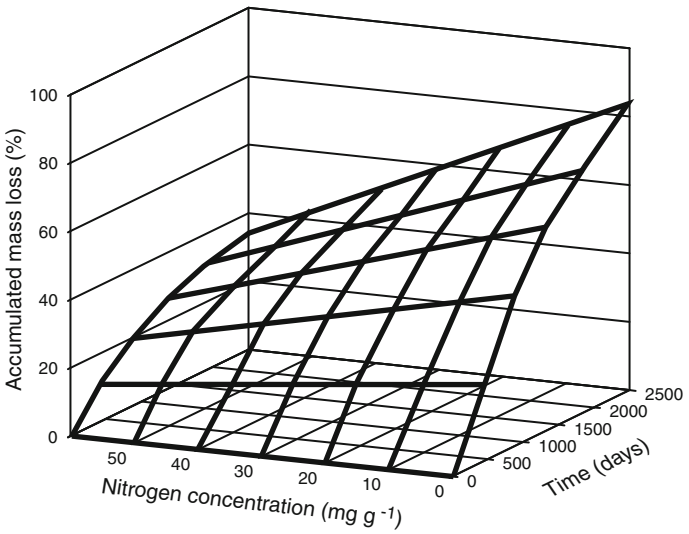

Fig. 6.8 Illustration of the negative relationship between accumulated AUR mass loss changing with time and litter N concentrations. $R^2_{adj} = 0.677$, $n = 82$. Data originate from seven litter types incubated experimentally in a Scots pine stand (Berg and Ekbohm 1991). Although there is a relationship to N we cannot exclude the effect of Mn on AUR mass-loss pattern. There was a highly significant relationship between concentrations of N and Mn with $R^2 = 0.325$ ($n = 89$)

6.3.2.7 How Should We Regard the Retardation of Litter Decomposition Caused by Lignin?

We reviewed the chemical and biological aspects of lignin degradation in Chaps. 2 and 3. As discussed above, elevated N levels may suppress the degradation of lignin and, at raised concentrations, the effect may be proportional to the N concentration. The two effects, biological and chemical, have so far not been separated at the level of litter decomposition, or the level of lignin/AUR degradation in litter. However, Berg and Matzner (1997) discussed effects of N additions to humus that suggested that both a biological and a chemical effect could be hampering the decomposition. In Chap. 2, we compared N levels in needle litter with N levels in pure laboratory cultures that were suppressing lignin degradation. In the relatively N-poor brown Scots pine needle litter, there were between 40- and 100-fold higher N concentrations than was needed to suppress lignin degradation in a laboratory culture. Of course, much of the N in litter would be relatively unavailable to the fungi as compared to the N in the culture media. However, with initial concentrations of N in litters ranging up to nearly 3 %, the N levels in litter are up to 800 times as high as concentrations that have a suppressing effect on lignin degradation in pure cultures of fungi.

The effect of added N on respiration rate from humus was seen within hours (Berg and Matzner 1997), indicating a microbial mechanism. We may expect that a repression of fungal ligninase synthesis occurs also in litter, as a result of the relatively high levels of N present. The chemical reaction between N and the decomposing lignin is slow at the low pH values (around 4) in boreal needle litter. Still, in a laboratory experiment, the reaction proceeded at a rate of 14–19 μg N day^{-1} g^{-1} litter (Axelsson and Berg 1988). The reaction rate was limited by N availability, and using Scots pine needle litter as a substrate, Axelsson and Berg (1988) found that the reaction rate increased with increasing N concentrations.

So far, the 'effect of lignin' on decomposition rate has been illustrated by relating the increasing AUR concentrations and decreasing mass-loss rates. As concentrations of AUR and N both increase about linearly to accumulated mass loss, we may speculate using this fact. A higher concentration of AUR would thus reflect a higher percentage of a group of compounds resistant to decomposition, with a magnitude of the effect that is dependent on the litter N concentration, and the kind of organisms that have invaded the litter. We can distinguish some cases that represent the extreme possibilities, and our generalized discussion is based on incubation of litter on the forest floor, not in laboratory systems.

If N-sensitive white-rot fungi invade the litter and dominate, we should find that the N concentrations, increasing with accumulated mass loss, are hindering the degradation of lignin to an increasing extent. Thus, the overall decomposition of the litter will be increasingly hindered. In this case, raised N levels could result in a lowered litter decomposition rate. The white-rot fungi as a group have the ability to degrade lignin fast when N levels are low, so any effect of N should be clearly distinguishable (Chap. 3). An effect like this may be expected in a nutrient-poor system in which N-sensitive fungi dominate.

Another possibility is that white-rot fungi that are not sensitive to raised N levels invade the litter. The lignin degradation of such a population would not be hindered by raised N concentrations, and lignin would thus not be a barrier to litter degradation at higher N concentrations. In such cases, either there would be no correlation between raised lignin levels and decomposition rate or, perhaps more likely, there would be no increase in lignin levels.

Brown-rots would not degrade lignin completely, and after the disappearance of the unshielded holocellulose, the raised lignin concentrations would hinder litter decomposition. This would apply to both N-sensitive and N non-sensitive species.

Considering the decomposition of foliar litter, the most likely scenario when litter is incubated on the ground is invasion by a mix of fungal species. For example, Osono and Takeda (2001) found over 100 different fungal taxa on the decaying leaves of Japanese beech. Thus, we would expect that both sensitive and non-sensitive white rots and brown rots would participate in the degradation. Such a mix of species would result in a moderate suppression of lignin degradation at low N levels, while higher N levels would have a stronger effect. Differences between systems would be reflected in the slope of the decomposition rates for lignin/AUR and for litter. Thus, a high initial litter N level would have a stronger rate-retarding effect on litter decomposition than a litter with lower N incubated

under the same conditions. We also speculate that a system richer in N would have relatively more fungi not sensitive to N, while really nutrient-poor systems would have a relatively high frequency of N-sensitive fungi, thus allowing a stronger retardation of litter decomposition in the latter type of system (Eriksson et al. 1990; Hatakka 2001). Based on the cases reported in the literature, suppression is normal for foliar litter.

It is a well-known phenomenon that as litter decomposes, the N level increases (Fig. 5.5). The rate of increase observed in N concentration is normally in proportion to the initial concentration (Chap. 5), meaning that the higher the initial N level, the greater the relative increase in N concentration with increasing mass loss.

During decomposition, there is an increase in the concentration of the normally resistant AUR and its recombination products (Fig. 5.2). Traditionally, this has been explained by the fact that the lignin-degrading microorganisms normally grow very slowly, and that lignin as a chemical compound is normally resistant to decomposition, while the unshielded cellulose and hemicelluloses in litter are decomposed considerably faster. This traditional picture of AUR resistance to degradation appears to be valid only under certain circumstances, however, and the degradation rate of AUR in litter has been related to the concentrations of N and Mn in litter (Chap. 2; above) and the physiology of the lignin-degrading organisms present (cf. Chap. 3). Most studies on litter decomposition are made on foliar litter where the levels of N have been high enough to influence the microbial degradation of lignin and possibly the formation of more resistant N-containing humus compounds, thus creating an image of AUR/lignin as being more recalcitrant.

When the decomposition has reached a certain magnitude, the (foliar) litter contains material that is rich in lignin and its condensation products. At this stage, the remaining cellulose and hemicelluloses are shielded and protected by lignin and newly formed lignin-like compounds (cf. Chaps. 2 and 5). This has as a consequence that in late decomposition stages, the degradation rates of cellulose and the different hemicelluloses are similar to that of lignin/AUR, whereas they are higher during earlier stages (Chap. 2). Through the effect of N in the late decomposition stages, the degradation of AUR products regulates the decomposition of the whole litter (Berg and Ekbohm 1991).

We may speculate that part of the rate-retarding effect of AUR could be dependent on the increasing N level of the decomposing litter, N exerting a suppressing effect on lignin degradation (cf. Fig. 2.2). Still we do not know whether this rate-retarding effect of increasing AUR levels should be ascribed to the simultaneously increasing N concentration in the litter. For decomposing Scots pine needle litter, the same AUR level showed a stronger retardation at warmer and wetter sites than at colder and drier ones (Fig. 7.7). The concentration of N increases relatively faster at warmer and wetter sites (Fig. 5.15), which means that higher N concentrations do occur in litter at sites where the proposed effect of AUR is stronger. The retarding effect of N should not be assumed to apply more

generally across different ecosystems, but it has been observed and confirmed in the cases described here (cf Chap. 10).

6.3.2.8 Early and Late Stages as Related to ^{13}C NMR Analyses

We have presented results from NMR analyses on decomposing litter and may relate them to the three-phase model. Do they support the model and how may we analyze that? There are unfortunately few studies that we may use.

The study of Klotzbücher et al. (2012) showed a degradation of lignin already from the start of the incubation as well as a degradation of the lignin-derived phenolics.

A study of hinoki cypress and Japanese cedar (Fig. 2.6) indicates that O-alkyl C (cellulose, hemicellulose) disappears heavily in the first year with a mass loss of 48.2 and 37.1 %, respectively. In the same period, aromatic C, which may cover lignin, tannins, and phenolic compounds, has a much smaller net loss. This may be a certain fraction of low molecular phenolics that are more easily decomposed. Also, tannins are more readily decomposed than lignin. Thus, aromatic C gives both the more recalcitrant lignin and more readily degraded tannins and cutins.

We may see (Fig. 2.6) that O-Alkyl C had decreased heavily at the sampling after 1 year. However, we may apply an early suggestion to define the late stage, namely the stage in which the degradation of lignin dominates the decomposition of litter. Such a definition may include influence of nutrients, for example, that of P (positive) for an early stage and that of Mn (positive) for a lignin-dominated stage.

We may investigate two further studies, namely that of Preston et al. (2009b), using foliar litter of trembling aspen and black spruce (Fig. 6.9) and that of De Marco et al. (2012) (Fig. 6.10). For aspen leaf litter, there was a heavy loss of O-alkyl plus di-O-alkyl instantly. Also, a heavy loss of aromatic C plus phenolic C took place, whereas for aspen litter, there was a slight increase in methoxy C, which may suggest that true lignin was not degraded from the beginning of the incubation, but possibly tannins. In contrast, it appears that black spruce litter had a loss of methoxy C in the same time interval (the interval from 100 to 60 % mass remaining). That loss was slower than the average and may indicate the possibility of a short early stage or none. We may remember the initial lignin/AUR degradation of another spruce litter (Norway spruce; Fig. 6.11).

Analyzing different fractions and using the resolution of ^{13}C NMR, we may have a tool to apply the definition of change in rate-limiting factors based on true lignin. In order to summarize the modification occurring with decomposition in the molecular composition of aromatic components, the methoxyl-C-to-phenol-C ratio (signal intensity in the 60–45 ppm interval over that in the 160–145 ppm interval; App III) has been suggested as an index for lignin degradation (Spaccini and Piccolo 2012). We may apply that onto a decomposition study of black locust and black pine foliar litter. A lower value of methoxy-C-to-phenol-C ratio for the

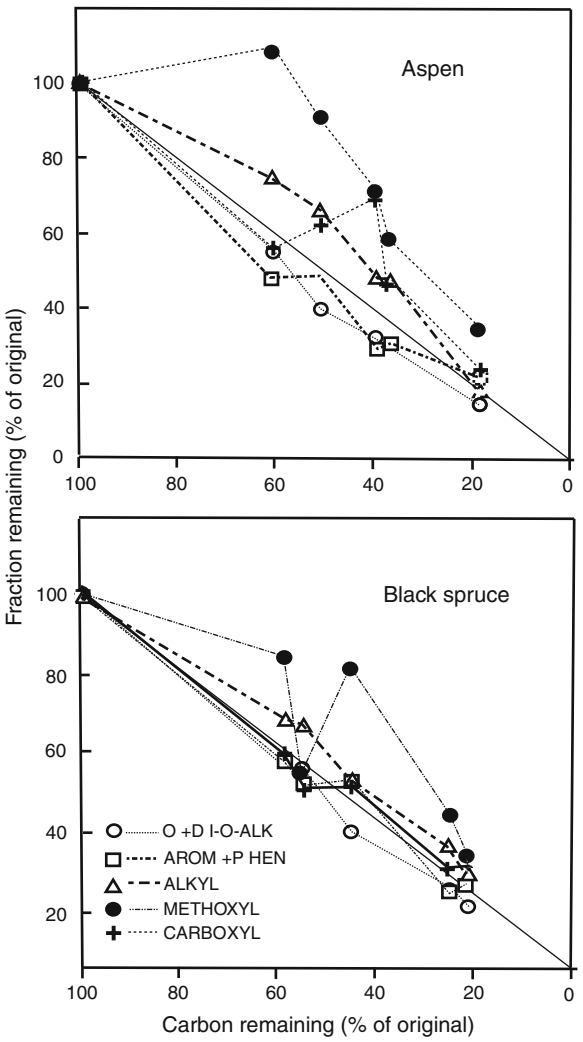

Fig. 6.9 Remaining mass of carboxyl-C, O-alkyl-C, aromatic-C, and aliphatic-C in decomposing foliar litter of trembling aspen and black spruce. From Preston et al. (2009b)

newly shed litter of black locust confirmed the larger contribution of tannin components to the phenolic region of NMR spectra (Spaccini and Piccolo, 2012).

The NMR analysis shows that the masses of phenol C and methoxy C decrease in both litter species (Fig. 6.10) during the early decomposition process. In contrast, the methoxy-C-to-phenolic-C ratio, indicating the relative contribution of lignin component to the phenolic region (Spaccini and Piccolo, 2011), increased in both litter species and the increase was higher in black locust litter than in that of black pine. Further, in black locust litter, the methoxy-C-to-phenol-C ratio was negatively correlated to litter decay rate. This was consistent with the results of the proximate analysis.

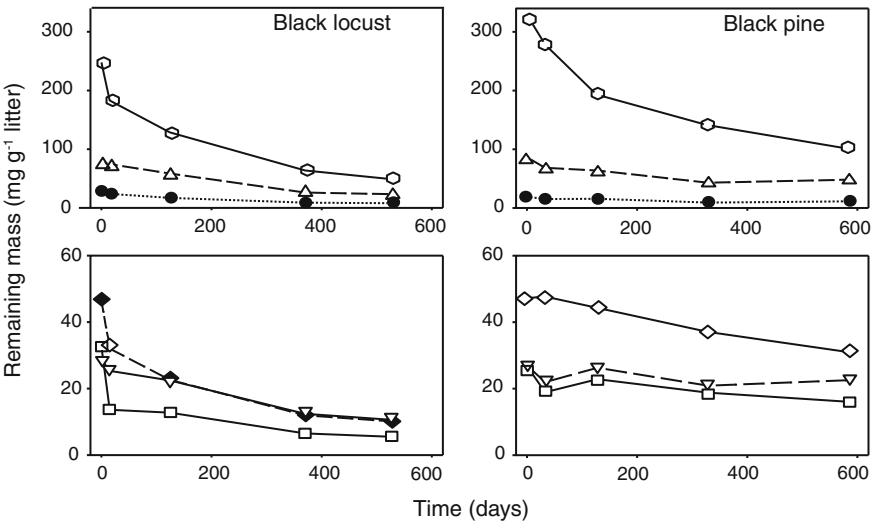

Fig. 6.10 Remaining mass of six fractions of carbon in newly shed and decomposing litter of black pine and black locust ($n = 3$). (○) O-alkyl-C, (△) alkyl-C, (●) carbonyl-C, (◆) aryl-C, (▼) methoxy-C, (□) phenol-C. From De Marco et al. (2012)

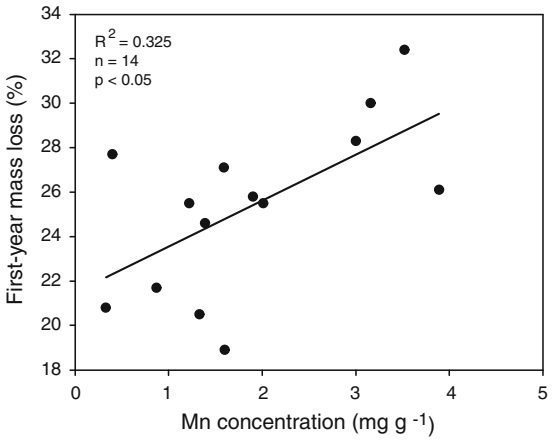

Fig. 6.11 First-year mass loss of local Norway spruce needle litter related to initial concentration of Mn. The needle litter was incubated at 14 sites in a gradient across Sweden (Berg et al. 2000)

Applying the data for ^{13}C NMR, De Marco et al. (2012) distinguished an initial period up to 15 days for black locust and 33 days for black pine litter, characterized by loss of relatively more decomposable phenolic C (in tannins), and in the region for methoxy C. The successive periods showed a more stable amount of two C fractions that likely reflect the more stable moieties of true lignin, namely phenolic C and methoxyl C (Fig. 6.10). The switch between stages was approximately

defined to an accumulated mass loss of about 40 % for black locust and about 28 % for black pine.

6.4 Litter at Humus-Near or Limit Value Stage

6.4.1 General Comments

Limit values for decomposition may be calculated for many litter species, provided that decomposition has been followed far enough through the decay process (Chap. 2). After an inventory of existing decomposition studies, Berg (2000b) and Berg et al. (1997) published a total of 128 limit values of which 106, encompassing 21 species, originated from forest sites that were natural and not disturbed. Among different litter species, the limit values were found to differ (Howard and Howard 1974; Berg and Ekbohm 1991; Berg et al. 2010). Also, the newly presented data from LIDET (Currie et al. 2010) give a wide range in limit values.

Limit values have been related negatively to initial N concentrations and positively to those of Mn. Berg et al. (1996b) presented the hypothesis that the amount of litter remaining at the limit value was regulated by lignin remains that had become recalcitrant as low molecular weight N compounds started a formation of complexes, a process that was in turn enhanced by the raised litter N levels. The relationships were empirical and suggestions for causal relationships included factors that influence lignin degradation and modify the lignin structure. Currently, we can state that the empirical relationships have been found to be more general and the recalcitrance of the remaining litter has been validated, but still there is no clear theory. In a search for possible factors regulating the limit value, relationships have been found with litter concentrations of N, Mn, Ca, and AUR, all of which have a potential causality. Reviews containing increasing numbers of limit values have been published (Berg et al. 1996b, 2010; Berg 2000b), and the main patterns observed have not changed.

6.4.2 General Relationships

Higher Mn values are related to higher limit values. We have seen highly significant relationships between limit values and initial Mn concentrations (Berg et al. 1996b), with $R^2 = 0.372$ and $p < 0.001$ for $n = 25$) for natural, undisturbed systems. With 127 sets of available data for deciduous and coniferous litter, limit values related to litter Mn concentrations gave a highly significant, positive relationship ($R^2 = 0.169$, Table 6.6; Fig. 6.12a). The data included litter from natural and manipulated (e.g., fertilized) forests. The dataset was dominated by

Table 6.6 Linear regressions between limit values and initial concentrations in litter of Mn, N, and Ca

Nutrient/litter group	R	R^2	n	$p<$
Available data, natural and fertilized systems				
Mn	0.411	0.169	127	0.001
N	−0.471	0.222	163	0.001
Ca	0.055	0.003	138	ns
All deciduous litter				
Mn	0.362	0.131	44	0.05
N	−0.261	0.068	44	ns
Ca	−0.045	0.002	47	ns
All coniferous litter				
Mn	0.513	0.263	74	0.001
N	−0.660	0.436	86	0.001
Scots pine needle litter alone				
Mn	0.485	0.235	35	0.01
N	−0.683	0.466	42	0.001
Norway spruce needle litter natural systems[a]				
Norway spruce, natural and fertilized systems				
Mn	0.522	0.272	26	0.01
N	−0.420	0.176	26	0.05
Ca	0.400	0.160	26	0.05
Oak species[b]				
Common oak				
Mn	−0.195	0.038	21	ns
N	−0.239	0.057	21	ns
Ca	−0.456	0.208	21	0.05

All available data were used both combined and subdivided into main groups and genera/species. Data from DELILA II database, Davey et al. (2007) and Berg and Johansson (1998).
[a] No significance to N, Mn or Ca, $n = 13$
[b] Available data encompassing 4 temperate oak species, no significance to N, Mn, or Ca. $n = 28$

pine ($n = 55$) and spruce ($n = 26$), whereas 8 deciduous species had 44 values of which common oak had 21. We may note that some subgroups in that dataset such as Norway spruce from natural systems and common oak did not give significant values when analyzed separately.

For selected groups of litter such as deciduous ($n = 44$) and coniferous ($n = 83$), positive relationships were seen between Mn and limit values with $R^2 = 0.382$ and 0.263, respectively. In addition, for local needle litter of *pine* sp., a significant relationship was seen using backward elimination ($p = 0.0014$) and for local Scots pine $p = 0.019$ (Chap. 2; Berg et al. 2010). In contrast, limit values for spruce needles from natural systems did not have any significant relationship to Mn (Table 6.6). Considering such a difference between pine spp. litter and that of Norway spruce, it may be of value not to combine species and genera when detailed analyses are wanted.

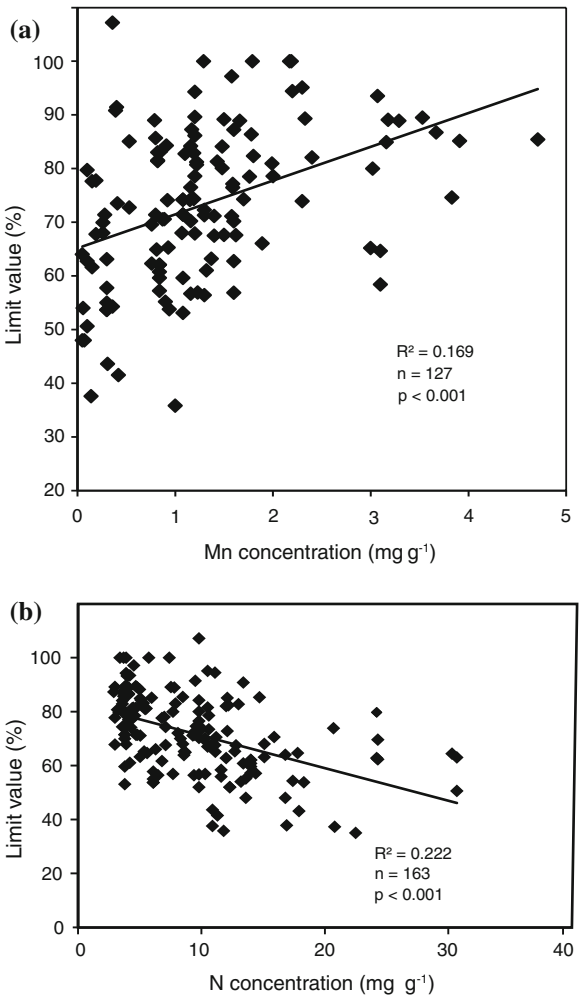

Fig. 6.12 Limit values for coniferous and deciduous litter related to two parameters. **a** Initial concentrations of Mn ($n = 127$). **b** Initial concentrations of N ($n = 163$). In each case, there was a highly significant relationship

Considering that Mn is being released about linearly to litter mass loss and has a not very regular pattern of concentration change (Berg et al. 201Xb) with accumulated mass loss, we may speculate about an effect on decomposition that is different from that/those of N, with a continuously increasing concentration. The Mn release rate was linear to litter Mn concentration, and we cannot exclude the possibility that the mobility of Mn is a critical factor (cf Sect. 5.4).

Higher N levels in the litter are related to lower limit values. When the available 163 limit values for foliar litter decomposing in natural systems were regressed against concentrations of nutrients and AUR, it was seen that N concentration gave a highly significant, negative relationship ($R^2 = 0.222$; $n = 163$; $p < 0.001$) (Fig. 6.12b, Table 6.6). The relationship using all available data was negative meaning that the higher the initial concentration of N the lower the limit

value, with a smaller proportion of the litter being decomposed. Behind this observation, there may be a causal relationship that is valid both for litter in late decomposition stages and for humus. The discussion that was applied onto 'litter in late stages' (cf. Chap. 2) may also be used in this case. The possible reasons for the relationships between limit values and N were discussed above and in Chap. 2.

The fact that in this large dataset the relationship to N concentration was significant indicates a general relationship to N over a good number of species in deciduous and coniferous ecosystems in boreal and temperate forests. In addition, initial litter N concentrations ranged from 3 to 30 mg g^{-1}. Although highly significant, the R^2 value was still low (0.222) when including all 163 limit values. This probably depends on the fact that in this broad dataset, there are several factors potentially influencing the limit value, which increase the variability of the data. Since data were collected for different forest ecosystems, with litter being incubated on soils with different properties and in different climate zones, this is not surprising.

A large difference between two systems was reported by Berg et al. (2003), namely a Scots pine system with a humus N level of 11.8 mg g^{-1} and a silver fir system with an N level of 38.2 mg g^{-1} and a generally higher level of the other nutrients. With such differences, the soil microorganism populations would have adapted to the different levels.

Higher AUR concentrations are related to lower limit values. Using all available limit values, Berg et al. (1997) noted a negative relationship to initial AUR concentrations in litter. Such a relationship may be expected, as lignin may to be an important component in the nucleus of the recalcitrant part. When all litter species were investigated, the relationship was weak, with an R^2 value of 0.044 for 112 measurements, whereas for single species, for example spruce litter, the relationship was stronger with $R^2 = 0.551$. The relationship between AUR concentration and limit value is not necessarily a simple one; although lignin's importance may strongly influence limit values, we may expect its role to be influenced by variables such as N and Mn.

*Heavy metal***s.** A very N-rich system could be expected to have a higher percentage of lignin-degrading organisms that are not sensitive to N (cf. Chap. 3). This could mean that the limit values are ruled to a lesser extent (or not at all) by the concentration of N, while other factors such as the levels of heavy metals may be important. Heavy metals have been measured, and relationships have been noted in data originating from two very contrasting sites (Berg et al. 2003). No clear global relationships were apparent from these studies. However, the heavy increase in, for example, Pb and Cu concentrations in decomposing litter (Chap. 5) suggests that we may expect an effect.

Groups of litter species have different empirical relationships. The observed relationships between N and Mn concentrations and limit values were also seen for selected groups of litter. The coniferous litters as a group gave a highly significant relationship between limit values and litter N concentrations ($R^2 = 0.436$, $n = 86$, $p < 0.001$; Table 6.6) as did Mn ($R^2 = 0.263$, $n = 74$). Berg et al. (2010) also found enough studies using local Scots pine and other local pine species to allow a

special investigation of the factors regulating the limit value for that specific litter species, and found a highly significant, positive relationship between Mn concentrations and limit values ($p = 0.0014$, $n = 42$).

For all available data for Norway spruce needle litter from undisturbed systems, a significant relationship was found between limit values and the concentrations of Ca ($R^2 = 0.160$, $n = 26$, $p < 0.05$) and Mn ($R^2 = 0.176$, $n = 26$, $p < 0.05$) but none to N (Table 6.6). However, there was no relationship to N concentrations. Davey et al. (2007) found that limit values for leaf litter of common oak were best related to initial Ca concentrations. We may speculate that at least in some cases, the groups suggested above (e.g. Table 6.1) would be applicable on the limit value stage.

For deciduous litter as a separate group, the limit values were positively related to litter concentrations of Mn ($R^2 = 0.131$, $n = 44$, $p < 0.05$) but not to N or Ca (Table 6.6).

Nutrient and heavy metal concentrations as indicators of limit values. The fact that significant relationships exist between limit values and initial concentrations of N and Mn suggests a regulating mechanism. However, until causal relationships are demonstrated, the effects of initial concentrations of these elements should be viewed as empirical indices only.

These indices may be regarded in different ways. For a nutrient such as N, concentrations increase linearly with accumulated mass loss, and mainly in proportion to the initial concentration (cf Fig. 5.14; Berg et al. 1999b); thus, the use of initial N concentration should not cause any problem when used as an index. Similar reasoning may be applied for some heavy metals. For Cu, Pb, and Fe, the concentrations in later stages reflect the initial ones as their concentrations increase (cf. Chap. 5) at least in the so far recorded cases. However, for some nutrients and heavy metals, with Mn as an example, mobility is pH dependent. With this element, the concentration pattern appears less predictable during decomposition and we may see (Fig. 5.9) that we cannot find any regular pattern in concentration change. It remains to be determined how we should interpret the relationship between limit values and their concentrations. Although new findings have been made as regards the regulation of enzymatic activity by Mn, these studies have not yet led to a clear understanding of the effects of Mn in more complicated litter and soil systems.

6.4.3 Do Limit Values Indicate a Stable Fraction?

Can we describe the properties of the recalcitrant remains? Do limit values indicate a more or less complete halt in the litter decomposition process? Although limit values for litter mass loss have been estimated for a variety of litters by using asymptotic functions, we cannot conclude that such limit values indicate a complete recalcitrance to biological degradation for the remaining organic matter. Instead, the residual organic matter could very well consist of a moderately

stabilized fraction that decomposes very slowly or a fraction that just does not decompose in a given environment, whereas a changed environment or disturbance could allow further degradation. However, this would not mean that the discovery of an apparent final mass-loss value should be considered trivial, especially if the limit value could be related to climate and litter properties, such as Mn concentration, nutrient status, or other environmental factors.

Couteaux et al. (1998) applied both a three-factorial model and a limit value function to direct CO_2 measurements of decomposing Scots pine needle litter close to the limit value, and to the humus formed in the same stands. They measured k values for decomposition of a stable fraction in the magnitude of 0.0001–0.00001 % per day. These k values correspond to a decomposition rate of about 1 % per 30 and 300 years, respectively. That study included an analysis of stable, meta-stable, and labile components (Table 10.2), where the stable fraction comprised c. 80 % of the material and may be considered as rate limiting.

The estimated limit values may thus illustrate a fraction that is highly stabilized and thus decomposes at a very low rate. Even if this should be the case, the limit value concept is no less useful, especially if we can connect this recalcitrance in litter to its chemical properties, for example to the initial concentrations of lignin or some nutrient, or possibly to climate (cf. Chap. 10).

6.5 Does Chemical Composition Influence Leaching of Compounds from Humus?

If the stabilized litter remaining at the limit value forms humus in, for example, an organic layer, we may use different observations on humus to discuss the stability of the remaining fraction. We comment on the relationship between respiration rate and humus N concentration (Fig. 7.10).

Published observations indicate the existence of a disintegration or decomposition mechanism for humus that appears to be initiated by high acid or high N loads in the soil system. Very high N loads, for example from atmospheric N deposition, appear to promote a disintegration of humus, probably as a consequence of heavily increased microbial activity. This theory was forwarded by Fog in 1988. He suggested that a higher concentration of N in litter/humus would result in an increased production of soluble organic matter (DOM or DOC). His ideas were based on the functioning of the group of lignin-degrading organisms that are called ‘soft rots’ (Chap. 3). Worrall and Wang (1991) briefly reviewed the literature and added their own observations to show that at least some soft-rot fungi need high levels of N in their surroundings in order to carry out decomposition. Therefore, in an N-rich environment, they can, to a certain extent, replace white-rot organisms. Soft-rot degradation of lignin yields remains of incompletely degraded lignin that react with organic N compounds, a reaction that leads to water-soluble products. Fog’s (1988) conclusion was that high N concentrations

increase the formation of water-soluble compounds, resistant to degradation, but decrease the amount of humus that is formed, as might occur in a mor layer. Ulrich (1981) has described a similar process and called it a 'disintegration of humus.' David et al. (1989) reported higher concentrations of soluble organic matter with increasing acidity.

Guggenberger (1994) concluded that the mobilization of DOC is not ruled exclusively by a low pH. On the contrary, he makes the reasonable conclusion that high inflows of total N suppress the complete lignin degradation carried out by white-rot organisms but increases the general microbial activity. He supports the conclusion by Fog (1988) that the more N-tolerant soft-rot fungi produce partial degradation products that are more water soluble, especially the N-containing compounds. He also proposes that a generally higher microbial activity will give a greater production of microbial metabolites.

We may compare this to the isolation of N-tolerant white-rot fungi (Chap. 3) from N-rich surroundings and conclude that the phenomenon described by Guggenberger (1994) and Fog (1988) could be due simply to a wider spectrum of fungal species. The common property among these fungi could be a tolerance of high N levels. Connected to the above observations is a comparison of amounts of humus in mineral soil under Douglas-fir and red alder. Cole et al. (1995) found that in the more N-rich alder stand, greater amounts of C compounds were leached into the mineral soil from the humus layer. While it is difficult to base wider conclusions on this study alone, the observation that an N supply in a naturally richer environment is part of a mechanism for formation of DOC that later precipitates in the mineral soil, does fit Fog's (1988) hypothesis.

Chapter 7
Climatic Environment

7.1 Introduction

Climate has a dominant effect on litter decomposition rates on a regional scale, whereas litter quality dominates on a local level (Meentemeyer 1984). Thus, at a given site and climate, one should expect differences in mass-loss rates of litters to be related primarily to their chemical and physical properties. Many studies have demonstrated such relationships (Fogel and Cromack 1977; Aber and Melillo 1982; Upadhyay and Singh 1985; McClaugherty et al. 1985; Dyer 1986). As the decay of litter progresses through time, the constituents that regulate the rate of mass loss can change. Berg and Staaf (1980a) presented a schematic model of these litter decay stages, later modified by Berg and Matzner (1997; Chap. 6). Thus, early-stage decomposition is primarily controlled by climate and concentrations of main nutrients, especially N and P, whereas lignin decomposition exerts the dominant control in the later stages. The delivery of heat and moisture to the litter will exert a control over the rate at which the decay phases postulated by Berg and Staaf (1980a) can proceed. Thus, in one climatic regime, the early, nutrient-controlled phase could persist while in other regimes, this phase could be quickly passed (Dyer et al. 1990).

Analyses of decay dynamics so far have been conducted using widely different litter types, at sites in different climatic regimes and in different forest types. Thus, when considering the regulation of decomposition, it is difficult to separate the influence of climate from the influence of litter quality. With the increasing emphasis on understanding the impact of climate changes on the broad-scale patterns of biological processes, we need to expand our consideration of the decomposition processes from substrate and site-specific studies to a broader regional context. At this larger geographical scale, our attention must turn to climate.

In this chapter, we have focused on litter decomposition in climate gradients and present results from seven main climatic gradients. Part of these studies was carried out in stands with monocultures and part of the gradients had stands of different species and genera. The monocultures had either, Norway spruce, or Scots pine or stands with monocultures of Scots pine and other pine species. One

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7_7,

gradient was based on oak spp. (genus *Quercus*). We suggest that the results are sufficiently contrasting to illustrate that different patterns should be expected among species in climatic transects.

Like in most decomposition studies, there are fewer studies with focus on late stages also in gradients. We first present data for first-year mass loss, and in a later section, we discuss decomposition data in relation to early and late stages.

7.2 Microbial Response to Temperature and Moisture

The soil microbial community encompasses several hundred species in the soil of a particular stand (Torsvik et al. 1990; Bakken 1997). The microbial community has a rich adaptability to both different moisture and temperature regimes (Chap. 3), but both moisture and temperature can be limiting. Unless there is enough moisture, often above about 10 % water-holding capacity, water may be so limiting that raising temperatures would not result in higher microbial activity. Likewise, in an energy-limited system, such as at low temperatures, higher moisture would not necessarily result in higher activity.

The microbial response to temperature should be regarded as the sum of the responses from the entire microbial community. Those bacteria and fungi having their temperature optima at say 15 °C are less active at 10 °C and nearly inactive closer to freezing point. However, at zero and even below, psychrophilic organisms carry out a clear heterotrophic activity. These organisms belong to completely different species from those active at higher temperatures. In systems in cold climates, the microorganisms would thus be adapted to the prevailing climatic conditions.

A microbial response to variability in climate would thus be dependent on the availability of both nutrients and carbon sources (see the review by Panikov 1999). A lack of an essential nutrient or available carbon source relative to the needs of the microbial population would thus result in a lack of response to a variation in climate. In situations where substrate quality poses a severe limitation on decomposition, changes in climate can have relatively little effect on decomposition rates.

7.3 Effects of Variation in Weather and Topography

7.3.1 Decomposition at One Site: Variation in Weather

Within a single site, there is a clear variation in litter decomposition rates among years that may be due to a variation in weather. When Scots pine needle litter was incubated at its own site, the first-year mass loss as determined over 19 measurements ranged from 21.1 to 33.8 % (Fig. 7.1), giving a range factor of 1.6.

There was no difference in annual mass loss between litter samples incubated in the spring and in late autumn just after litter fall. Average values for both sets were close to the general average value of 27.8 % $year^{-1}$ mass loss.

However, there are differences in decomposition rates between periods of the year determined by temperature and rainfall patterns and intensity. Two summers were characterized as warm with extended drought periods, whereas the other summers were moist. The variations in soil temperature were much more pronounced between different winters than between summers. Of the winters, three had soil temperatures well below zero degrees, which also caused high water tension in the soil. The other winters were both moister and warmer, mainly because of thicker snow packs. An early snowfall prevented the soil from becoming completely frozen. Under these conditions, the soil water was always unfrozen, which means that decomposition took place under the snow cover. In fact, for one particular one-year period, the main part of the decomposition took place during the winter.

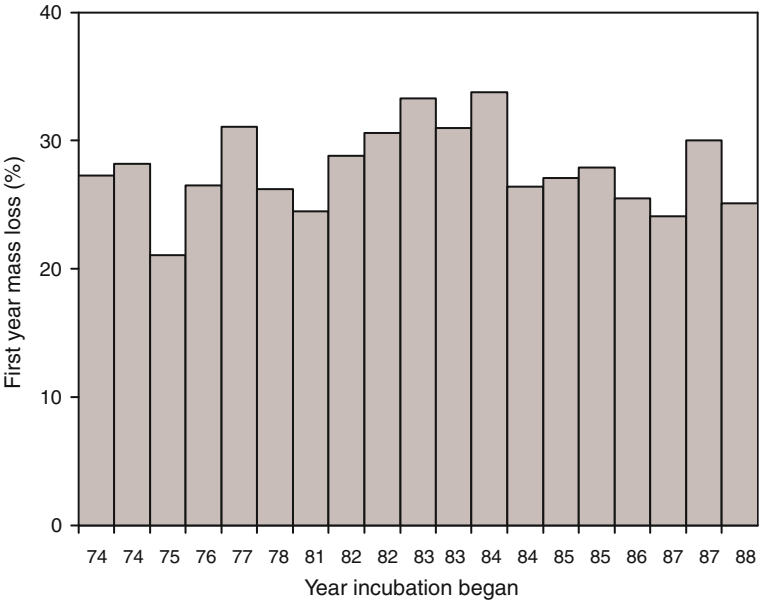

Fig. 7.1 First-year mass loss from Scots pine needle litter incubated in an 120–150-year-old Scots pine forest at the former site of the Swedish Coniferous Forest Project (SWECON) at Jädraås, Sweden. The first incubation was made in 1974 and the latest in 1988. In some years, incubations were made in both spring and autumn (Berg unpublished; Andersson unpublished)

7.3.2 *Effects of Local Topography*

Topography, notably slope and aspect, can influence microclimate. Slope position can influence water dynamics and possibly litter accumulation. Topography is clearly important in soil formation, but its role in decomposition dynamics is not as well documented. In a forest, the canopy often moderates microclimate in the forest floor (see example in App II) and microrelief assumes importance as a rate-regulating factor.

Topographic heterogeneity can have a large effect on the distribution of litter on the forest floor (Dwyer and Merriam 1981). In an American beech–sugar maple forest in southern Quebec, Canada, they observed that the mass of litter accumulated on the forest floor varied from 416 $g \cdot m^{-2}$ on high sites to 1,210 $g \cdot m^{-2}$ on level ground to 2,438 $g \cdot m^{-2}$ on low sites, a factor of nearly six. The three sites also had very different levels of soil moisture and soil temperature. After 16 months, mass loss ranged from 10 % on high sites to nearly 40 % in low sites. Examination of bacterial populations followed the same trend, with the lowest populations on the high sites. Thus, the topography influenced the accumulation of litter and the microclimate, which influenced the microbial community and resulted in altered initial decay rates. Even though decomposition was faster at the low sites, the downslope movement of litter more than offset the enhanced decay and increased the litter accumulation. Accumulation of soil organic matter was not reported.

In many northern forests, pit and mound topography creates a microtopography with sufficient relief to influence decomposition. The results of studies on the effects of pit and mound topography seem to contradict the results of Dwyer and Merriam (1981, above). For example, Beatty and Stone (1986) found that decomposition was slower in pits and McClellan et al. (1990) found no difference between decomposition of cellulose (filter paper) in pits and mounds. Dwyer and Merriam (1981) worked in a site that had warm, dry summers, in contrast to McClellan et al. (1990) whose sites were in cool, wet southeast Alaska where water was unlikely to be limiting. Less clear is why Beatty and Stone, working in New York State, USA, found lower decay rates in pits. Perhaps, the pits in their study held water so well that the soil became hydric and the decomposition went through periods of anaerobicity.

When these studies are taken together, it becomes clear that the underlying factor influencing decomposition rate is really microclimate. Whether or not microtopography influences decay rates, and nutrient cycling depends on whether or not the topography causes variation in microclimate, especially moisture.

7.4 Decomposition Over Climatic Gradients

We will review some major studies on decomposition in different climatic gradients, of which two cover Asia and Europe, and several have a focus on Northern Europe. Six of the studies investigated one genus or one species of needle or leaf litter:

- *Gradient 1 with 105 identified litter species* covered Asia and Europe from 68° 59′ N to 05° 30′ N and from 08° 30′ W to 142° 10′ E. This gradient had 83 broadleaf litter species and 22 coniferous. Among their data, Kang et al. (2009) identified three main genera, namely pine spp., spruce spp., and oak species. We discuss these data sets as separate gradients (below). Table 7.1, Figs. 7.2 and 7.3.
- *Gradient 2 with Scots pine* located mainly on glacial till in which local Scots pine needle litter was incubated once or twice. Twenty-two stands/sites were located between 66° 08′ N, near the Arctic Circle and 55° 39′ N, at about the latitude of Copenhagen in southern Scandinavia.
- *Gradient 3 was composed of pine spp*. in forests located mainly on sediment soils in which unified Scots pine needle litter was incubated. The gradient encompassed mainly stands with Scots pine but also sites with stands of Austrian pine, Corsican pine, stone pine, maritime pine, Monterey pine, red pine, and loblolly pine. This gradient included 39 sites ranging across Europe from northernmost Finland (69° 45′ N) to southernmost Spain at (38° 07′ N) and southernmost Italy (39° 24′ N). Five North American stands ranged from 41° 41′ N to 31° 28′ N and 83° 32′ W to 81° 18′ W (Ohio and Georgia) (Figs. 7.4 and 7.5).

Table 7.1 Linear regressions of first-year mass loss of foliar litter versus mean annual temperature (MAT) and annual precipitation (MAP). All litter types and species combined (All litter), as well as coniferous, broadleaf and *Pinus*, *Picea,* and *Quercus* as separate groups

Litter group	Intercept		MAT		MAP		*n*	R^2_{adj}	p
	C	p	A	p	B	p			
All litter	1.250	<0.001	0.035	<0.001			295	0.293	<0.001
Coniferous	3.207	<0.001	0.024	<0.001			116	0.119	<0.001
Broadleaf	3.469	<0.001	0.027	<0.001			179	0.150	<0.001
Pinus	3.208	<0.001	0.026	<0.001			87	0.116	<0.001
Picea	3.291	<0.001	−0.006	=0.819			18	0.000	=0.819
Quercus	3.425	<0.001	0.015	=0.375			54	0.000	=0.375
All litter	3.153	<0.001			0.045	<0.001	295	0.362	<0.001
Coniferous	3.162	<0.001			0.025	<0.001	116	0.079	<0.001
Broadleaf	3.337	<0.001			0.039	<0.001	179	0.287	<0.001
Pinus	3.176	<0.001			0.027	<0.100	87	0.020	=0.100
Picea	3.219	<0.001			0.055	<0.010	18	0.305	=0.001
Quercus	2.911	<0.001			<0.055	<0.001	54	0.361	<0.001
All litter	3.085	<0.001	0.018	<0.001	0.032	<0.001	295	0.407	<0.001
Coniferous	3.152	<0.001	0.019	<0.001	0.012	=0.212	116	0.124	<0.001
Broadleaf	3.233	<0.001	0.012	=0.015	0.033	<0.001	179	0.307	<0.001
Pinus	3.258	<0.001	0.029	=0.003	−0.010	=0.600	87	0.109	=0.003
Picea	2.965	<0.001	0.012	=0.602	0.056	=0.011	18	0.273	=0.036
Quercus	2.815	<0.001	0.007	=0.582	0.055	<0.001	54	0.352	<0.001

The data were not evenly distributed and the first-year mass loss is log-normalized; ln(FML) = C + A(MAT) + B(MAP). From Kang et al. (2009)

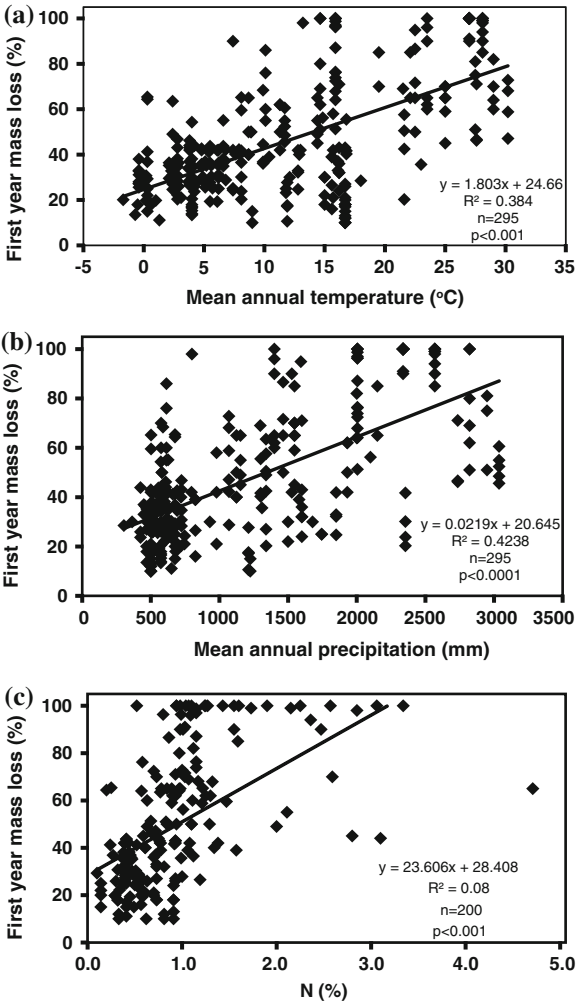

Fig. 7.2 First-year mass loss for 105 litter species (broadleaf and coniferous) combined in a climatic gradient ranging from close to the equator in East Asia to northernmost Scandinavia (Gradient 1). **a**. First-year mass loss related to site MAT. **b**. First-year mass loss related to site MAP. **c**. First-year mass loss related to litter N concentration. We may note that several litter species reach 100 % accumulated mass loss already after 1 year. There was no relationship to litter AUR concentration. Data from Kang et al. (2009)

- *Gradient 4 with different pine species*, ranging from northern Scandinavia to south China (Kang et al. 2009).
- *Gradient 5 with Scots pine*. This gradient had sites along a west to east gradient of continentality. Sites were located between 52° and 53°N and from Berlin in the west (12° 25′ E) to the Russian/White Russian border in the east (32° 37′ E) (Breymeyer and Laskowski 1999).
- *Gradient 6 with Norway spruce* stands located on glacial till in which local litter was incubated once. Fourteen sites were used, located between 66° 22′ N, close to the Arctic Circle in Scandinavia, and 56° 26′ N in southernmost Sweden

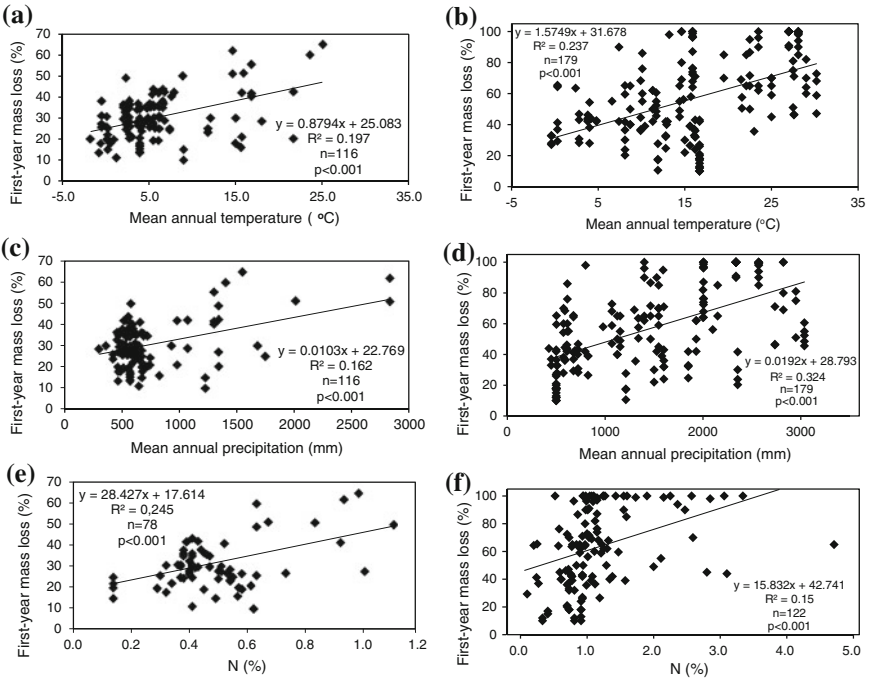

Fig. 7.3 First-year mass loss for coniferous (**a**, **c**, **e**) and broadleaf (**b**, **d**, **f**) litter. Related to site MAT, MAP as well as litter N concentration (Gradient 1). **a** and **b** give first-year mass loss related to site MAT for coniferous and broadleaf litter, respectively. **c** and **d** give first-year mass loss related to site MAP for coniferous and broadleaf litter, respectively. **e** and **f** give first-year mass loss related to litter N concentration for coniferous and broadleaf litter, respectively. We may note that several of the broadleaf litter species reach 100 % accumulated mass loss already in the first year. There was no relationship to litter AUR concentration. Data from Kang et al. (2009)

(Tables 7.2, 7.3, and 7.4). This gradient coincides mainly with that of Kang et al. (2009) who added Glehns spruce and a few more Swedish data.

- *Gradient 7 with oak spp.* Leaf litter with MAT ranging from 0.3 °C to 25°, and MAP from 449 to 2,822 mm. The geographical range covered Europe and Asia from 0° 30′ W to 142° 10′ E.

The decomposition data from Gradients 1, 2, 4, 6, and 7 were related to both climate and substrate-quality data. Climate data were those given in cited papers (e.g., gradients 1 and 4) or calculated according to Meentemeyer (1978), for example, for gradients 2, 3, and 6. The climate indices are listed in Table 7.5 along with indices for substrate quality.

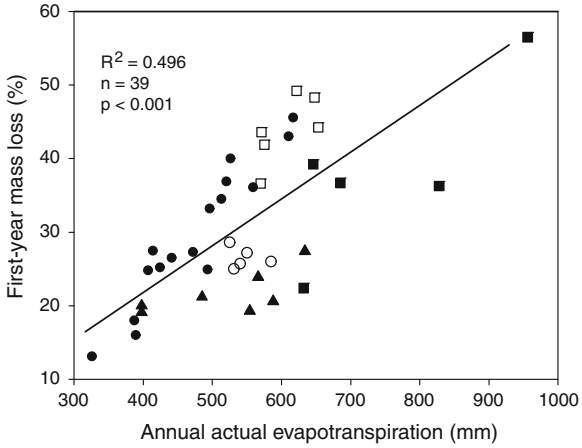

Fig. 7.4 Bivariate plot of average first-year litter mass loss versus actual annual evapotranspiration (AET). (●) Scots pine sites in an intensively studied Fennoscandian-NW-continental gradient ranging from northern Finland to central Holland; (□) pine sites close to the European west coast or sites relatively exposed to Atlantic climate; (▲) pine sites around the Mediterranean; (○) central European Scots pine sites (Poland) with characteristics of inland climate; (■) pine sites in the eastern inland of the United States. ($n = 39$; Tables 7.8, 7.9) (Berg et al. 1993a)

7.5 Multi-Species Gradient Across Asia and Europe

7.5.1 First-Year Mass Loss versus Climate and Litter Chemical Composition

The 295 values for first-year mass loss used by Kang et al. (2009) had a wide span in chemical composition and the litter had been incubated at a wide range of climates. Thus, initial N concentrations ranged from 0.1 to 4.8 % and for AUR from 4 to 50 %. Annual average temperature ranged from −1.7 to 30.2 °C and MAP from 443 to 3,040 mm.

Using literature, they found data for 83 broadleaf litter species and 22 coniferous, which were investigated together and divided into main subgroups such as coniferous and broadleaf as well as genera. Data were collected from sites ranging from the equator to northernmost Scandinavia. Not all litter-quality variables were always available, and they found 200 sets with N and 124 sets with AUR concentrations.

The first-year mass loss (1st yr ml) values ranged from 10.0 to 100 % with initial N concentrations ranging from 0.1 to 4.8 % and those of AUR from 4 to 50 %. Using natural log–transformed 1st year ml, they calculated simple and multiple regressions between 1st year ml and MAT and MAP.

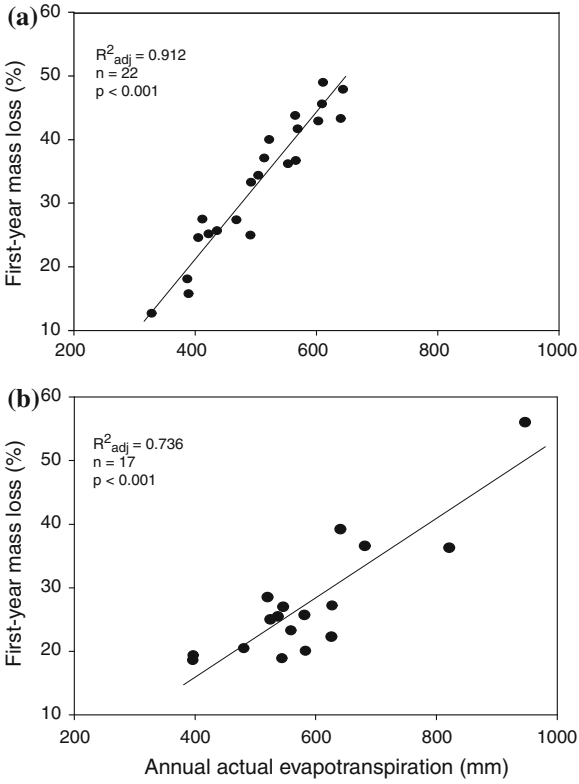

Fig. 7.5 Bivariate plot of average first-year litter mass loss versus actual evapotranspiration. **a** Scots pine sites in a Fennoscandian-NW-continental transect and pine sites close to the European west coast, relatively exposed to Atlantic climate ($n = 22$). **b** Mediterranean sites, central European ones, and North American ones ($n = 17$). A unified Scots pine needle litter was used. (Berg et al. 1993a) (cf Table 7.8)

Table 7.2 Linear relationships of first-year mass loss of Norway spruce needle litter to climatic and substrate-quality factors

Variables	R	R^2	$p<$
Mn concn	0.570	0.325	0.05
AET, Mn concn, Mg concn	0.644	0.415	0.05

The litter, collected locally, was incubated in a climate gradient (No 6) ranging from the Arctic Circle in Sweden to the latitude of Copenhagen ($n = 14$). All climate and substrate-quality variables listed in Table 7.5 were tested

We may see (Fig. 7.2) that there was a highly significant linear relationship between first-year mass loss for available data (all litter; $n = 295$) and MAT as well as MAP. A multiple regression improved the relationship (Table 7.1). Including initial N concentration also improved the relationship and R^2_{adj} increased from 0.407 to 0.578.

For all available data (all litter, $n = 295$), R^2_{adj} was 0.407 with MAT and MAP as independent variables (Table 7.1). MAT as a single factor gave an R^2_{adj} of 0.293 and MAP 0.362. The relationships between 1st year ml and N concentration were

Table 7.3 Equations for the linear relationship between annual mass loss in years 2–5 and AUR concentrations at the start of each year in decomposing Norway spruce needle litter incubated at 14 sites in Scandinavia (Gradient 6). (Berg et al. 2000)

Site	Slope	Intercept	R	n	$p<$
Significant relationships (*Group 1*)					
5 Stråsan	−0.09631	55.5266	−0.709	18	0.001
111 Hässlen	−0.07393	48.2824	−0.851	13	0.001
113 Tönnersjöheden	−0.09399	57.0367	−0.973	5	0.01
10 Mästocka	−0.11077	65.05364	−0.960	5	0.01
114 Farabol	−0.10636	65.16445	−0.969	5	0.01
104 Tveten	−0.10874	66.37035	−0.955	5	0.05
102 Kungs-Husby	−0.03942	38.60125	−0.933	4	0.1
Non-significant relationships (*Group 2*)					
109 Ätnakobbo	0.04882	2.90427	0.801	4	*ns*
108 Västbyn	0.03572	15.61122	0.197	5	*ns*
112 Månkarbo	−0.03309	38.60966	−0.911	3	*ns*
103 Tomta	0.013382	19.7723	0.207	5	*ns*
100 Dimbo	0.037064	12.28549	0.386	5	*ns*
101 Grensholm	0.021138	12.904	0.351	4	*ns*
105 Remningtorp	0.002265	28.00804	0.063	5	*ns*

Table 7.4 Linear relationships between the slope coefficients from the Group 1 litter in Table 7.3 and substrate-quality variables. Only statistically significant ($p < 0.05$) slopes were used in this investigation. $n = 7$. (Berg et al. 2000)

Equation	R	R^2	$p<$
Slope = f (Ca)	0.946	0.895	0.01
Slope = f (AUR)	−0.823	0.677	0.05

highly significant in both linear and exponential models ($p < 0.001$), but the fits were better in the latter with $R^2_{adj} = 0.408$ for all litter ($n = 200$). Kang et al. (2009) investigated for any effect of AUR concentration on the first-year decomposition and found none.

To determine relative influences on first-year mass loss, data for MAT, MAP, and N were transformed using the program Standardize Transform (SPSS, 1997) (see Sect. 4.4.2). In a multiple regression equation, the values of the coefficients indicate their contributions to the variation in 1st year ml. To show the differences in effect of MAT, MAP, and N within an equation, they used t test. A similar test was also made for the effects of MAT, MAP, and N between equations representing different groups (Table 7.6). It appears that for 'all litter,' MAP dominated as a rate-limiting factor followed by N.

First-year mass loss of coniferous and broadleaf litter as separate groups—climate and litter quality.

In a next step, Kang et al. (2009) subdivided their data into the main categories broadleaf and coniferous litter. Both groups had significant linear relationships ($p < 0.001$) between 1st year ml. and MAT and MAP as independent variables in

Table 7.5 Climate and substrate-quality variables toward which litter mass loss was regressed in studies of litter decomposition in gradients (gradients nos. 1–3 and 6.). The climate variables were calculated according to Meentemeyer (1978) and Thornthwaite and Mather (1957). For convenience, some acronyms are used in this chapter

Description of variable acronym	Acronym
Annual mass loss of litter (%) either as first-year or as annual mass loss in later decomposition stages	ML
Climate variables	
Average temperature for July (°C)	JULT
Average annual temperature (°C)	MAT
Total annual precipitation (mm)	MAP
Potential annual evapotranspiration (mm)	PET
Actual annual evapotranspiration (mm)	AET
Soil moisture surplus (mm)	
Soil moisture deficit (mm)	
Substrate-quality variables	
Concentration of water solubles at the start of each one-year period (mg g^{-1})	
AUR concentration, initial or at the start of each one-year period (mg g^{-1})	
Nitrogen concentration, initial or at the start of each one-year period (mg g^{-1})	
Phosphorus concentration, initial or at the start of each one-year period (mg g^{-1})	
Potassium concentration, initial or at the start of each one-year period (mg g^{-1})	
Calcium concentration, initial or at the start of each one-year period (mg g^{-1})	
Magnesium concentration, initial or at the start of each one-year period (mg g^{-1})	
Manganese concentration, initial or at the start of each one-year period (mg g^{-1})	

Table 7.6 Linear regressions of standardized first-year mass loss (StandFML, %) of foliar litter (ln(FML)) against standardized MAT (StandMAT, °C), standardized MAP (StandMAP, dm), and standardized initial N concentration (StandN, %). 'All litter' stands for broadleaf and coniferous litter combined. The function used was ln(FML) = D + A(MAT) + B(MAP) and C(N). From Kang et al. (2009)

Group	Intercept		StandMAT		StandMAP		StandN		*n*	R^2_{adj}	*p*
	D	*p*	A	*p*	B	*p*	C	*p*			
All litter	0.094	=0.054	0.070[a]	=0.277	0.666[b]	<0.001	0.189[a]	=0.002	200	0.578	<0.001
Coniferous	0.117	=0.255	0.327	=0.043	0.061	=0.626	0.199	=0.129	78	0.204	<0.001
Broadleaf	0.133	=0.044	−0.032[a]	=0.671	0.802[b]	<0.001	0.156[a]	=0.024	122	0.563	<0.001
Pinus	0.147	=0.228	0.445[a]	=0.041	−0.268[b]	=0.082	0.280	=0.093	56	0.223	<0.001
Picea	0.000	=1.000	−0.111	=0.615	0.599	=0.015	−0.005	=0.098	18	0.221	=0.093
Quercus	0.153	=0.147	−0.138[a]	=0.224	0.786[b]	<0.001	0.151[a]	=0.171	41	0.626	<0.001

Within an equation, different letters after the coefficients (StandMAT, StandMAP, and StandN) indicate a significant difference, for all litter, coniferous, and broadleaf $p < 0.001$, for *Pinus* and *Quercus* $p < 0.05$. Between functions, significant differences were found between coniferous and broadleaf for MAT and MAP ($p < 0.001$) and N ($p < 0.01$). Significant differences were found between *Pinus* and *Picea* ($p < 0.001$) for Intercept, MAT, and N

single or multiple regressions (Table 7.1, Fig. 7.3). In a single regression for broadleaf litter, MAT gave an R^2_{adj} of 0.150 and MAP 0.287 whereas for coniferous, the corresponding R^2_{adj} values were 0.119 and 0.079, respectively, both at

$p < 0.001$ (Table 7.1). In a multiple regression, broadleaf litter gave an R^2_{adj} of 0.307 ($n = 179$) and for coniferous R^2_{adj} became 0.124 ($n = 119$).

There was a higher variation among the first-year mass loss values for broadleaf litter samples than for coniferous (Fig. 7.3). Further, broadleaf litter generally had higher 1st year mass loss under the same climatic conditions as compared to coniferous litter. Thus, 1st year ml reached 100 % for broadleaf litter at a MAT of 15 °C and above and at a MAP of 1,500 mm, but only c. 60 % for coniferous litter at the same MAT and MAP (Fig. 7.3).

For coniferous and broadleaf litter, the relationships between 1st year mass loss and N concentration were highly significant in both linear and exponential models ($p < 0.001$), but the fits were better in the latter with 0.173 for coniferous ($n = 78$) and 0.210 for broadleaf litter ($n = 122$) in comparison with the linear model ($R^2_{adj} = 0.154$ for coniferous and 0.131 for broadleaf litter). Kang et al. (2008) also investigated for any effect of AUR concentration on the decomposition in the first year and found no effect in any group. For coniferous litter, AUR concentrations ranged from c. 20 to 40 %, and for broadleaf litter from c. 4 to 50 %.

The relative influences using standardized data (Table 7.6) indicate differences between the groups coniferous and broadleaf as regards the coefficient for MAT (negative for broadleaf and positive for coniferous) as well as for MAP which had a higher value for broadleaf litter. Within the group broadleaf, the coefficients for MAT and N were not different but less influential than MAP.

First-year mass loss for litter of Scots pine and other Pinus spp.

Local litter. When investigating the data of Gradient 2, ranging over Scandinavia, Johansson et al. (1995) determined the effects of climate and litter-quality variables on mass-loss rates. They used long-term average climatic values when relating first-year mass loss to climate variation (Table 7.7) and found that MAT gave the best fit with a value for R^2_{adj} of 0.518. Annual actual evapotranspiration (AET) gave almost as good a fit with an R^2_{adj} of 0.505. Potential evapotranspiration and average temperature in July (JULT) were also significantly related to mass loss, but MAP, water surplus, and water deficit did not give any significant relationships. AET had previously been distinguished as a superior climate index at broad, continental scales (Meentemeyer 1978, 1984; Berg et al. 1993a, b). As the R^2_{adj} value for AET was close to that obtained using MAT, Johansson et al. (1995) used it as a basis for further analysis.

On this scale, they found no relationships between first-year mass loss and initial concentrations of water solubles, N, P, or AUR. None of these factors was significant, probably because the variation in climate across the 22 sites overwhelmed the control by substrate quality. Thus, for this litter type, the first-year mass loss supports the traditional image of a climate dominance over a region.

Unified litter—Gradient 3. In a more specific investigation, a set of sites with numerous observations was investigated. This set of 13 sites in Scandinavia and the northwestern part of continental Europe had mass-loss measurements over a period of between 6 and 19 years. Of the single climate factors, AET gave a highly

Table 7.7 Linear relationships between first-year litter mass loss, and climate factors in a climatic gradient from the Arctic Circle in Scandinavia (north–east) to the latitude of Copenhagen in the South–West (Gradient 2). Local Scots pine needle litter was incubated at 22 stands/sites. All climate and substrate-quality variables listed in Table 7.5 were tested ($n = 28$). (Johansson et al. 1995)

Climate factor	Slope (SE)	Intercept (SE)	R^2_{adj}	$p<$
MAT	2.729 (0.498)	20.869 (5.812)	0.518	0.001
AET	0.134 (0.025)	−30.162 (5.890)	0.505	0.001
PET	0.143 (0.027)	−37.522 (5.955)	0.493	0.001
JULT	3.871 (1.787)	−28.6645 (7.856)	0.120	0.05

significant relationship ($R^2_{adj} = 0.867$, $p < 0.001$; Table 7.8). It is likely that the multiple years of observations gave an average mass-loss rate more representative of the climatic norms used in this study as compared to the one-time incubation in Gradient 2, using local litter.

Substrate-quality factors alone did not give any significant relationships, but the inclusion of initial N concentration or water solubles as a substrate-quality index somewhat improved the relationship; for AET plus N concentration, an R^2_{adj} value of 0.885 was obtained (Table 7.8). The addition of other climatic factors added very little to explain the observed variation. This part of the world's boreal forests is energy limited (Berg and Meentemeyer 2002) and the relationships may be improved by selected temperature functions.

Unified litter—All sites—Gradient 3 extended to encompass monocultures of different pine species. Using 39 pine sites, Berg et al. (1993a, b) incubated standardized needle litter samples in regions with AET ranging from c. 330 to 950 mm and with a highly standardized site selection and design. The sites ranged over

Table 7.8 Coefficients of determination for linear correlations between first-year mass loss of unified Scots pine needle litter and selected climatic factors, as well as some substrate-quality factors. Sites, from Gradient 3, were grouped and investigated separately as well as in combinations of groups. All correlations presented here are significant at $p < 0.001$. (Berg et al. 1993a)

Independent variables	R^2	R^2_{adj}	Types of pine stands in gradient
Scandinavian—northwestern European sites ($n = 13$)			
AET	0.878	0.867	Scots pine only
AET, N concn.	0.895	0.885	
Scandinavia—continental Europe north of the Alps and the Carpathians ($n = 23$)			
AET	0.647	0.630	Scots pine only
AET, water sol.	0.748	0.736	
Scandinavian—northwestern European plus Atlantic sites ($n = 22$)			
AET	0.916	0.912	Scots, Austrian, Monterey, and maritime pine
Mediterranean plus central European and North American sites ($n = 17$)			
AET	0.753	0.736	Scots, stone, Monterey, and red pine
AET, water sol	0.766	0.750	
AET, JULT	0.761	0.745	

differing climates across Western Europe from boreal northernmost Finland to subtropical sites in southern Spain and southern Georgia (USA). This means that the gradient included different climate types such as maritime and inland climates as well as Mediterranean.

Unified litter was incubated two or three times a year at the different sites. First-year mass loss ranged from about 10 % at the northern-most boreal site to 56 % at a subtropical Georgia site.

The best positive correlations were obtained for the relationship between first-year mass loss and AET ($R^2 = 0.509$) and MAP ($R^2 = 0.323$) both with $p < 0.001$, and average temperature (MAT, $R^2 = 0.203$, $p < 0.05$). Of the climatic variables, water deficit also gave a small but significant correlation (Table 7.9).

First-year mass loss was plotted against the best single variable (AET) using all sites (Fig. 7.4). The progression in rates from the arctic to the subtropical sites is readily apparent. Some of the scatter can be attributed to the use of long-term climatic means rather than information about the weather during incubation. For example, the Georgia sites should have higher rates of mass loss in normal years than those that were observed, because incubation occurred in an extremely dry year. Some of the variation must also be caused by variations among local site conditions and litter quality. Although the litter originated from the same site and stand (unified litter), there were some differences in chemical composition among years. The N concentration in the incubated litter ranged from 3.4 to 4.1, P from 0.19 to 0.21, S from 0.32 to 0.38, and Ca from 2.3 to 7.1 mg g^{-1} (cf. Table 4.5).

Atlantic climate sites. This climate type, with rainy summers and moderate winters, encompasses all Scandinavian and northwest European sites. The 13 highly standardized sites in the long-term Scandinavian gradient (part of No 3), the sites relatively close to the Atlantic coast (in the Netherlands, France, NW Spain, and Portugal) with an Atlantic climate ($n = 7$), and data from two eastern Finnish sites, had similar relationships between first-year mass loss and AET (Fig. 7.5). All of these sites had low water deficit with the exception of one that was located very close to the coast. With the similar responses the 22 decomposition values were combined for an analysis versus climate. Comparing AET and first-year mass loss

Table 7.9 First-year mass loss of unified Scots pine needle litter in 39 pine forests (Gradient 3) as a function of some single climatic factors as well as multiple ones. A broad regional scale was used across Europe from an arctic site close to Barents Sea to southern Spain and southern Italy and subtropical sites in southern Georgia, USA. Tested variables are given in Table 7.5. (Berg et al. 1993a)

Independent variables	R^2	R^2_{adj}	p	Comments
AET	0.509	0.496	<0.001	
MAP	0.323	0.304	<0.001	
MAT	0.203	0.181	<0.01	
PET	0.187	0.165	<0.05	
Water deficit	0.097	0.073	<0.05	Def. gave a negative relation
AET, JULT	0.689	0.681	<0.001	JULT gave a negative relation
AET, JULT, MAT	0.716	0.708	<0.001	JULT gave a negative relation

gave a very good fit ($R^2_{adj} = 0.912$; Fig. 7.5a). This relationship was not improved by the addition of other climatic factors or substrate quality.

Sites with warm, dry summer climate. The relationships obtained for the Atlantic climate sites were significantly different from those for Mediterranean and inland sites. Although AET had similar ranges for the two climate types, the pattern and temporal distribution of temperature and precipitation was of importance. Combining the mass-loss values for the sites characterized by dry and warm summers resulted in a set of sites encompassing those with a Mediterranean climate, sites in Central Europe, and in the American Midwest. A linear regression of mass loss versus AET gave a significant relationship ($R^2_{adj} = 0.736$, $n = 17$, $p < 0.001$; Fig. 7.5b). The relationship was not improved by further climatic factors indicating little contribution to the relationship by seasonality, or by substrate-quality factors.

Latitudinal gradient. In a different approach, Breymeyer and Laskowski (1999) investigated a latitudinal gradient (No 5) with increasing degrees of continentality ranging from Berlin in the west (12° 25′ E) to the Russian/White Russian border in the east (32° 37′ E). This transect was oriented along a gradient of increasing continentality. With increasing continentality, the MAT decreased, temperature amplitudes and MAP increased, while in the same direction, the first-year mass loss decreased. Their experiment thus indicated that the distribution of the climate over the year is of importance for mass-loss rate, which was also seen in the comparison of Atlantic and inland climates (above).

Comments on regional comparisons—Atlantic versus inland climates. Berg et al. (1993a, b) showed that general broad-scale climatic control of mass-loss rates in pine needle litter could be modeled. Their results also show that regions have differing responses that may be related to climate patterns. This means that the slopes and intercepts of the relationship can vary between different climates (Fig. 7.5). Effects of climate patterns may be direct or indirect. The forest-floor environments are indeed different under pine forests of different regions, even though macroclimatic AET values are similar. Increasing continentality may result in changes in the composition of ground vegetation (Roo-Zielinska and Solon 1997, 1998), which may change the ground climate and other environmental conditions important for decomposition.

In this comparison, climatic variables that respond to seasonality and continentality were included, but none of these variables could help explain lower rates in the Mediterranean and inland sites. The mix of years and sites used suggests that this is not simply the result of experimental error (Berg et al. 1993a). Furthermore, the results using the Fennoscandian and Atlantic sites are very similar to those found by Meentemeyer and Berg (1986) using earlier data sets for Fennoscandia and weather records for the actual incubation period. Their regressions using AET versus needle litter mass loss had intercepts and slope coefficients as well as R^2 values similar to those found here. The functional basis for these differences among climatic zones remains unclear.

7.6 Climate and Decomposition of Spruce (*Picea*) Needle Litter

7.6.1 First-Year Mass Loss

Over a climatic gradient (No 6), the decomposition rate of Norway spruce needle litter was more closely related to substrate quality than to climate. Norway spruce needle litter appears to be a substrate with properties very different from those of the different types of pine needle litter (cf. Chaps. 4 and 6), and over the gradient, this was reflected in a switch from climate control to one of the substrate qualities already for first-year mass loss. For example, in a North–South gradient along Scandinavia from the Arctic Circle (66° 22′ N) to the latitude of Copenhagen (56° 26′ N, climate indices did not show any significant relationship to first-year mass loss (Berg et al. 2000). In their synthesis, Kang et al. (2009) using in part overlapping data found no relationship to MAT (range −1.3 to 7.4°).

The lack of a climatic influence on the decomposition of Norway spruce litter, both for the first year of incubation and in later years, makes it differ greatly from previous studies using other litter types, notably Scots pine needles (Berg et al. 1993a, b). In other words, the decomposition of Norway spruce litter does not depend on site-specific energy and water inputs to the ecosystem but on other, more powerful influences. For Norway spruce litter, site climate based on long-term averages was very poorly related to decomposition rate, even though the variation in AET in the 1,600-km-long transect ranged from 371 to 545 mm. This suggests that soil microclimate is not an important control on litter decay rates in Norway spruce stands.

For some of the Norway spruce plots in this gradient, Berg et al. (1984) reported that first-year mass loss of a standardized preparation of Scots pine needles could not be correlated to climatic indices. They had incubated unified Scots pine needle litter in paired stands of Norway spruce and Scots pine, and although decomposition of the litter incubated in the Scots pine stands was regulated primarily by climate, the decomposition of that incubated in the nearby stands of Norway spruce, on the same soil and under the same climate, could not be related to any climatic factor.

Soil microclimate in spruce forests is poorly described by local temperature, precipitation, and water-balance variables. Spruce trees produce dense canopies, but in a gradient study, Berg et al. (2000) found no effect of canopy cover and basal area indices on litter decay rate. In contrast, the decomposition of Scots pine litter incubated in a pine stand follows ground microclimate fluctuations very well (Jansson and Berg 1985). The results suggest that for decomposition of Norway spruce litter other factors may be involved, such as substrate quality and possibly different microflora in spruce, as compared to Scots pine stands. Ground climate in the spruce forests may not be related as closely to macroclimatic factors and

averages as in the adjacent pine forest (Johansson et al. 1995). Under the dense spruce canopies, water could be limited due to interception, in which case temperature differences would have little effect. This appears to be a reasonable conclusion since decomposition of Scots pine needles in spruce stands was also unrelated to climate.

Dead Norway spruce needles may stay on the branches for long periods and become partly decomposed before being shed. This means that the early phase of decomposition (Berg and Staaf 1980a) occurs before litter fall, and that at least part of the litter was already in a late phase of decomposition when collected. Hence, the concentrations of compounds such as lignin, N and P, will be higher than in directly shed litter and concentrations of water solubles will be lower. Further, mobile nutrients, such as *K*, will be leached, resulting in lower concentrations (Laskowski et al. 1995). Thus, a dominant influence of the substrate cannot be excluded. However, only one out of eight substrate-quality factors, namely initial Mn concentration, correlated positively with first-year mass loss ($R^2 = 0.325$, $p < 0.05$; Table 7.2, Fig. 6.11). The relationship between Mn concentration and first-year mass loss is based on a causal relationship for the role of Mn as a rate-stimulating agent for lignin degradation (cf. Chaps. 2 and 3).

7.7 Climate and Decomposition of Oak Species (*Quercus*) Leaf Litter

7.7.1 Climate versus First-Year Mass Loss

The gradient (No 7) with oak spp. leaf litter encompassed both deciduous and evergreen species and several climates. MAT ranged from 0.3 to 25 °C, and MAP from 449 to 2,822 mm. The geographical range covered Europe and Asia; from 06° 30′ W to 142° 10′ E.

When Kang et al. (2009) related first-year mass loss of oak leaf litter to MAT, there was no relationship ($R^2_{adj} = 0.000$; $n = 54$; Table 7.1). On the other hand was MAP significant ($R^2_{adj} = 0.361$). They had 41 studies with nitrogen analyzed for and found a positive relationship ($R^2_{adj} = 0.076$; $p = 0.045$). Using standardized 1st year ml and standardized MAT, MAP, and N concentration ($n = 41$), they found that MAP had the strongest influence on decomposition and those of MAT and N concentration were not significant. It appears that oak leaf litter behaves in a different way as compared to, for example, that of pine spp. We may refer to Sect. 6.3.1 describing decomposition of common oak litter with a strong influence of Mn on litter mass loss.

7.8 Decomposition in Climate Gradients and the 3-Stage Model

7.8.1 Scots Pine Litter

7.8.1.1 Early Stage

At a given site, different litter materials decay at rates that are largely dictated by their chemical and physical properties (Berg and Staaf 1980a; Berg and Ekbohm 1991). These relationships may be unique to a site and its decomposer organisms. Therefore, predictions of decay rates for other sites cannot be made with confidence on the basis of the effect of substrate quality at a single site. The analysis of decay dynamics at a site must include the combined effects of both climate and litter-quality variables. We have seen that N concentration may have an effect on the early-stage mass-loss rate (Gradient 3) in addition to MAT and MAP. Still, the magnitude of the effect may vary with climate.

Relationships between substrate properties and climate in a gradient. In part of the stands belonging to Gradient 3, pine litters of different chemical composition were incubated at 11 sites (Table 7.10). This gradient included sites in Finland, Germany, The Netherlands, and Sweden. For each site, the litter-quality variables (concentrations of N, P, and water-soluble constituents) were regressed against annual mass loss (Berg et al. 1993a). Most of the regressions, even considering the low number of litter types at each site, were significant ($n = 4$, $p < 0.1$). Examination of the intercepts and slope coefficients for each regression equation at each site suggested a consistent change in coefficients that was influenced by climate similar to what was found by Dyer (1986).

Berg et al. (1993a) analyzed the set of intercepts and slope coefficients for the 11 sites with respect to each of the climatic variables. Their analysis revealed the degree to which the coefficients vary with climate. For concentrations of both N and P, the intercepts were strongly and positively related to annual potential evapotranspiration (PET), and the slope coefficients were related to precipitation

Table 7.10 Chemical composition of four experimental Scots pine and lodgepole pine needle litters incubated at part of the sites in Gradient 2. (Berg et al. 1993a)

Litter type	Ws	Es	AUR	N	P	S	Mg	Ca	Mn	K
	Concentration [mg g^{-1}]									
Scots pine										
Brown, natural	164	113	231	4.8	0.33	0.55	0.49	4.42	0.79	1.07
Brown, fertilized	135	91	265	7.0	0.33	nd	0.37	2.50	0.70	1.02
Green natural	199	63	284	13.4	1.47	0.98	0.85	2.82	0.41	4.90
Lodgepole pine										
Brown, natural	103	42	381	3.9	0.34	0.62	0.95	6.35	0.95	0.56

Ws water solubles, *Es* ethanol solubles

(MAP) at the site. Thus, the intercepts appear to be driven mostly by annual temperature (temperature is a main component of PET), and the slopes of the relationship (mass loss vs. quality) by the gross water supply (precipitation).

These relationships were described empirically using derived linear equations based on data from a boreal to temperate climatic gradient (Berg et al. 1993a).

$$\text{Mass loss}_{\text{Phos}} = (-29.3 + 0.111(\text{PET})) + (0.749 + 0.013(\text{MAP}))(\text{P concn}) \tag{7.1}$$

Equation (7.1) shows the relationship between mass-loss rates and potential evapotranspiration (PET) and initial phosphorus concentration. The first term in parenthesis is actually an intercept determined by the site's PET (mm). The second term is the slope coefficient and is determined by the annual precipitation at the site (mm). The initial P concentration is the independent variable.

$$\text{Mass loss}_{\text{Nitr}} = (127.3 + 0.100(\text{PET})) + (-0.067 + 0.0022(\text{MAP}))(\text{N concn}) \tag{7.2}$$

Equation (7.2) is completely analogous to Eq. 7.1 and demonstrates the relationship between climatic variables, N concentrations, and annual mass-loss rates.

The expanded model for the influence of initial concentrations of N and P at any particular site may be written as nomograms (Fig. 7.6). This nomogram was constructed from Eq. 7.1. Selected PET values are shown on the left vertical axis, annual precipitation on the horizontal axis and predicted mass-loss rates on the right vertical axis. The figure provides predicted loss rates for PET values between 400 and 600 mm, variable precipitation (from 200 to 650 mm) and initial P concentrations of 0.15(a), 0.30(b), 0.60(c), and 1.20(d) mg g^{-1}. Thus, PET determines the intercepts and precipitation (MAP) determines the slopes. Using this nomogram, the mass-loss rate at a given site can be predicted on the basis of initial P concentrations.

These relationships (Fig. 7.6; Eqs. 7.1 and 7.2) also suggest that most of the regional variation in early-stage mass-loss rates in Scots pine forests across northern Europe is driven by temperature/heat constraints (Berg and Meentemeyer 2002). As precipitation increases, the differences in mass-loss rates for litter of differing P concentrations became larger. The sites used in this investigation all had an Atlantic climate (cf. above) and we could expect that the corresponding relationships for Mediterranean and continental sites would be different.

Figure 7.6 illustrates an alternative approach to comparing the roles of climate and litter quality in determining mass-loss rates across a large geographical area. Even small changes in climate can produce greater changes in early-stage decay rates than large differences in litter quality. Thus, it is not surprising that in this type of system, quality variables are important at local scales but their influences are less significant when viewed over a larger scale. Nevertheless, the equations described here should permit predictions of the influence of litter quality across a broad area of northern European pine forests, especially those with Scots pine.

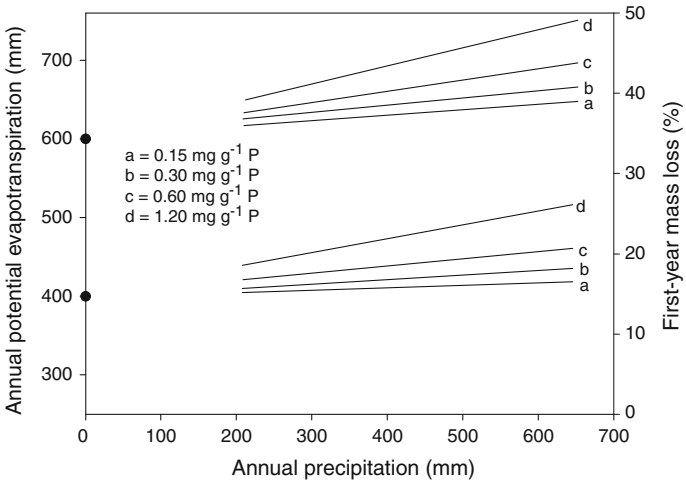

Fig. 7.6 Relationships among first-year mass loss (%), potential evapotranspiration (PET), annual precipitation, and initial P concentration in litters. To investigate the effect of differing litter qualities under different climates, four chemically different litter types were incubated at 11 sites (part of gradient 2, Table 7.10). Nomogram constructed from Eq. (7.1). Selected potential evapotranspiration (PET) values are shown on the *left vertical axis*, annual precipitation on the *horizontal axis* and predicted mass-loss rates on the *right vertical axis*. The figure provides predicted loss rates for PET values of 400 mm (*lower set of graphs*) and 600 mm (*upper set of graphs*) and four initial P concentrations of 0.15 mg g^{-1} (**a**), 0.30 mg g^{-1} (**b**), 0.60 mg g^{-1} (**c**), and 1.20 mg g^{-1} (**d**). (Berg et al. 1993a)

Is there a transition stage between the early and the late stage?
We may use annual mass loss (cf. App II) and data for gradient 2 (Scots pine local litter). With samplings several times a year at regular intervals, Berg et al. (201Xa) calculated overlapping annual mass losses. They divided their litter into groups based on the accumulated mass loss. One group was identified as having 10–20 % accumulated mass loss, another 20–30 % and a third, 30–40 %. Thus, the groups represented stages with the early stage passed to different extent. Starting with litter in different stages of decomposition, they calculated annual mass loss for sites over the gradient. We may see that the newly incubated litter responded well to the variation in climate and had a steep slope (Fig. 7.7b). The same was found for the annual mass loss of little decomposed litter (the 10–20 % group). For the more decomposed litter, the slopes decreased as the climate effect decreased (Fig. 7.7b).

7.8.1.2 Late Stage

Lignin/AUR concentrations increase during decomposition of litter (cf. Chap. 5), and raised AUR concentrations have been related to decreased litter decomposition

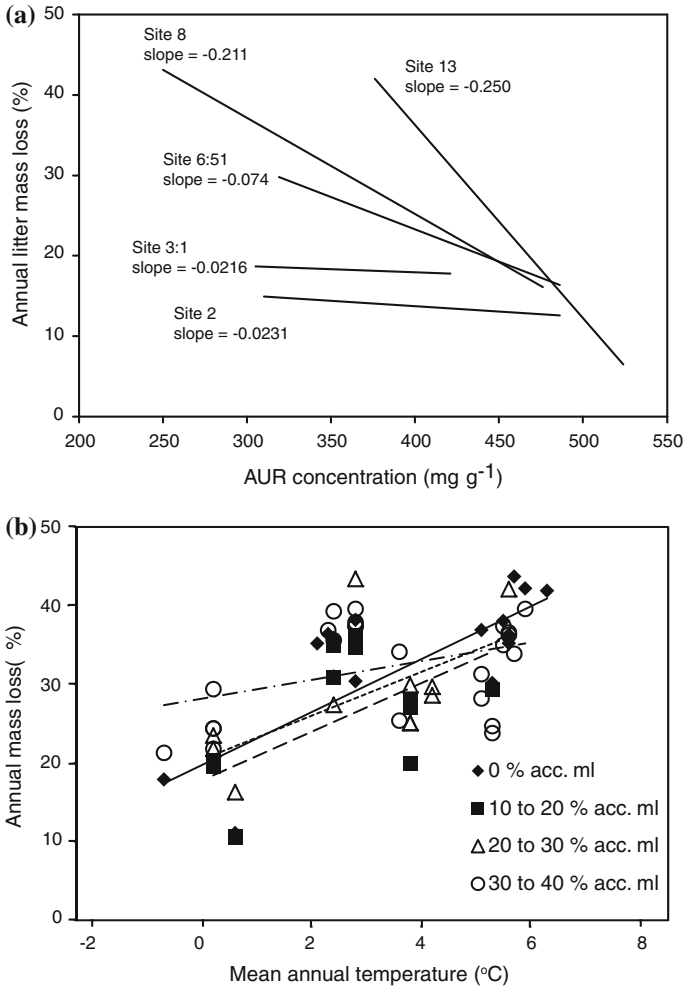

Fig. 7.7 **a** Plot of annual litter mass loss versus litter AUR concentrations at the start of each year. The forest stands ranged between the Arctic Circle in Scandinavia and Lüneburger Heide, northwest Germany (Site 13;Table 7.11). **b** Annual mass loss of local litter of Gradient 2. The first relationship is based on first-year mass loss starting at 0 % accumulated mass loss (◆). The second (■) is based on litter decomposed to the interval 10–20 % accumulated mass loss and for 1 year. The third (▲) is based on litter decomposed to the interval 20–30 % accumulated mass loss and 1 year after that. The fourth (●) is based on litter decomposed to the interval 30–40 % accumulated mass loss and one year after that. The relationships with progressively more shallow slopes thus illustrate the effect of decomposition level on the temperature dependence of the decomposition

rates (Fogel and Cromack 1977). The rate-dampening effect on litter mass-loss rates acting through lignin/AUR concentrations can be described with a negative linear relationship (Berg and Lundmark 1987), which for some pine litter species,

may begin as early as 20 % mass loss. In earlier work, Meentemeyer (1978) and Berg et al. (1993b) related mass-loss rates to AUR concentrations and demonstrated a variation with geographical location.

Johansson et al. (1995) calculated slopes for the relationship between AUR concentration and annual mass loss in a 2,000-km-long climatic gradient (part of Gradient 2) and found negative relationships. The steepest slopes were obtained for the southern sites that were warmer and wetter and, thus, had initially higher mass-loss rates than the more northern ones (Fig. 7.7a). In fact, for three dry, nutrient-poor northern sites, the slopes became so shallow that the R^2 values became very low (Table 7.11). Thus, the slope for the southernmost site, no. 13 at Lüneburger Heide, northern Germany (Fig. 7.7a), was -0.250 % mg^{-1} g^{-1}, but a value of -0.023 % mg^{-1} g^{-1} was determined close to the Arctic Circle in Sweden. The slopes for the sites in south and central Sweden were in between (Fig. 7.7a). The lengths of the lines define the intervals between highest and lowest AUR concentration used for the relationship.

The range in AUR concentration values could influence the slope. However, Johansson et al. (1995), using two sets of data (for sites 13 and 6:51; Fig. 7.7a) to isolate a range with the same AUR concentration interval, made a comparison of the slopes and found that they remained the same. In a further step, they used the slopes at each site and compared them to climate. They performed a second set of linear regressions and found that the best fit was that between slope and AET (Fig. 7.8), with an R^2_{adj} of 0.528. Other climatic variables gave significant

Table 7.11 Calculated slope coefficients for the relationship between annual mass loss and increasing AUR concentration in Scots pine needle litter at the start of each one-year period (cf. Fig. 7.7a). Data are taken from a gradient with local Scots pine needle litter incubated at sites ranging from the Arctic Circle in Scandinavia to Lüneburger Heide, northwest Germany. (Johansson et al. 1995)

Site	Slope	SE	R^2	R	n	$p<$
2 Harads	−0.0231	0.0144	0.076	−0.276	33	Ns
3:1 Manjärv	−0.0216	0.0421	0.036	−0.189	7	Ns
3:2 Manjärv	−0.060	0.0597	0.173	−0.416	9	Ns
3:3 Manjärv	−0.132	0.0209	0.278	−0.527	8	0.05
4:23 Norrliden	−0.0815	0.0217	0.453	−0.673	19	0.01
6:51 Jädraås	−0.0734	0.0240	0.227	−0.476	34	0.01
17:2 Kappsjön	−0.1751	0.0473	0.774	−0.880	6	0.05
18:2 Anundberget	−0.1874	0.0551	0.794	−0.891	5	0.05
103:1 Tomta	−0.045	0.0593	0.055	−0.235	12	Ns
102:1 Kungs−Husby[a]	−0.107	0.0353	0.568	−0.754	9	0.05
105:1 Remningstorp[a]	−0.166	0.043	0.65	−0.806	10	0.01
101:1 Grensholm[a]	−0.148	0.0518	0.577	−0.760	8	0.05
107 Sänksjön[a]	−0.166	0.043	0.65	−0.806	8	0.01
8 Nennesmo	−0.230	0.0516	0.665	−0.815	12	0.01
10:1 Mästocka	−0.228	0.0533	0.901	−0.949	4	Ns
13 Ehrhorn	−0.250	0.0334	0.846	−0.920	12	0.001

correlation with slope as well, for example, PET and MAP with values for R^2_{adj} of 0.413 and 0.405, respectively. They also combined all data in a multiple regression analysis with AET, AUR, and their product as independent variables. This analysis showed a strong significance for all three terms in the model, and an adjusted coefficient of determination (R^2_{adj}) of 0.346 ($n = 196$; $p < 0.0001$), thus explaining 34.6 % of the variation. This offers support for the conclusion that the relationship between litter mass-loss rate and lignin/AUR at a site is dependent on, or related to, the values of the climatic factors, especially AET. However, this relationship is empirical and the underlying causal factors are not known.

The causal mechanisms behind the relationship between AUR concentration and mass-loss rate could depend on the litter N concentration (Chap. 6). That the mass-loss rates were affected more strongly by increasing AUR concentrations in warmer and wetter climates, means that the degradation of lignin/AUR was more hampered at such stands. The litter N concentration increased more quickly in litter incubated in stands located at higher AET (Chap. 5), which may be a partial explanation. We can reiterate that conditions that are initially rate stimulating may, in later stages, become rate inhibiting.

It appears that when litter has entered late decomposition stages, its decomposition rate is affected more by increasing lignin/AUR concentrations at sites with higher AET values, namely under warmer and wetter conditions. It also seems that the slopes of the AUR versus mass-loss relationship tend to converge at an AUR concentration a bit higher than 500 mg g^{-1} litter, suggesting that the mass-loss

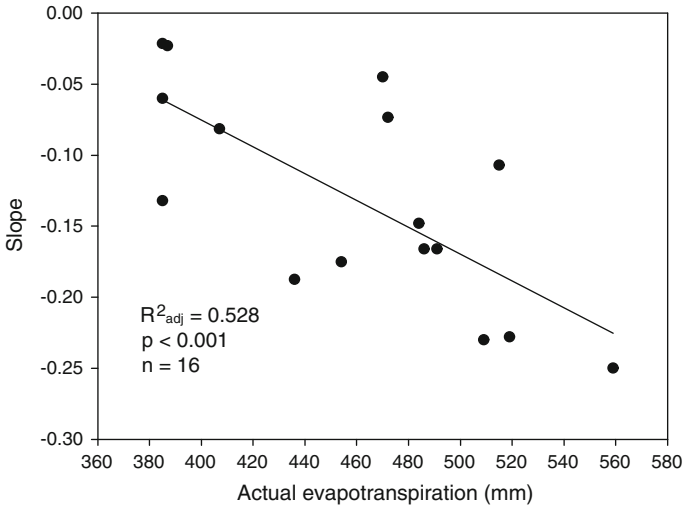

Fig. 7.8 Bivariate plot of slope coefficients (Table 7.11; cf. Fig. 7.7) versus actual annual evapotranspiration (AET) for 16 sites in a climatic gradient (No 2). The slope coefficients originate from the relationship between litter AUR concentration and annual litter mass loss. From Johansson et al. (1995)

rates approach a similar value at this level of AUR concentration, irrespective of climate. Thus, at very late, humus-near stages, decomposition rates would not be driven principally by climate factors (cf Fig. 7.10).

An experiment by Dalias et al. (2001) may confirm this observation. They investigated the effect of different temperatures during decomposition on the decomposability of the residual litter substrate. Using humus from five coniferous sites in a gradient from 64° 00′ N in Sweden to 43° 07′ N at the Mediterranean, they incubated a ^{14}C-labeled straw material at 4, 16, and 30 °C. They let the straw decompose to the same level of mass loss as measured through the released $^{14}CO_2$. Then, the material was reincubated and the release of $^{14}CO_2$ showed that the highest mineralization rate took place in samples that had been originally incubated at 4 °C and the lowest in those originally incubated at 30 °C (Fig. 7.9). Their interpretation was that when litter decomposed under higher temperatures, its residual compounds were more recalcitrant.

7.8.2 Norway Spruce

7.8.2.1 Climate versus First-Year Mass Loss

Over a climatic gradient (No 6), the decomposition rate of Norway spruce needle litter was more closely related to substrate quality than to climate. Norway spruce needle litter is a substrate with properties very different from those of different

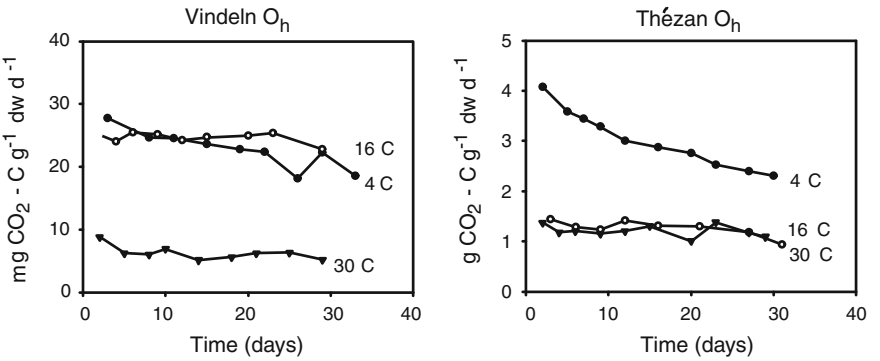

Fig. 7.9 Mean daily respiration of $^{14}CO_2$ per gram dry, partly decomposed wheat straw. Wheat straw had been incubated and was partly decomposed in the humus at five sites in a climatic gradient ranging from north Sweden to the Mediterranean. The straw was reincubated at 4, 16, and 30 °C in the laboratory. Decomposition was allowed to proceed until about the same mass loss in all cases (as measured from $^{14}CO_2$), the litter was reincubated at the standard temperature of 23 °C and the activity was compared among the litters incubated at different temperatures. The highest activity was found for litter that had been incubated at the lowest temperature. (Dalias et al. 2001)

types of pine needle litter (cf. Chaps. 4 and 6), and over the gradient, this was reflected in a switch from climate control to one of the substrate qualities. For example, in a north–south gradient along Scandinavia from the Arctic Circle (66° 22′ N) to the latitude of Copenhagen (56° 26′ N, none of the climate indices (MAT, MAP, AET, PET, JULT, water deficit, water surplus) showed any significant relationship to first-year mass loss. Of eight substrate-quality variables investigated (N, P, K, Ca, Mg, Mn, AUR, water solubles), Mn was the only one that was significant (Sect. 6.3.1; Fig. 6.11).

7.8.2.2 Late Stage

Individual sites. In Gradient 6, Berg et al. (2000) compared annual mass loss for Norway spruce needle litter to current litter AUR concentrations in the same way as was done for Scots pine needle litter (cf. Fig. 7.4). We can compare these two approaches using slope coefficients for the negative relationship between changes in AUR concentration with time, and annual mass loss. For Norway spruce needle litter, the AUR concentration at the start of each one-year period was regressed against the mass loss over that one-year period, to obtain a slope for each of the 14 sites, describing the effect of AUR on litter mass loss. The values included were clearly those of the late stage (years 2, 3, 4, and 5). AUR concentration correlated negatively with litter decay rate for 7 of the 14 sites. Berg et al. (2000) combined these into one group (Group 1, Table 7.3). For the 7 other sites (Group 2), there were no such effects related to AUR (Table 7.3).

In both groups, the intervals for AUR concentrations were similar, with 227 to 524 mg g^{-1} for Group 1 and 286 to 513 mg g^{-1} for Group 2. The litter in Group 2 had a wide range in Mn concentrations (0.41 to 7.7 mg g^{-1}). For Group 1, the range was clearly narrower (0.3–3.0 mg g^{-1}). When Berg et al. (2000) selected the corresponding range in Mn concentrations for the Group 2 litter, namely excluded all data outside the interval 0.3 to 3.0 mg g^{-1}, no significant relationship to Mn concentration was found.

Combined data. When combining all data for late stages (Group 1 and Group 2) with the Mn concentration interval from 0.3 to 7.7 mg g^{-1}, Berg et al. (2000) found a highly significant relationship between Mn concentrations and mass loss ($R^2 = 0.372$, $n = 59$, $p < 0.001$. The effects of Mn on lignin and AUR degradation have been discussed above (Chap. 3). Using all the data for late stages (Group 1 plus Group 2), including all gradient data plus all data from an experimental site (B. Berg unpublished, $n = 95$) they found that Mn concentration correlated positively with annual mass loss ($R^2 = 0.356$, $p < 0.001$; Table 6.5).

7.9 A Series of Limiting Factors

In later stages of decay, increasing AUR concentrations have been found to correlate negatively with lower decay rates. However, the nutrients influence the prevailing microflora, thus influencing both the degradation rates of AUR/lignin and the litter substrate. The succession of the latter may be regulated by the composition of nutrients. The effects of N (Eriksson et al. 1990) and Mn (Perez and Jeffries 1992; Hatakka 2001) have been discussed earlier (Chap. 6). Lignin-degradation rates as reflected through its concentration may limit litter decomposition rates if essential elements required for microbial degradation of lignin (e.g., Mn) are limiting. At the other extreme, high concentrations of an element such as N could suppress microbial degradation of lignin. Such nutrient interactions may be complex, but the composition of the microbial community, including the lignin-degrading fungi, depends greatly on both litter degradability and concentrations of nutrient elements. If the degradation of lignin is the primary rate-regulating factor in the late phase decomposition, factors such as the concentration of nutrients that influence lignin degradation will also influence the decomposition of the whole litter.

For the litter of Norway spruce, the effect of lignin/AUR was related to Mn concentrations. Within a narrow concentration interval (0.3–3.0 mg g^{-1}), Mn was not related to litter degradation rate. However, with the wider range of litter Mn concentrations (0.4–7.7 mg g^{-1}), mass-loss rates appear to be influenced by the litter concentrations of Mn and the relationship was clearer. At high Mn concentrations, microbial lignin degradation thus may be facilitated. AUR concentration itself was less important but would increase in importance when Mn was limiting. The differing concentrations of Mn in litter could be dependent on site (soil) properties (Berg et al. 1995a), and the availability/mobility of Mn in the mineral soil could thus be an important site property for determining the rate of litter decomposition. The counteracting effects of Mn and N in the late stage may be simultaneous or express themselves in a sequence. To our knowledge, this has not yet been investigated.

A similar approach may be used when discussing the effect of Ca on lignin degradation by the microbial community (cf. below). Calcium may influence the lignin-degrading microflora and thus, through lignin-degradation rates, the litter decomposition rates. The higher the Ca concentration the steeper the slope for lignin concentration versus mass-loss rate ($R^2 = 0.895$, Table 7.4). This is possibly due to a higher lignin-degradation rate when Ca was not limiting, thus leading to less lignin regulation of litter mass loss.

7.10 Climate and the Decomposition of Humus and Litter in Humus-Near Stages

The idea of a low climatic influence on respiration from humus is in part supported by a study by Bringmark and Bringmark (1991) who made respiration measurements on humus in a climate transect along Sweden from the latitude of the Arctic Circle to that of the city of Copenhagen (66° 08′ N to 55° 39′ N). Incubating their samples at a standard temperature, they found higher respiration rates for the northern humus samples as compared to the southern ones. The relationship between latitude and respiration was highly significant ($R^2 = 0.41$; $n = 166$) with respiration expressed as mg CO_2 g^{-1} ash-free humus under standardized temperature and moisture conditions. Although this measurement was made on humus, the results have a clear similarity to those of Dalias et al. (2001) (Sect. 7.8.1).

Respiration rates from humus samples are often negatively correlated with the N concentration of decomposing humus (Berg and Matzner 1997; Bringmark and Bringmark 1991; Bringmark personal communication). Thus, respiration rates of humus samples collected in a gradient over Sweden and kept under standard climatic conditions, showed a significant negative relationship to N concentrations in the humus ($r = -0.650$, $n = 13$, $p < 0.05$; Fig. 7.10; Berg and Matzner 1997). Nitrogen concentrations were in the range of 1.0–1.9 %, and such a variation in N concentrations in humus could be a natural phenomenon (Berg et al. 1999b) rather than a pollution-related one. In another study, in which humus was collected from sites across Europe, from the Arctic Circle to the Mediterranean, a highly significant, negative relationship between respiration and N concentration was found (Laskowski personal communication).

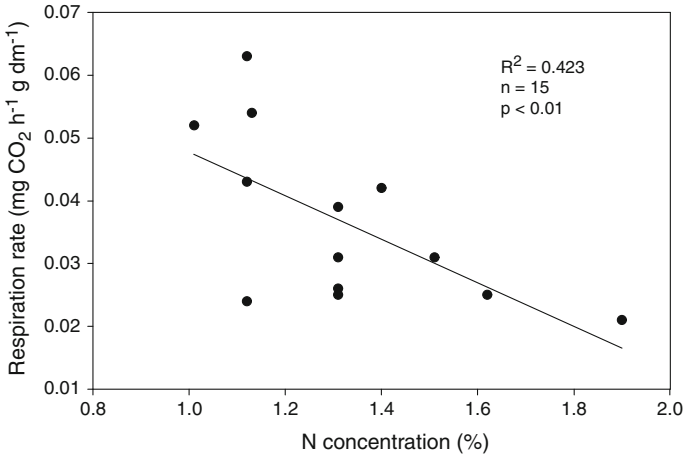

Fig. 7.10 A comparison between N concentration in humus (F and H layers) and CO_2 release rate from the same samples incubated under standard temperature and moisture conditions. Samples were collected in a gradient along Sweden. (Berg and Matzner 1997)

When investigating the literature on laboratory measurements of respiration rates from humus samples, we found both rates and the variation among studies to be very high (Berg unpublished). Thus, when recalculating amounts of CO_2 developed per hour or per day from a given ash-free sample to annual mass loss, the respiration rates often correspond between 10 and 100 % of the total humus mass per year (e.g., Persson et al. 2000), figures that do not agree with an accumulation of humus. We must conclude that such rates are not to be regarded as a quantitative measure of humus decomposition and cannot exclude that in some cases, the reported effects of rate-regulating factors may be in doubt.

Chapter 8
Decomposition of Fine Root and Woody Litter

8.1 Introduction

Most studies of litter decomposition in forests have focused on foliar litters because of their large amounts and relatively high nutrient contents. Foliar litter provides an important transfer of organic matter and nutrients to the soil, and the patterns of its deposition are temporally regular and spatially rather uniform. Woody and fine (small diameter) root litter can also contribute large amounts of organic matter to forest soils. Fine root litter inputs are highly variable across ecosystems, but in at least some ecosystems, they represent a transfer of organic matter and nutrients to the soil of the same magnitude as foliar litter. Woody litter is deposited sporadically in time and space. Its deposition may be trivial in managed forests.

Fine roots are variably defined, usually based on diameter, and represent a rapidly changing component of forest biomass. Fine root litter differs from woody litter in several key respects. They may comprise less than 2 % of the biomass present in a forest ecosystem, but they may contribute as much as 40 % of the annual production (Vogt et al. 1990). Fine roots and green leaves are among the most nutrient rich of plant tissues (Table 8.1). Furthermore, they have one of the highest surface area-to-volume ratios of any litter type. With all of these characteristics, we would expect fine roots to decay very rapidly, but that is not the case as will be discussed below.

According to Harmon et al. (1986), woody litter plays important but poorly studied roles in forest ecosystems. Woody litter includes stems, stumps, branches, twigs, and most roots, excluding those with a small diameter. These litter components enter the soil very erratically in space and time, often as a result of such sporadic events as strong wind, heavy snowfall, or freezing rain. Further, the tendency for the amount of woody litter fall to increase with stand age gives it a different pattern as compared to foliar litter. A single tree may fall as a result of a storm or death. The bulk of its biomass is concentrated along the bole and branches. The chemical and physical quality of this woody litter is quite different from foliar litters.

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7_8,

The amount of woody litter present in forests varies by two orders of magnitude from about 1 Mg ha^{-1} in dry tropical forests to 500 Mg ha^{-1} in old-growth coniferous forests in the Olympic Mountains in the Pacific Northwest of the United States (Agee and Huff 1987). However, most ecosystems fall into the range of 5–50 Mg ha^{-1} (Table 8.2). Woody litter often increases immediately after a harvest due to logging slash (McCarthy and Bailey 1997; Table 8.2). However, older managed stands can have less woody litter than do corresponding old-growth stands (Goodburn and Lorimer 1998; Table 8.2). Estimates have been made about the proportion of woody litter fall to foliar litter. Using the foliar litter fall as a reference in a mature Scots pine forest, the woody litter fall (cones excluded) made up c. 10 % and cones separately, c. 25 % (Berg et al. 1993d).

Not only is woody litter deposited unevenly, it comes in a huge array of sizes and conditions. Clearly, the diameter of the woody debris will influence surface area-to-volume relationships in a way that results in more rapid decay of smaller diameter pieces. Furthermore, wood can undergo extensive decay before falling to the ground. This could be due to pathogens on living trees or saprophytic organisms on snags. In contrast, a storm may blow over or break limbs from a living tree.

One of the most important aspects of woody litter in terms of its decomposition is its extremely low nutrient content. This means that organisms that consume wood must either consume very large quantities in order to extract sufficient nutrients or that the nutrients must come from outside the substrate. Such a low nutrient environment would be most suitable for organisms with low nutrient demands. Further, the lignin degradation by white rot, which often is suppressed by high N concentrations may be less inhibited (Sect 2.5.3; Chap. 3). A comparison of initial nutrient concentrations in wood, fine roots, and leaves is shown in Tables 8.1 and 8.3.

Table 8.1 Representative concentrations of nutrients in living leaves, wood and fine roots

	Concentrations as % of dry matter				
	N	P	K	Ca	Mg
Leaves[a]	2.28	0.19	1.45	1.26	0.29
Wood[a]	0.30	0.03	0.21	0.32	0.046
Fine roots[b] (0.6 mm)	2.00	0.10	0.23	0.21	0.05

For leaves and wood, values are averages for four species groups: European white birch, common oak, filbert, and European ash. For fine roots values are taken from a northern hardwood forest containing sugar maple, yellow birch, American beech, and red spruce

[a] Swift (1977) and [b] Fahey et al. (1988)

Table 8.2 Mass of dead wood on the ground in selected types of forest stands

Forest type	Location	Mass (Mg ha^{-1})
Coniferous stands—boreal and temperate		
Douglas-fir—hemlock[a]	Oregon/Washington, USA	500
Boreal fir-spruce[b]	Newfoundland, Canada	4–22
Rocky Mt. spruce-fir[c]	Colorado, USA	52
Ponderosa pine[d]	Colorado, USA	3–5
Deciduous stands—boreal and temperate		
Aspen[e]	Alberta, Canada	15–25
Southern maple[f]	Tennessee, USA	14
Northern hardwood[g]	New Hampshire, USA	21–30
Hemlock-hardwoods[h]	Wisconsin/Michigan, USA	16
Mixed oak[i]	Kentucky, USA	16–22
Southern beech[j]	New Zealand	300
Managed temperate stands		
Northern hardwood—even-aged[k]	Wisconsin/Michigan, USA	6
Northern hardwood—selection[k]	Wisconsin/Michigan, USA	15
Northern hardwood—old-growth[k]	Wisconsin/Michigan, USA	29
Appalachian hardwood 2 years[l]	Maryland, USA	55
Appalachian hardwood 25 years[l]	Maryland, USA	17
Appalachian hardwood 80 years[l]	Maryland, USA	19
Appalachian hardwood >100 years[l]	Maryland, USA	33
Tropical stands		
Tropical thorn woodland[m]	Venezuela	1
Tropical very dry[m]	Venezuela	1
Tropical transition[m]	Venezuela	3
Tropical moist[m]	Venezuela	18
Tropical low montane moist[m]	Venezuela	21
Tropical montane wet[m]	Venezuela	18

[a] Agee and Huff (1987)
[b] Sturtevant et al. (1997)
[c] Arthur and Fahey (1990)
[d] Robertson and Bowser (1999)
[e] Lee et al. (1997)
[f] Onega and Eickmeier (1991)
[g] Gore and Patterson (1986)
[h] Goodburn and Lorimer (1998)
[i] Tyrell and Crow (1994)
[j] McCarthy and Bailey (1997)
[k] Muller and Liu (1991)
[l] Stewart and Burrows (1994)
[m] Delaney et al. (1998)

Table 8.3 Concentrations of N, water soluble compounds, and AUR in wood and fine roots from some boreal and temperate tree species

Species	N (mg g^{-1})	Water-solubles	AUR
Coniferous wood			
Norway spruce[a]	0.39	37	271
White pine[b]	0.40	15	221
Coniferous fine roots			
Norway spruce[c]	3.5	210	330
Scots pine[c]	2.5	134	273
White pine[b]	9.3	135	253
Deciduous wood			
European beech[a]	0.92	35	228
Red maple[b]	0.90	22	125
Trembling aspen[a]	0.55	39	197
Silver birch[a]	0.64	26	195
Deciduous fine roots			
Black alder[d]	12.8	nd	254
Hybrid poplar[d]	9.4	nd	262
Sugar maple[b]	16.7	196	338

[a] Staaf and Berg (1989), [b] Aber et al. (1984), [c] Berg et al. (1998), [d] Camiré et al. (1991) *nd* not determined

8.2 Woody Litter Decomposition

8.2.1 Methods

8.2.1.1 Decay Classes for Coarse Wood (Logs)

The state of decay of logs is often categorized using decay classes. Decay classes are based on visual and physical properties of wood. Although different investigators have given somewhat different definitions to each decay class, this approach is widely used, and a general scheme for decay classes is given in Table 8.4. Much of the recent literature has used a five-stage progression of decay, designated as decay classes I through V. This concept was first articulated by Maser et al. (1979) for coniferous trees and has been recently adapted to deciduous trees by Pyle and Brown (1998). One of the problems with this system is that objects as large as logs do not decay uniformly. First, logs are composed of different quality substrates (e.g., inner and outer bark, sapwood, heartwood) each of which decays at a different rate and begins to decay after different lag periods (Schowalter 1992). Furthermore, a particular log may be invaded by fungi with different mechanisms for decomposing wood (Boddy et al. 1989) and thus may contain parts in several different decay classes (Pyle and Brown 1999).

Table 8.4 System of decay classes used in wood decay studies. Modified from Maser et al. (1979) and Pyle and Brown (1999)

Characteristic	Decay class				
	I	II	III	IV	V
Bark attached tightly	+	–	–	–	–
Wood not stained	+	–	–	–	–
Bark present, perhaps loose	+	∀	–	–	–
Twigs retained	+	∀	–	–	–
Wood solid, resistant	–	+	∀	–	–
Log surface may flake, fall into shreds	–	–	+	–	–
Log solid but decay clearly evident	–	–	∀	+	–
Logs easily broken into large pieces	–	–	–	+	–
Log easily crushed	–	–	–	+	∀
Log more than 85 % powdery	–	–	–	∀	+
Log shape oval to nearly flat	–	–	–	∀	+

+ Present; ∀ present or absent; – absent

8.2.1.2 Mass-Loss Rates: Percent Loss and Decay Constants (k)

Many reports of wood decay use a decay constant, calculated in the sense of Olson (1963), see Eq. (9.1). It can be calculated based on a single point, using Eq. (8.1).

$$k = \frac{-\ln\left(\frac{M_t}{M_0}\right)}{t} \tag{8.1}$$

where M_t is mass at time t and M_0 is initial mass ($t = 0$).

The decay-rate constant, k, can also be calculated using multiple points over time and fitting a linear regression to the line formed by the natural log of mass versus time. The slope of this regression line is $-k$. This latter approach is better than the single-point approach because it includes data taken over the course of decay. However, most litters, and especially wood, seldom decay at a constant rate and the use of k can thus be misleading (cf. Chap. 9). For example, Fig. 8.1 shows both percentage mass loss and the changing value of k during decomposition of logs. Whenever available, we present decomposition data as a percentage of the initial mass that is lost; however, many studies present k-values, and we report those also.

8.2.1.3 Estimating Mass Loss in Coarse Wood

Litter. Litterbags have been the dominant technique for studying foliar litter decomposition. For coarse wood, the sheer size and the long life expectancy of the log make litterbags inappropriate. Most studies have relied on density changes to estimate mass loss, though this approach is not without its own problems. Volume

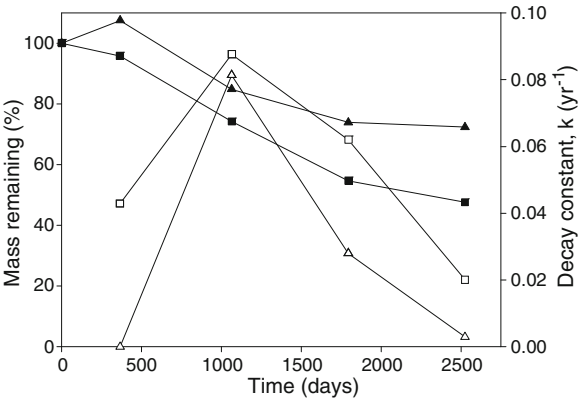

Fig. 8.1 Percentage of initial mass remaining and decay-rate constants (*k*, sensu Olson 1963) during each measured period for red pine and red maple logs incubated under a temperate climate in a red pine plantation and an adjacent mixed hardwood forest at Harvard Forest, Massachusetts, USA. *k*-values were calculated for each interval of the study. The figure indicates that the rate reaches a maximum in the 2nd to 4th year after which it declines. (■) Red maple % mass remaining (▲) red pine % mass remaining, (□) red maple *k*, (Δ) red pine *k*. (C. McClaugherty unpubl.)

displacement in water as a means of determining bulk density is commonly used, but it becomes less accurate as wood enters later stages of decay and loses its structural integrity. Further, bulk density measures do not account for losses due to fragmentation and removal by tunneling arthropods. The methods for studying woody detritus have been well summarized by Harmon and Sexton (1996).

Litterbags have been used to study the decay of wood chips (see below). This technique allows for a more direct comparison of wood with foliar litter, as a substrate, by eliminating the differences caused by the volume of the log.

8.2.2 Decomposition Rates versus Climate

Mass-loss rates of woody litter vary dramatically among climatic zones (Table 8.5) and among litter species. Yin (1999) has presented a very thorough compilation of woody debris decay studies. Temperature appears to be the most important climatic variable for large logs, at least in a wide range of tropical systems (Chambers et al. 2000), perhaps because the volume of the logs makes them able to buffer changes in moisture. In fact, too much moisture could suppress log decay by creating zones of low oxygen availability. However, the variation in decay rates among species within a single climate can be greater than the variation in a single species across a range of different climates. The differences can generally be attributed to substrate quality, though this term is somewhat hard to define for wood.

Table 8.5 Representative decomposition rate constants (k, year^{-1}, see Eq. 8.1) for large woody debris

Ecosystem	Location	k
Boreal coniferous[a]	S Norway	0.033
Boreal coniferous[b]	NW Russia	0.019–0.108
Temperate deciduous[c]	Tennessee, USA	0.086
Temperate deciduous[d]	Indiana, USA	0.018–0.045
Temperate deciduous[e]	New Hampshire, USA	0.096
Temperate mixed[f]	Minnesota, USA	0.042–0.080
Temperate mixed[g]	Michigan/Wisconsin, USA	0.021
Temperate coniferous[h]	British Coloumbia, Canada	0.022
Tropical evergreen[i]	Brazil	0.015–0.67
Tropical dry[j]	Mexico	0.008–0.615

[a] Næsset (1999)
[b] Harmon et al. (2000)
[c] Onega and Eikmeier (1991)
[d] MacMillan (1988)
[e] Arthur et al. (1993)
[f] Alban and Pastor (1993)
[g] Tyrell and Crow (1994)
[h] Stone et al. (1998)
[i] Chambers et al. (2000)
[j] Harmon et al. (1995)

It is possible that physical factors relating to wood structure, such as porosity, play a more important role in regulating decomposition than do different nutrient levels. Thus, in an experiment with trembling aspen and European beech wood sticks incubated for a year in the forest floor, the more porous aspen wood lost more than 50 % of its initial mass, while the less porous beech had a barely measurable mass loss (B. Berg unpubl.).

Mass-loss rates change over time as logs become more decayed. McClaugherty (unpubl.) has followed decay of red maple and red pine logs for 7 years in a temperate deciduous forest and an adjacent red pine plantation at the Harvard Forest (Fig. 8.1). The species decay at different rates, but both have similar patterns of decay. The decay during the first year was very slow (not measurable in red pine). The highest decay rates occurred in the interval between years 1 and 3. The decay rate then slowed in the subsequent periods. Schowalter et al. (1998) observed a similar phenomenon in oak logs, describing their decay with a two-phase exponential decay model. They suggested that a slower, third exponential decay phase would likely emerge as decomposition proceeded.

The kinetics of decay in coarse woody debris is complicated because different parts of the log may be undergoing attack by microbial species or communities with very different metabolic abilities. In the simplest sense, an entire log could be invaded by either white-rot or brown-rot fungi.

Smaller diameter woody debris has been less well studied. Erickson et al. (1985) compared the decay of logging residue in two diameter classes in a variety

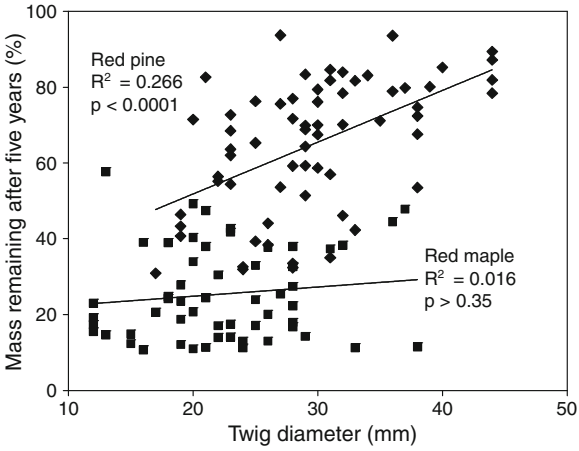

Fig. 8.2 Mass remaining after 5 years of field incubation of twigs (<5.0 cm diameter). Twigs were incubated in a mature red pine plantation or in a mixed mesophytic forest dominated by red oak and red maple. Study was conducted at the Harvard Forest (Massachusetts, USA). (◆) Red pine, (■) red maple. (C. McClaugherty unpubl.)

of temperate coniferous forest ecosystems in Washington State, USA. They found that smaller diameter (1–2 cm) twigs decayed much slower than did the larger diameter (8–12 cm) pieces and attributed this to the fact that smaller diameter fragments dried more quickly, thus suppressing decay. In their study, decay-rate constants (k) for small diameter slash ranged from 0.004 to 0.011, much lower than for most large or coarse woody debris (Table 8.5).

Twigs (<5 cm diameter) of red pine and red maple, tethered to nylon strings on the forest floors of a red pine plantation and a red maple—red oak forest, respectively, in Massachusetts, exhibited highly variable mass loss (Fig. 8.2, McClaugherty unpubl.). After 5 years, red pine twigs had lost considerably less mass (35.0 %) than had those of red maple (74.6 %). Diameter had no effect on mass loss from red maple twigs. A linear regression for pine twig mass loss versus diameter was significant ($p < 0.001$), but the R^2 was only 0.266.

8.2.3 Carbon Dioxide Release

Decomposition of wood has also been measured as CO_2 release or respiration. This method allows for more instantaneous assessment of C flux as compared to periodic mass-loss measurements. In a pair of studies, Marra and Edwards (1994, 1996) measured respiration from logs in decay classes I through III and V (they did not measure decay class IV), in a clear-cut and an old-growth forest on the Olympic Peninsula (Washington State, USA). As expected in this seasonal environment, respiration reached a maximum in summer and a minimum in winter. Variability was greater in the clear-cut, but overall, there was no difference between the clear-cut and old-growth forest. Species did differ, however, with western hemlock logs having higher respiration rates than those of Douglas-fir. This reflects the greater amount of inhibitory secondary compounds such as

tannins and extractable phenols found in the wood of Douglas-fir (Kelsey and Harmon 1989). The results are similar to other studies that have compared the decay of these two species (Graham and Cromack 1982).

8.2.4 Organic Chemical Changes

Studies of chemical changes during litter decay began in the early twentieth century. Among the early studies, Rose and Lisse (1916) described the chemical composition of fresh, partially decayed and 'completely' decayed Douglas-fir wood. 'Completely' decayed means that the wood has lost its structural integrity and would correspond to decay class V (Table 8.4). They noted the resistance of lignin to decomposition and suggested the possibility of connecting decayed organic matter and lignin residues to humic substances in the soil. Bray and Andrews (1924) demonstrated that different fungi acted differently on the cellulose and lignin of wood (cf. Chap. 3), with brown-rots acting only on cellulose. Using more recent technology, namely ^{13}C-NMR, Preston et al. (1990) characterized the chemical changes in decaying heartwood of Douglas-fir, western hemlock and western red cedar. They distinguished changes in the relative amounts of C in carbohydrates, lignin, aliphatic groups, and the sum of carboxyl plus carbonyl groups. Douglas-fir and hemlock wood followed the more classic pattern, with a rapid decline in carbohydrate-C to less than 10 % of original amount and an increase in the relative amount of lignin C. In contrast, western red cedar wood showed little change in its organic chemical composition, even though density had declined, and the physical structure had collapsed.

The loss of holocellulose dominates mass loss, at least during the initial stages of wood decay. Figure 8.3 shows the amounts of lignocellulose, lignin, and extractives remaining in wood chips of red maple and white pine during 42 months of decay on the forest floor of Black Hawk Island, Wisconsin, USA. Although red maple wood lost considerably more mass than that of white pine, both species exhibited similar patterns of mass loss and change in chemical composition. Mass-loss patterns were similar to those observed earlier: slow during the first year, faster during the second year, and then slower again in the third year.

8.2.5 Changes in Nutrient Concentrations

Woody litter contains relatively small amounts of nutrients, especially when compared to foliar and root litter (Tables 8.1 and 8.3). However, there is no clear agreement on the nature of nutrient dynamics in woody debris. Most investigators have found that decomposing wood accumulates some elements (e.g., N, P), retains some, and releases still others (e.g., K). Alban and Pastor (1993) studied

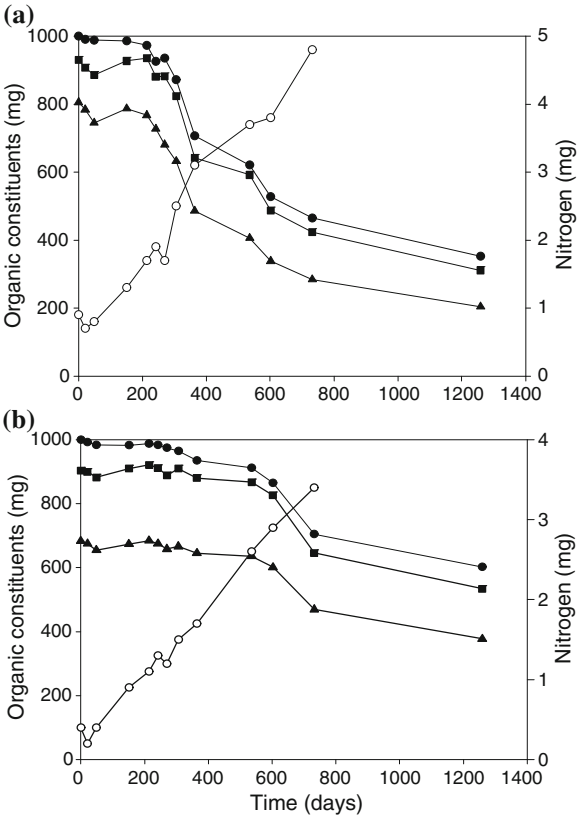

Fig. 8.3 Changes in amounts of some organic constituents and N over time in wood chips incubated in litterbags on the forest floor of a sugar maple forest on Black Hawk Island (WI, USA). Organic constituents are expressed as mg g^{-1} of initial material. Nitrogen is expressed in mg g^{-1} of initial material. **a** Red maple wood. **b** White pine wood. (•) Total organic matter; (■) lignocellulose; (▲) AUR; (○) total N. (C. McClaugherty unpubl.)

logs of aspen, spruce, red pine, and Jack pine that had decayed for 11–17 years and compared the amounts and concentrations of nutrients in the original logs with those in the decayed logs. The concentration of N increased by an average factor of 4.3 from 1,090 to 4,698 ppm. Concentrations of P also increased in all four species, with the average increase from 120 to 348 ppm, a factor of 2.9. Potassium concentrations remained about the same, with the average concentration increasing from 731 to 784 ppm. Concentrations of Ca increased from 2,225 to 5,784 ppm, and Mg increased from 206 to 504 ppm. Initial concentrations of all nutrients were higher in aspen wood than in that of the conifers, but the nutrient concentrations increased by a larger factor in the three conifer species. In a study of Sitka spruce and western hemlock, Graham and Cromack (1982) found that N accumulated (net transport into the wood) in western hemlock, but not in Sitka spruce, though the concentration of N increased in both species. Concentrations of other elements (P, Ca, Mg, K, and Na) did increase, but their amounts did not increase.

When comparing net movement of nutrients over the entire span of decomposition (all five decay classes) for Douglas-fir wood, Means et al. (1992) observed that N and K were lost, Ca and Mg were accumulated, and P and Na were

accumulated and then released, with no overall net change. In a northern hardwood forest, Arthur et al. (1993) examined the change in nutrients in logs that had been on the ground for 23 years following a clear-cut. They estimated that during that time, the logs had released, as a percentage of initial content, 31 % of N, 68 % of P, 77 % of Mn and between 86 and 93 % of Ca, K, Mg, and Na. At different stages of decay and for different nutrients, logs may be either net sinks or net sources of nutrients for the soil.

Krankina et al. (1999) measured the concentrations of 12 nutrients (N, P, K, Ca, Mg, Al, Cu, Fe, Zn, Na, B, and Mn) in decaying logs of Scots pine, Norway spruce and a birch species in northwestern Russia. They found that nearly all nutrients showed an increase in concentration as logs passed through decay classes III, IV, and V. The exceptions were K, which did not increase in pine and birch logs, and B, which did not increase in spruce and pine logs. Although concentrations of many of the elements increased, there was no net accumulation of nutrients over the course of decay, except for Al, which accumulated in wood of pine and birch, and Na, which was retained throughout decay.

N_2-fixation. With the low N concentration in wood, even low N_2-fixation rates could be important in influencing the N concentration of the wood during its decay. N_2-fixation has been noted in decaying logs and may be of importance in the N dynamics of wood decay. Using acetylene reduction to estimate the potential for N_2-fixation, Larsen et al. (1978) found that brown-rotted wood was more likely than white-rotted wood to support N_2-fixation and that there were differences between species, with Douglas-fir wood having higher rates. Jurgensen et al. (1984) and Griffiths et al. (1993) found that the N_2-fixation potential increased as decay proceeded. The amount of N_2-fixation in rotting wood is generally low, but potentially important to the N dynamics of the log (Larsen et al. 1982).

Fungal transport. Fungi that decompose wood can be important in transporting nutrients into or out of the decaying wood. Although the actual work of decay is done by hyphae penetrating the wood, nutrients are transferred to, and accumulated by, two particular fungal structures that are on or above the surface of the wood: rhizomorphs and sporocarps. Sporocarps are the fruiting bodies or reproductive structures of fungi, and they often appear on wood during the first decade of its decay. Their tissues are greatly enriched in nutrients compared to their woody substrate. Harmon et al. (1994) found that fungi had concentrations of N, P, and K that were 38, 136, and 115 times, respectively, as great as the concentrations in the logs on which the fungi were growing. This enrichment occurs largely by mycelial transport from the log and the surrounding environment into the sporocarp. Although small in mass, the fungi transferred measurable amounts of nutrients out of the logs and into the sporocarps, clearly against the nutrient gradient. The amounts of nutrients found in the sporocarps as a percentage of the total amounts initially present in the logs were 0.9–2.9 % for N, 1.9–6.6 % for P, and 1.8–4.5 % for K.

After fungi have decayed a substrate, they must eventually forage for new substrates, reproduce sexually, or perish. In many basidiomycetes, fungal hyphae can aggregate into cords or rhizomorphs and grow until they encounter suitable

substrate. The cords can form long-lived networks that have the ability to transport e.g. C and P over one meter (Boddy and Watkinson 1995). For both fruiting bodies and rhizomorphs, nutrients are moved and concentrated.

Although wood is low in nutrients, it demonstrates a wide variety of decomposition patterns. Because of its low nutrient status, its decay may be more dependent on the exogenous supply of nutrients. Given this wide diversity of nutrient dynamics, it is not at present possible to define a general conceptual model for changes in nutrient concentrations during wood decay. The variability among the example studies given above may be due to species, environmental and methodological differences.

8.3 Fine Root Decomposition

Estimates of root litter input are highly variable. Because of the difficulty of measuring root processes, few studies on fine root litter production have been done. Similarly, root decomposition is below ground and difficult to examine without significantly disturbing the system. Nevertheless, fine root litter may represent a large input of organic matter into ecosystems, and the decay of roots has implications for organic matter and nutrient dynamics in ecosystems.

It is important to note that fine roots are markedly different from larger diameter roots. The definition of fine roots cannot be made solely on the basis of diameter because species differ. Fine roots can be defined to include root tips and small diameter roots without secondary growth. Thus, fine roots have, in general, about the same diameter or less than root tips. In fact, root tips may be slightly larger in diameter due to mycorrhizal coverings.

8.3.1 Fine Root Litter

8.3.1.1 Amounts of Litter

In contrast to aboveground litter, it is not possible to directly measure fine root litter production. A variety of methods have been used to approach this problem. Several investigators have used sequential measurements of live and dead roots to develop estimates of production, mortality, and decomposition (Persson 1980; McClaugherty et al. 1982; Santantonio and Hermann 1985). This mass-balance approach assumes that decreases in living biomass are due to death, which is therefore litter production. Timing and frequency of sampling are important in this technique. Kurz and Kimmins (1987) analyzed this method using a computer simulation and found that the estimates were very sensitive to violations of the assumptions and that estimates could be either too high or too low.

Rhizotrons (direct viewing through underground windows or tubes, Hendrick and Pregitzer 1992; Burke and Raynal 1994) allow for direct observation, but some disturbance of the rooting environment is inevitable. Another method involving elemental budgets was proposed by Nadelhoffer et al. (1985) and developed further by Raich and Nadelhoffer (1989). In this technique, fine root production is estimated by using fine roots to 'balance' the nutrient budget.

With all these techniques (see review by Hendricks et al. 1993), we are still not able to precisely measure the transfer of fine root litter to the soil. Vogt et al. (1996) reviewed the literature and found 41 data sets that included estimates on below-ground litter transfer. The values were derived from different investigations, and the methods were not comparable. Nevertheless, the estimates for below-ground litter input, which is predominantly from fine roots, ranged from 100 g m^{-2} $year^{-1}$ in a northern hardwood forest in New Hampshire, USA, to 1,262 g m^{-2} $year^{-1}$ in a Pacific silver fir forest in Washington State, USA, with a mean of 436 g m^{-2} $year^{-1}$. These values are similar to the amounts of foliar litter fall.

8.3.1.2 Chemical Composition of Fine Roots

Fine roots have rather high AUR concentrations as compared to wood and foliage (Table 8.3), in the range of 25–50 % (Vogt et al. 1991). Nitrogen concentrations also tend to be relatively high, generally in the range of 1–2 %, especially as compared to wood (Tables 8.1 and 8.3), but other nutrients are less predictable. Because of their location in the soil, fine roots may accumulate elements such as aluminum (Dahlgren et al. 1991). Furthermore, the tips of many, if not most, fine roots in forests are mycorrhizal. The mycorrhizal association may have a direct influence on chemical composition due to the presence of fungal biomass, as well as indirectly, by influencing nutrient concentrations in the root environment and possibly influencing the decay resistance of the root (Harley and Smith 1983).

8.3.2 Mass-Loss Rates

Researchers have had considerable difficulty reconciling the apparent high productivity of fine roots in forest ecosystems with the apparent low decomposition rate of fine root litter in forests (Fahey and Hughes 1994). It is unclear whether the problem is due to errors in the production estimates, or the decomposition estimates, or both.

Litterbag methodology. Most studies of mass loss in fine roots have utilized a litterbag approach, though some have used sequential measures of dead and live root mass (see above). Litterbags are generally filled with excised live roots that are dried, killing at least a proportion of the attached mycelia. For foliar litter, the bags are generally filled with newly senesced material. Another difference in comparison with foliar litter is that fine root litter remains in the place where the

roots die, possibly already attached to, or at least closely surrounded by saprophytic microorganisms. Removing fine roots from this environment and placing them into a litterbag and reburying them is much more drastic than placing leaves or needles into litterbags. Nevertheless, litterbags continue to be used, and so far, there have been no definitive studies that show if or how much litterbags modify the decay of fine roots. Realizing that fine root decay studies are subject to a rather large and uncertain amount of error, we will nevertheless proceed to summarize some of these studies.

Intact soil core methodology. Soil cores are harvested, ideally for one tree species. To decrease the variability, they may be sampled at a predetermined distance from the tree. The intact cores are transferred to plastic pipes and inserted into the soil for different time periods. At harvest, the fragmentation may be less if the cores are soaked in water. The residual fine roots are sorted out, removed, and sorted into size class. After drying, the remaining mass is compared to roots from cores that not were incubated (e.g., Dornbusch et al. 2002; Sun et al. 2012).

Studies on fine root mass loss. Selected first-year mass losses (%) for a variety of fine roots are given in Table 8.6. In boreal forests, first-year mass loss ranged from 19 to 40 %, with much of the variability due to climate (Berg et al. 1998). One study from Puerto Rico compared two species, Sierra palm and Tabonuco, a tropical hardwood tree. The roots from the hardwood tree almost completely disappeared after 1 year, while the palm roots lost only 37–43 % (Bloomfield et al. 1993). In this case, climate was similar, so the differences between the two species were most likely due to differences in chemical composition.

Decomposition of fine roots of sugar maple and white pine roots was followed in a 10-year litterbag study in a temperate sugar maple forest on Black Hawk Island, Wisconsin, USA (McClaugherty unpubl.; Fig. 8.4). After 10 years, sugar maple fine roots had lost 56.5 % of their initial mass, and white pine fine roots had lost 66.4 %. White pine roots lost more mass than sugar maple roots during their first year of decay. After that, decay rates remained constant. This illustrates again that relying on first-year mass-loss rates to predict longer term decomposition may be incorrect.

Using the two species Chinese birch and Korean pine, Sun et al. (2012) made a comparison of the two methods litterbag and intact cores and found no difference in litter mass-loss rate. Further, they found that the high initial rate decreased and that the litter entered a very slow phase, which may indicate a limit value.

*Factors that influence fine root decay rate*s. Silver and Miya (2001) collected and analyzed 176 data sets on root decomposition. Their analysis included broadleaf, coniferous and graminoid roots, and sites with latitudes ranging from 4°N to 66°N. Using a stepwise multiple regression, they found that AET, root Ca concentrations, and C-to-N ratios accounted for 90 % of the variability in early stage root decay rates (*k*-values). They concluded that, on a broad scale, root chemistry was the primary determinant of root decomposition rates, with secondary roles for climate and environmental factors. Looking at fine roots only (defined here as <2 mm in diameter), conifer roots decayed much more slowly than broadleaf roots. It is noteworthy that their results show a greater importance

Table 8.6 First year mass loss of fine roots in a variety of ecosystems

Species/system type	Diameter (mm)	Mass loss 1st year (%)	Comments
Boreal			
Scots pine[a]	2–3	19.3–40.9	Sweden, latitudinal climatic transect, 18 sites
Norway spruce[a]	2–3	27.4–39.7	Sweden, latitudinal climatic transect, 12 sites
Lodgepole pine[a]	2–3	29.8–35.3	Sweden, 4 sites
Norway spruce[b]	<1	23.5	Estonia
Norway spruce[b]	1–2	21.6	Estonia
Temperate			
N. hardwoods[c]	<1	17	White Mountains, New Hampshire, USA
N. hardwoods[d]	<0.5	30	Adirondacks, New York, USA
N. hardwoods[d]	0.5–1.5	17.4	Adirondacks, New York, USA
N.hardwoods[d]	1.5–3.0	20.9	Adirondacks, New York, USA
White pine[e]	<3	21.5	Sugar maple forest, Black Hawk Island, USA
Sugar maple[e]	<3	15.4	Sugar maple forest, Black Hawk Island, USA
Tropical			
Tabonuco[f]	<2	99.8–99.9	Puerto Rico, tropical montane rain forest
Sierra palm[f]	<2	36.7–43.4	Puerto Rico, tropical montane rain forest

[a] Berg et al. (1998)
[b] Lõhmus and Ivask (1995)
[c] Fahey et al. (1988), northern hardwoods mean for sugar maple, American beech, yellow birch, and red spruce
[d] Burke and Raynal (1994), northern hardwoods sample from forest dominated by sugar maple, American beech, yellow birch and red maple
[e] Aber et al. (1984)
[f] Bloomfield et al. (1993)

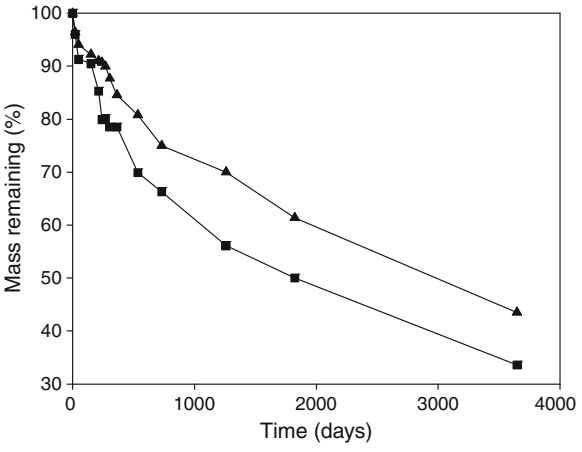

Fig. 8.4 Mass remaining in fine roots incubated in litterbags over a 10-year period in a sugar maple forest floor on Black Hawk Island (WI, USA). (▲) sugar maple; (■) white pine (C. McClaugherty unpubl.)

of chemistry than climate, which is in contrast to what has been observed for most foliar litter species (cf. Chap.7). Silver and Miya (2001) suggest that because roots are buried in the soil, they are more buffered from climatic conditions.

Studies in boreal and temperate forests have also indicated that the chemical composition of fine roots influences their decay rates. For example, Camiré et al. (1991) noted that fine root decay rates appeared to be inversely related to their initial N concentrations. They based this on their own findings with black alder and hybrid poplar roots and in comparison with results of Berg (1984) and McClaugherty et al. (1984).

A study of coniferous root litter was undertaken in a climatic transect across a region ranging from the Arctic Circle (66°N) in Scandinavia to Berlin (52°N) in NE Germany. The study was carried out in coniferous monocultural forests. Berg et al. (1998) used data from 37 sites at which root litter of three coniferous species, namely Scots pine, lodgepole pine, and Norway spruce, had been incubated.

When they combined all data, the linear relationships to climatic factors and chemical composition were poor. In spite of the considerable climatic difference between sites, there was no strong relationship between any climatic variable and the first-year mass loss (range 17.0–40.9 %). For the first-year mass loss, the average annual temperature (MAT) was the most rate-regulating factor for all litter species combined, with an R^2_{adj} of 0.186. Substrate-quality indices had a weak influence. Thus, for the whole region, AUR concentration was significant with an R^2_{adj} of 0.142. When combining MAT and AUR concentration, the R^2_{adj} value became 0.262.

For pine and spruce litters as separate groups, the R^2 increased, but still, the factor MAT dominated. For the pine group, the R^2_{adj} reached a value of 0.346. Also, the N concentration in the fresh pine root litter gave a significant relationship ($R^2_{adj} = 0.232$).

For the root litter of Norway spruce, the average temperature in July was the strongest rate-regulating climatic factor with a value for R^2_{adj} of 0.381. A combination of temperature in July and the initial litter P concentration gave an R^2_{adj} value of 0.713, thus explaining about 71 % of the variation. Temperature in July and initial Ca concentration explained about 45 %. Berg et al. (1998) concluded that the decomposition of spruce root litter was more dependent on energy input than that of pine and that for both groups, energy was the main rate-regulating factor. However, fine root decay is perhaps less sensitive to temperature changes than is foliage litter decay (Silver and Miya 2001).

8.3.3 Changes in Chemical Composition

Fine roots are chemically similar to foliar litter, so one would expect that their organic chemical composition would change during decay with a pattern similar to

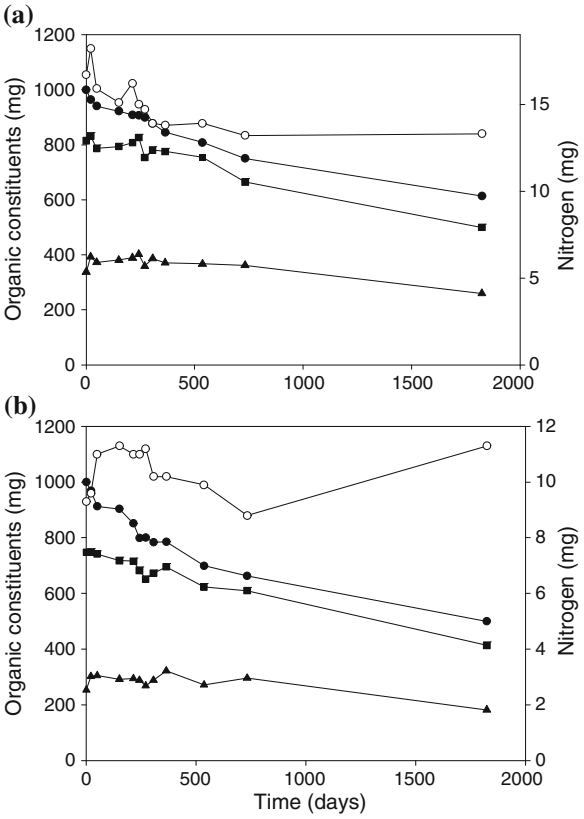

Fig. 8.5 Changes in amounts of some organic constituents and N over 5 years in fine roots incubated in litterbags on the forest floor of a sugar maple forest on Black Hawk Island (WI, USA). Organic constituents and nitrogen are expressed as mg g^{-1} of initial material. **a** Sugar maple fine roots. **b** White pine fine roots. (•) Total organic matter; (■) lignocellulose; (▲) AUR; (○) total N. (C. McClaugherty unpubl.)

that for foliage litter. Although many studies have reported initial chemical composition of fine roots, few have followed the chemical composition during decay.

The changes in chemical composition of fine roots during 5 years of decay in litterbags in a temperate sugar maple forest (Black Hawk Island, WI, USA) are shown in Fig. 8.5 (McClaugherty unpubl.). For white pine and sugar maple, most of the mass loss during the first year could be explained by the loss of soluble substances. Subsequent losses were largely due to a decline in polymer carbohydrates. Lignin declined rather slowly, beginning after the first year of decay.

The concentration of N in the root litters was initially high, 16.7 and 9.3 mg g^{-1} in sugar maple and white pine, respectively. Nitrogen contents varied during decay, but there was no clear pattern as is generally seen for foliar and wood litters (Fig. 8.5).

Chapter 9
Models that Describe Litter Decomposition

9.1 Introduction

Models serve a variety of functions for ecologists, but all ecological models are abstract representations of biological systems expressed in either mathematical or symbolic terms. Models may serve as hypotheses to be tested, or as tools to predict behavior of the ecosystem or one or more of its subsystems. In a concise review, Moorehead et al. (1996) distinguished three groups of decomposition models.

Some models are empirical and most of these are statistically based. For example, regression models relate parameters in a system. These models are useful for identifying or indicating the strength of hypothesized relationships, but cannot, by themselves, reveal causality. Empirical models are often useful for prediction, but they are, or at least should be, limited to the range of data from which they were developed. Extrapolation, however tempting, can be misleading.

Mechanistic models are another general class of models. They are often analytical in nature, using a system of equations to describe complex processes. Such models have proven very useful for gaining insight into ecosystem behavior, and for developing and testing general theories.

A third group of models is simulation models. They are created to simulate the behavior of a system, in a way that allows researchers to manipulate initial conditions, or other aspects of the model, to investigate potential outcomes. Simulation models may use a combination of mechanistic and empirical components to achieve their goal. Ecosystem simulation models often include a decomposition submodel.

In reality, models are often hybrids of these types. Empirical or data-based models may be based on a mechanistic understanding of processes. From a different perspective, theoretical (theory-based) models can be made more specific by validation with experimental data, and by using data to determine parameters. Simulation models often use such hybrids to enhance their ability to predict.

One of the challenges facing those who model decomposition is the large number of factors that influence the rates and patterns of litter decomposition. Thus, a single model or a relatively simple approach would not likely give a generally applicable description of the decomposition process. Factors that influence decomposition can

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be highly interactive, variable, and even hard to measure. These factors include microbial ingrowth, climate, variation in weather between years and different levels of nutrients, heavy metals, and lignin/AUR. Considering the complexity of the decomposition process, we should expect a set or system of functions, each specific for different litter types and conditions. Such a set of functions in relation to litter type and ecosystem remains to be established. In this chapter, we simply describe empirical functions that have been found to fit particular types of litters.

The concept of 'kinetics' for litter decomposition is not used here in the same way as it is for enzymatic or chemical reactions, for which there are well-defined systems with, for example, zero-order, first-order, or second-order reactions. Rather, the mathematical descriptions of the litter decomposition process have used functions that simply fit to, and describe the process, as well as possible. These fits are sometimes related to short-term decomposition, covering just part of the process, often less than 50 % mass loss. The models describe the decomposition as regulated by the sum of different effects on the decomposition process. Effects that are often used in these models are litter chemical composition, soil or site richness and variation in climate over the period of incubation.

There are, of course, several mathematical functions that may be used to describe the litter mass-loss process, alternatively the change in remaining amount (Howard and Howard 1974), but the models we present here have been the most commonly used. The most widely used mathematical model—the single exponential model (Jenny et al. 1949; Olson 1963)—is often used for very early stages of litter mass loss, but frequently unable to fit observations from later phases of decomposition (Eqs. 9.1 and 9.2). A slightly more complex model uses a double exponential with two decay rate constants. These two decay constants can relate to two different components of litter, or to two different phases of decay (Lousier and Parkinson 1976) (Eq. 9.3). A further development of the idea that it is necessary to use differing rates for different substrate-quality compartments is the triple-exponential model (Couteaux et al. 1998). This model divides litter into three substrate-quality components, each with a different decay rate, and estimates separate rate constants for each. With the different rate constants that are produced from this model, it has been possible to estimate the potential decomposition rates for very late stages.

A different approach is represented by the models that allow us to estimate and quantify a stabilized fraction of litter. There are different functions that may be used for this, and we have selected two that have been applied to larger sets of decomposition data. One (Eq. 9.5) is based on an asymptotic function that estimates the decomposition rate as the derivative of the function at each point of the graph, and ultimately reaches an asymptote, which commonly has been observed at a level between 50 and 100 % mass loss. An alternative function is based on the single exponential (Eq. 9.1) to which an asymptote has been added (Eq. 9.7). We will discuss both functions.

Investigators working from a mechanistic perspective have proposed general models that could also lead to an asymptotic function. Among the first was Carpenter's (1981) model. His model was based on the idea that litter constituents could be placed on a continuum of decomposability. Furthermore, the model

allows that during the decay process, particular components could be transformed into substances of either higher or lower decomposability. Carpenter's model produced declining decay rates and has provided improved fits to the decay data for aquatic vegetation.

Ågren and Bosatta (1998) presented a mechanistic model that considers the continuing change in the quality of litter during its decomposition. The model has been validated with empirical data (Joffre et al. 2001) and has been used to predict temperature responses of organic matter in coniferous forest soils (Hyvönen et al. 2005). These models and their applications are helping to minimize the gap between empirical and theoretical studies in the ecology of decomposition.

In this chapter, we focus on empirical models, though as stated above, the best empirical models have a mechanistic foundation. In practice, different types of models may be used for the same dataset, and the fit of theoretical to observed data will give different levels of statistical significance. However, the utility of a given model as a predictor is dependent not only on a statistical significance of the fit, but also on the causal relationships that support the specific model. We discuss and develop this in Chap. 10, asking what the models may be used for and what factors that may determine whether a given litter will follow a single exponential or an asymptotic model. In the present chapter, we present a group of regression models that appear to fit to most foliar litters.

9.2 Three Commonly Used Models

The models found in the literature may be divided into two main categories. However, considering the development in the last decade, such a division becomes somewhat artificial and we use it for the purpose of our discussion and presentation of them. Measured data normally determine what mathematical function that is applicable and often enough a given dataset fits to different models. The division we make here is based on the types of function.

The first group of models comprises those that describe the complete decomposition of the litter. More specifically, they are based on the assumption of complete degradation of the whole litter. This assumption, in turn is based on fixed rates. Similar models with two or three components have been developed (Lousier and Parkinson 1976; Couteaux et al. 1998).

Sometimes, the ash is subtracted from litter mass, for example at high concentrations (Sect. 2.3), and the model is applied onto the organic matter only (Faituri 2002). This subtraction of ash is important irrespective of what model that is being used, giving focus onto the organic matter.

A second group of models is based on the assumption that part of the litter is decomposing at an extremely low rate or not at all. There are different functions used to describe this and we present two. In support of these models, litter may have been analyzed for organic-chemical components of different stabilities as well as for nutrients. For example, if two main groups of organic matter are

Table 9.1 Some models used to describe the decomposition of litter

Formula	Comments	Characteristic	Reference
$M_t = A + Br^t$	Asymptotic	Leaves a residual	Howard and Howard (1974)
$L_t = m(1 - e^{-kt/m})$	Asymptotic	Leaves a residual	Berg and Ekbohm (1991)
$M_t = M_0 e^{-kt} + S$	Asymptotic	Leaves a residual	Harmon et al. (2009)
$M_t = M_0 e^{-kt}$	Single exponential	Leaves no residual	Jenny et al. (1949), Olson (1963)
$M_t = Ae^{-k_1 t} + Be^{-k_2 t}$	Double exponential	Leaves no residual	Bunnel et al. (1977), Lousier and Parkinson (1976)

degraded at very different rates, these degradation rates are estimated separately for each component. We discuss this in Chapter 10. Mathematical formulae for examples of these models are given in Table 9.1.

With regard to the litter types for which these models are applicable, we can distinguish two main classes: foliar and non-foliar litters. The above models have been applied primarily to foliar litter. The two major types of non-foliar litter are wood and roots. For wood, a critical characteristic is the extremely low nutrient concentrations, especially that of N (see Chaps. 4 and 8), that may change the decomposition pattern. We give attention to wood and root decomposition in Chap. 8. In the present chapter, we intend to focus on models that describe decomposition of foliar litter.

9.3 Models

9.3.1 Single Exponential

This model, first proposed by Jenny et al. (1949), and elaborated by Olson (1963), is an equation for first-order kinetics, the same as for radioactive decay. A basic condition for applying this equation is that the process runs at the same rate (constant fractional rate), irrespective of the amount of material left at any given point in time, and that one component ('unified chemical composition') is considered as active in the process.

The formula may be written (Wieder and Lang 1982):

$$M_t = M_0 e^{-kt} \tag{9.1}$$

and is often used in this form

$$\ln(M_t/M_0) = -kt \tag{9.2}$$

In these and subsequent equations, M_0 is the initial mass, M_t is the mass at a certain time, t, and k is the decay rate constant. The single exponential model is often used for predictive purposes, based on the assumption that the decomposition

rate is constant and that all material is decomposed. The 'half time' and 'mean residence time' of litter are also calculated, although the validity of this function in any specific case is open to question. Aber et al. (1990) suggested that this model works reasonably well for a variety of litters until only 20 % of initial mass is remaining (cf. Fig. 9.1). Because of its relative simplicity and its reasonably good fit for early stage of decay, this model is widely used (Gholz et al. 2000).

9.3.2 The Double Exponential

The double exponential model is a development of the single exponential and is based on the assumption that the litter substrate has two main substrate-quality components with different decomposition rates. Its construction is simply an addition of two factors each defining a part of the litter substrate.

$$M_t = Ae^{-k_1 t} + Be^{-k_2 t} \tag{9.3}$$

In this equation, t is time, and k_1 and k_2 are rate constants for quickly and slowly decomposing fractions of the litter. The amount of each fraction is given by A and B, respectively. Also in this case, the assumption is that the substrate is completely decomposed, initially at a higher rate and later by a lower one. The model appeared for the first time in the literature from the International Biological Program (IBP) Tundra Biome (Bunell et al. 1977), and in a paper by Lousier and Parkinson (1976) describing the decomposition of aspen leaf litter.

9.3.3 Asymptotic Models

We have described (Chaps. 2 and 6) that for several litter types, decomposition proceeds progressively more slowly, and may even approach zero, as decay progresses, which is most likely due to the retarded degradation of AUR, which in its turn may be related to the initial concentrations of Mn and N (Sect. 2.5) . Howard and Howard (1974) found that the amounts remaining after decomposition of some litter types approached a minimum level. They found that the model which best described this process was an asymptotic nonlinear model with three parameters: A, B, and r.

$$M_t = A + Br^t \tag{9.4}$$

M_t is the percentage of remaining litter mass, t is time in days, A and B are variable parameters, and r is an expression for the decomposition rate. By definition, the sum of A and B should be equal to 100 %, resulting in only two free parameters. By making a slight parameterization ($m = B$ and $k = B \ln r$), Berg and Ekbohm (1991) arrived at the following nonlinear model that they found more feasible to use (Fig. 6.3):

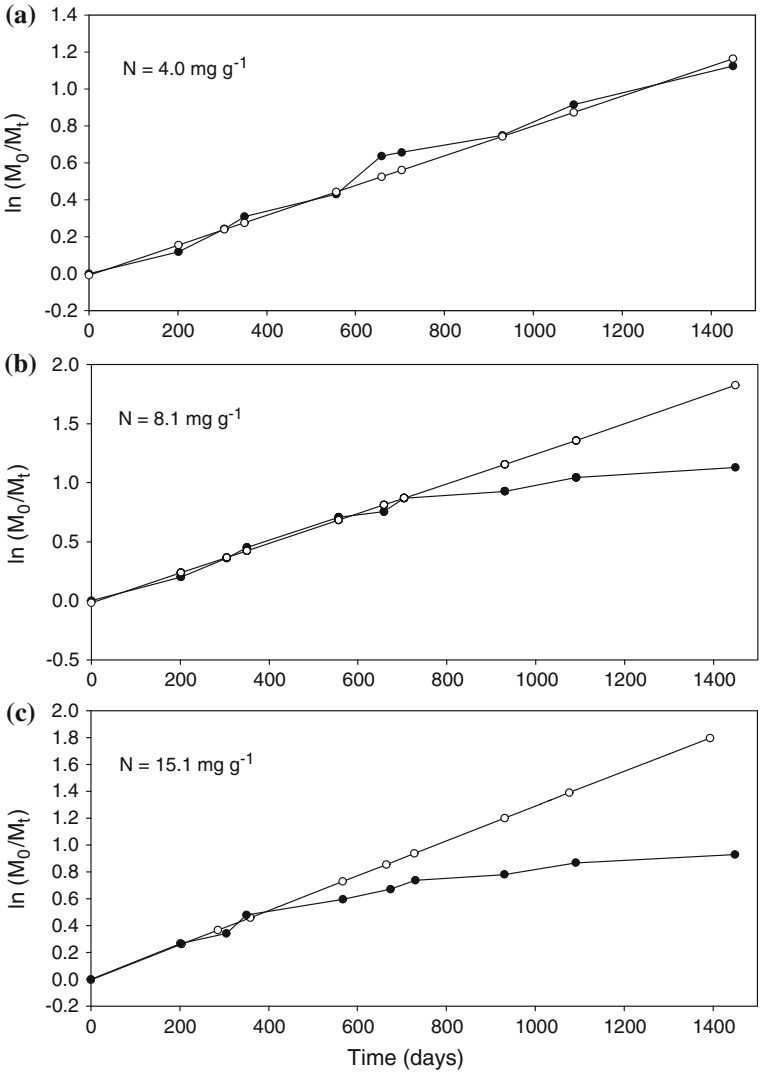

Fig. 9.1 Application of the single exponential model (constant-fractional-rate model) for Scots pine needle litter of three different nutrient (N) levels. On each plot, one line is estimated using all available data, specifically litter mass-loss values from 0 to c. 66–70 % for litter of different initial N concentrations (●), and the other is an extrapolation of the fractional rate as estimated for the early stages (◯), see Table 9.2. **a** For natural litter from a nutrient-poor plot, the rate was rather constant as seen in the comparison of the two graphs. **b** At a higher nutrient level (N concentration 8.1 mg g^{-1}), deviation from a constant rate starts at c. 58 % litter mass loss. **c** At an even higher nutrient level (N concentration of 15.1 mg g^{-1}), a deviation starts even earlier, at c. 38 % litter mass loss (Berg unpubl.)

$$L_t = m(1 - e^{-kt/m}) \tag{9.5}$$

where L_t is the accumulated mass loss (in percent), t is time in days, k is the decomposition rate at the beginning of the decay, and m represents the asymptotic level that the accumulated mass loss will ultimately reach, normally not 100 % and often considerably less (cf. Fig. 9.2). The k of this function is the derivative of the function at $t = 0$ and should not be directly compared to rate constants estimated with other models.

Model 9.5 gives a limit value using values for accumulated litter mass loss. However, the equation may be adapted to remaining mass:

$$M_t = m + (1 - m)e^{-kt/m} \tag{9.6}$$

in which M_t is remaining mass at time t, and m is the limit value given as percentage remaining mass.

A further equation has been proposed and applied, mainly after the Long-Term Intersite Decomposition Experiment Team (LIDET; Harmon et al. 2009; Currie et al. 2010). This equation is based on Eq. 9.1 and an asymptote is added:

$$M_t = M_0 e^{-kt} + S \tag{9.7}$$

where M_t is the remaining mass at time t, M_0 is initial mass, S is the asymptote, and k is the decomposition rate constant. In contrast to models 9.5 and 9.6, the intercept of eq. 9.7 is not zero. Thus, restrictions may be wanted for the intercept, for example, that the intercept falls between 95 and 105 % of the original mass (cf. Harmon et al. 2009).

The asymptote as estimated with these functions should not be regarded as an asymptote in a strict mathematical sense, but rather as a practical limit for decomposition separating a more readily decomposed part of the litter and one that is estimated not to 'decompose.' However, the fact that we may measure/estimate a low or no rate does not mean that the fraction defined by an asymptote (limit value) is completely stable. We may rather expect a potentially resistant fraction, with a resistance that may depend on litter type, its chemical composition as well as environment (Chap. 10).

9.4 Type of Model and Some Dominant Influencing Factors

9.4.1 Some Aspects of Litter Chemical Composition

We may illustrate the use of three models on a few examples of litter within the same species but with varying chemical composition (Table 9.2; Figs. 9.1 and 9.2).

Table 9.2 A comparison of k values estimated using the constant-fractional-rate model given in Eq. (9.2) (Olson 1963), for an early stage (m.l. < 40 %), for a late stage (40 % < m.l. < 70 %), and for early and late stages of decomposition combined (m.l. < 70 %).R^2 values within parenthesis. Using the asymptotic model and mass-loss values for both stages combined (Eq. 9.5), the initial rates and limit values were estimated. All litter types compared are Scots pine needle litter with different nutrient levels. Please note that the magnitudes of the k values (B and C) and the initial rate (D) are not comparable. *A* Litter type and initial composition. *B* Single exponential model—all data combined. *C* Single exponential model—two phases. *D* Asymptotic model. (Berg unpubl.)

A. Litter type and composition		Initial concentration [mg g^{-1}]	
Designation	Litter/treatment	N	P
1	Brown/unfertilized	4.0	0.21
2	Brown/unfertilized	4.4	0.32
3	Brown/fertilized 40 kg N/year for 6 years	4.4	0.3
4	Brown/fertilized 80 kg N/year for 6 years	7.0	0.34
5	Brown/fertilized 120 kg N/year for 6 years	8.1	0.42
6	Green	15.1	1.31
B. Single exponential model—all data combined			
Designation	m.l. < 70 %, n = 10–12		
	k values [$year^{-1}$]	Intercept	
1	0.2949 (0.980)	0.0128	
2	0.3103 (0.936)	0.0829	
3	0.3019 (0.948)	0.0790	
4	0.3179 (0.959)	0.0806	
5	0.2964 (0.911)	0.1365	
6	0.2602 (0.960)	0.1382	
C. Single exponential model—two phases			
Designation	m.l. < 40 %, n = 4–5	m.l. > 40 %, n = 5–6	
	k values [$year^{-1}$]	k values [$year^{-1}$]	
1	0.2949 (0.976)	0.2303 (0.984)	
2	0.3989 (0.953)	0.2029 (0.936)	
3	0.3880 (0.966)	0.2059 (0.969)	
4	0.4073 (0.977)	0.2267 (0.989)	
5	0.4592 (0.980)	0.1723 (0.928)	
6	0.4709 (0.991)	0.2025 (0.980)	
D. Asymptotic model			
Designation	Initial rate [% day^{-1}]	Limit value [%]	
1	0.0768	93.2	
2	0.1087	78.2	
3	0.1055	77.4	
4	0.1112	78.0	
5	0.1299	72.2	
6	0.1360	68.0	

In some cases, the retardation of decomposition can be related to the initial concentrations of specific nutrients/components. An example shows a clear effect of different nutrient levels on mass-loss rates as described by a single exponential. Six sets (Table 9.2) of Scots pine needle litter all have highly significant fits to the

single exponential model when all mass-loss data are used, encompassing 10–12 samplings and up to 70 % mass loss. All six sets have similar k values, ranging from 0.26 to 0.32 year^{-1}. This indicates similar overall rates for decomposition, with no trend in the k values, even though there is a clear trend in litter chemical composition. For example, N increases from 4.0 to 15.1 mg g^{-1} and P from 0.21 to 1.31 mg g^{-1}. Further, there is no relationship between nutrient levels and k values. The approximation that is made when using all data results in a consistently higher intercept as the linear regression adapts to the datasets (Table 9.2B). The increasing curvature with increasing nutrient levels is seen in Fig. 9.1. Here, we use the terms 'nutrient' and 'nutrient rich' in a more traditional sense, namely rich in main plant nutrients such as N, P, S, K, Ca, Mg, and we have used mainly N concentration to illustrate that. We will develop this in Chap. 10.

Comparing these results to those obtained when the datasets are split into an early phase with mass loss <40 %, and a later phase with mass loss >40 % but <70 % reveals greater variability among the six sets. The separation into phases made it possible to distinguish trends in the data and showed that k values for high-nutrient litter with mass loss <40 % are almost double those of low-nutrient litter. For brown litter, the initial rate (k, Eq. 9.3) is related to the initial concentration of nutrients such as P ($R^2 = 0.950$; $n = 5$). When calculating the rate for later stages only (mass loss >40 %), the rates are much lower than in the early phase (Table 9.2) and no trend is seen. Thus, splitting the single exponential into two phases may help us to resolve the process, and we may uncover large differences in rate between early and late phase of decomposition (Table 9.2). This example also indicates the limitations of the single exponential model. Such increasing intercepts will also be seen using Eq. 9.7. One approach is that taken by Harmon et al. (2009) to set restrictions on the intercept and reject the function when the intercept falls outside set borders, in that case 100 ± 5 %.

Figure 9.1 shows an example with three sets of Scots pine needle litter with different levels of nutrients, and we have compared the pattern of the first-order kinetics graphs to the initial concentrations of N. Fig. 9.1a shows a needle litter with low initial concentration of N (4 mg g^{-1}), one line shows the observed values for $ln\ (M_t/M_0)$ for this litter, and the other the constant fractional rate extrapolated. The two lines clearly cover each other, and there is no trend toward a retardation of the decomposition rate. Figure 9.1b shows a litter with an initial N concentration twice as high. We can see that the calculated function and the measured values start deviating after c. 700 days of incubation (at c. 58 % mass loss). For a set of needle litter with almost four times as high an initial N concentration (Fig. 9.1c), the deviation begins even earlier, namely after c. 400 days of incubation (c. 38 % litter mass loss). For the two further nutrient (N)-rich litter, there is a clear deviation from the single exponential model.

There is thus a clear deviation from the constant-fractional-rate model with increasing nutrient levels. The reasons for this could be a higher initial rate in the early stages, namely with increasing concentrations of N and P, which would be the effect of a limiting nutrient. There is also a rate-retarding effect on decomposition in the later stages, an effect that likely is related to the degradation of

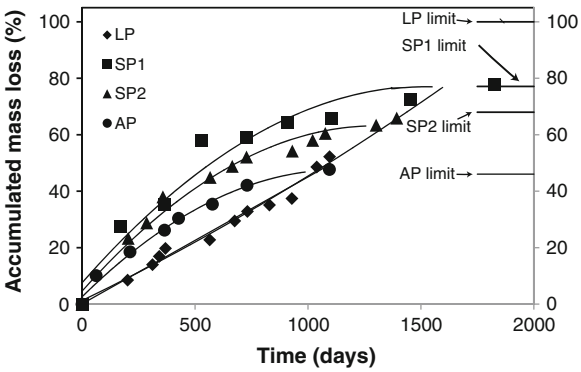

Fig. 9.2 Application of the limit value model (Eq. 9.5) to needle litter of pine spp. at different levels of Mn and N. A. Lodgepole pine. B. Scots pine. C. Scots pine. D. Aleppo pine. Data from Berg et al. (2010).

AUR. We discuss several alternatives to this retardation in Chap. 10. It is likely that more than one effect is active, resulting in lower rates in late stages. As a general observation—but without causality—the higher the nutrient (N) level the larger the deviation from a single exponential.

The decomposition of the litters discussed above may be described by an asymptotic function giving different limit values (Eq. 9.5) (Table 9.2). We have applied an asymptotic function onto four sets of pine litter data using Eq. 9.5, obtaining a set of limit values (Fig. 9.2). We may see that the functions follow the data and give different values for k and for the asymptote. The higher initial rate for a nutrient-rich litter gives a corresponding k value, and the limit value may be related to initial Mn concentration (Sect. 10.3.2; cf Fig. 10.1).

For what litter types would the constant-fractional-rate model be valid? The model fits well to the most 'nutrient-poor' litter (Table 9.2D, Fig. 9.1a). Although the fit is based on empirical findings, we may still speculate in that the nutrient levels play a role as was suggested. The mass-loss graphs for these litter types may be described by an asymptotic function that clearly indicates that the rate decreases to become close to zero. The fits for asymptotic models to the six sets of Scots pine needle litter are all highly significant, indicating that the model can describe the decreasing rate of the litter decomposition. The model also incorporates the extremely slow decomposition in the very late stages (Table 9.2D). The example above dealt with needle litter from Scots pine only. When applying the same comparison over some different litter species of different nutrient richness, we obtained about the same result as that shown in Fig. 9.1. We have extended this discussion in Chap. 10, referring to causality in litter chemical composition and discussing further litter species.

Different models may be applied to the same datasets with varying degrees of fit. One point in choosing a model is how far the decomposition pattern will be described. The technique of measuring litter decomposition as remaining amount or mass loss may allow the decomposition to be followed until c. 60–80 % accumulated mass loss, or until the process has come to a halt, which for some litter types may take place even earlier (Chap. 6). The present basis for our

discussion is that decomposition should have either reached a point where no further change can be measured, or be followed to at least 60–80 % mass loss, which sometimes may be impossible due to litter fragmentation.

Some observations from the LIDET project (Harmon et al. 2009) deserve to be presented and commented on. In a 10-year experiment using 27 sites and with 9 litter types sampled at one-year intervals, they obtained in all 234 combinations of site and litter quality to evaluate. Using the single exponential (Eq. 9.1), the double exponential (Eq. 9.3) and an asymptotic function (9.7) they found that an asymptotic model was statistically significant and explained more than 85 % of the variation in 107 combinations of site and litter quality. In the same investigation, they found that the double exponential was significant in 138 cases.

9.4.2 Extent and Quality of the Dataset

Often the patterns in later stages of decay are the most difficult ones to describe with a model. As a rule, datasets that cover only low values of accumulated mass loss fit well to the single exponential model. Likewise, small datasets with a low number of measured values can almost always satisfy a single exponential equation. In contrast, to test a set of measured values for the fit of a double exponential or an asymptotic function means a set of conditions on the dataset. Thus, a dataset with a low number of mass-loss values is not likely to give a significant limit value (asymptote). Since data often are collected over some years, annual and seasonal variation in weather will influence the mass-loss patterns, for example summer drought or frozen ground at winter. The best datasets tested so far have been those with a high number of samplings, ideally ten or more, and with some of the samples collected at exactly one-year intervals to minimize the effect of short-term weather variations or annual weather cycles.

The quality of a dataset is often determined by the number of replicates for each sampling, relative to the inherent variability of the data (see App II). For example, in the case of litter bags, a low number of replicates normally results in a scatter among the average values. Further, the study should ideally follow the accumulated mass loss far enough so that the measured values are within 20 % of the asymptotic value. This may be a problem related to some litter species, for example litter that starts fragmenting. Further, for some litter species the asymptote may be reached already during the field measurements.

Chapter 10
Some Possible Influences on Decomposition Pattern, Regression Model, Stable Fraction, and C Sequestration

10.1 Introduction

10.1.1 Background

Numerous factors, both internal and external to the litter, may decide the decomposition pattern. Further, when we want to describe the pattern using a model, also factors related to the collection of data may influence how well a decomposition model will fit. For example, sampling frequency, duration of the study, and number of replicate samples may be deciding (App II). Thus, the quality of the collected data will influence the development of a model.

Before evaluating a model, several questions must be answered. Given a model based on a particular litter type with a certain chemical composition, would the model be appropriate over a range of ecosystems? Over a range in climates? For a wide range in chemical composition? How much would a selected characteristic of the ecosystems, for example nutrient availability in the humus layers, influence the decomposition pattern and, in a later step, the fit of the model?

To our knowledge, there are no consistent answers to these questions. In addition, the specific microbial population of a site, having developed in relation to the local environment, is a critical factor and normally unknown. Thus, for a given litter type and litter species, the decomposition pattern and model may vary between different ecosystems and climates. Generally, we may expect all factors that influence decomposition rates to also have a potential influence on the general decomposition pattern and thus on type of model.

With close to 400 decomposition studies now investigated with regard to model fit, we have at least an empirical background to investigate some possible decomposition patterns. Most studies are lacking important information, however, mainly about soil chemistry but also in litter chemistry, to allow a complete and thorough analysis. Still, using the available information may help us to distinguish some main patterns.

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In a first attempt, we may simplify our discussion to models resulting in (1) complete decomposition and (2) those leaving a residue. For this, we may use the argument that the double exponential (Eq. 9.3) is a special case of Eq. 9.5, of which the latter allows us to estimate the rate at any point in time (Sect. 9.3.3). With the number of alternative equations thus reduced, we may argue that we just have to answer a question with 'yes' or 'no'. However, for the time being, we have no perfect tool to decide what litter fits to the complete decomposition model (for example Eq. 9.2) and what litter that fits to a limit value model (Eqs. 9.5 and 9.7). Still, we have enough data to present some suggestions.

Several long-term projects and studies have allowed the number of estimated limit values to increase considerably. The duration of the studies simply has made it possible to follow the decomposition process long enough to estimate statistically significant limit values and develop this type of model (Eqs. 9.5 and 9.7). Still, we have few data sets extensive enough to allow an evaluation of relative influence of both endogenous and exogenous factors. Considering the fact that limit values so far have been found to range from 49 to close to 100 % accumulated mass loss, it may be possible that just the real long-term studies may discover how widely spread the concept limit value (or stable residue) is.

Of the c 250 European data sets from decomposition studies that have been evaluated using the regression model 9.2—complete decomposition—and the limit value models 9.5 and 9.7, c 200 encompass foliar litter (Berg and Johansson 1998; Berg et al. 2010) (cf DELILA database; www.eko.uj.edu.pl/deco) and have given significant asymptotic limit values for practically all these data sets. In addition, Harmon et al. (2009) mention that over 200 studies in the LIDET project fulfilled the conditions for following an asymptotic function, which means a limit value.

In the last 20 years, the number of studies evaluating patterns and models has increased considerably. The recently reported study from the project LIDET covering the United States (Harmon et al. 2009) reported that out of 234 combinations of litter type and site c 95 % fulfilled the conditions of having a limit value (evaluated using Eq. 9.7). There was also litter that fitted best to a model indicating a complete decomposition (Eq. 9.2). The site locations ranged from northern Alaska (MAT −7.0 °C) to Panama (MAT 25.6 °C) and thus covered arctic to tropical climates.

We may see two groups of possible influences, namely (1) endogenous, (2) exogeneous ones. The former encompasses litter chemistry and litter physical properties. For the time being, we may combine them and call them just endogenous properties. Exogenous ones, e.g., soil nutrients, local climate as well as unknown environmental factors may be combined into external properties. There may be multiple influences caused by interactions between exogenous and endogenous ones that may complicate the interpretation of data. We have subdivided the chapter into sections dealing with the factors that have been suggested and observed.

10.1.2 Potential Influence

Substrate chemical properties (‘*substrate quality*’) have been related to type of model, using causal influence to decomposition of litter compounds. We have discussed earlier (Chaps. 2, 6) that degradation of lignin may create new compounds and a nucleus of lignin-like recalcitrant compounds. We present this in part as a speculation, but it appears that the degradation of this group of compounds, which may be lignin-like, is influenced by nutrients such as N and Mn, which have a causality to lignin degradation (Chap. 3), and we may assume that the degradation of this group of compounds is related to the same factors. Therefore, we discuss N and Mn and their effects on a group of compounds rather than that group of compounds per se (e.g., AUR), which still needs further resolution.

Litter type has been suggested (Harmon et al. 2009) to be a dominant factor for the level of the limit value. Although this has been observed, it may have a more clear meaning for litter species for which we have at least a limited set of chemical analyses.

Climate and some substrate chemical factors are related (Chap. 4). Still, in their cross-continental study, Harmon et al. (2009) using unified litter types commented on that decomposition went further at warmer and wetter climates, which means that the limit value was higher, and less of stable residue was left. We may comment on the indirect effect of climate on litter nutrient levels (e.g., N, Mn), which in their turn influence decomposition pattern.

Soil nutrient concentration is a complex concept and very rarely investigated in studies of litter decomposition. Often scientists are forced to use available data, which normally are very incomplete. Traditional soil terminology may be misleading. A term like ‘nutrient rich’ may mean rich in the main nutrients such as N, P, S, Ca, and K. Thus, it is possible that such a terminology taken from botany or plant ecology may be less useful. A nutrient that is not a main one for plant life may be important or deciding for the microorganisms decomposing litter. We have discussed the example with Mn, which has been related to lignin decomposition and to the limit value. Another, seemingly extreme example is that with sodium (Na) as a limiting nutrient (Kaspari et al. 2009), Thus, we may ask what factors were important in the difference between ‘nutrient-poor’ and ‘nutrient-rich’ litter.

In this chapter, we intend to discuss the above factors one by one and relate to decomposition pattern, which in its turn may determine a model type. One main reason to investigate the pattern is simply the storage time for the stable fraction of organic matter (carbon) in the ground. Storage time is ruled by the mass-loss rate and the amount decomposing at that rate. As part of such a study, we may see two main cases; (1) complete decomposition at a constant rate and (2) stabilized residue including the size of the stable fraction decomposing at a very low rate. We focus on the size of stable residue as calculated by a limit value.

10.2 Two Main Patterns and Two Main Models?

Several foliar litter types decompose more quickly initially when the litter is newly shed, with a decreasing rate in later stages as the litter 'ages'. This decrease has been discussed above (Chaps. 2, 6). Other foliar litter species decompose with a constant rate.

A basic question in evaluating the decomposition pattern is 'what criteria can we use to predict a pattern?' How do we test for and decide that a certain model fits better or is more valid than another to a given set of data? We have just a few relationships based on causality, so a discussion about patterns versus causality is more close at hand than a discussion about an absolute fit. Like in other sciences, we also have empirical relationships lacking causality, which need to be considered.

By considering just two main patterns, we may reduce the question to the estimation of a significant limit value, which means a value that is statistically significant and lower than or equal to 100 %. With a nonsignificant limit value or one well above 100 % and a well significant relationship for Eq. 9.2 (single exponential), we should have a pattern that means a complete decomposition. So, in a first step, we may reduce the question of model type to one about the litter leaving 'stable' residue or not, thus according to Eqs. 9.5 and 9.7.

'Stable' residues may be of different magnitude. A limit value of say 50 % accumulated mass loss leaving a stable residue of 50 % may fit the models 9.5 and 9.7 and so does a model leaving a limit value at 80 % mass loss and leaving 20 % as 'stable' remains. Whereas model 9.2 has just the complete mass loss, Eq. 9.5 may give a range of limit values, and although our question is one of yes or no, we may take advantage of the different limit values to develop and identify factors that may influence both type of model and level of the limit value. We thus may distinguish a range of limit values from those below 50 to 100 % with 100 % decomposition being one of several limit values.

10.3 Specific Factors that May Determine a Pattern and a Model?

10.3.1 Litter Type versus Litter Chemistry Revealing a Pattern

In a paper in 1993, Berg and Ekbohm suggested that decomposing needle litter of lodgepole pine would have an average limit value very close to 100 %. They compared to litter of Scots pine which also had a clear limit value, but significantly lower. That study was based on six sets of studies in paired stands of lodgepole pine and Scots pine. From such a test, it is possible to conclude, maybe a bit

prematurely, that litter species is an important parameter. Lodgepole pine needle litter thus should decompose completely as determined by Eq. 9.2 or should follow 9.5 which gives a limit value of 100 %, whereas Scots pine litter follows a limit value pattern.

However, we may relate each individual limit value to a parameter of a possible causality, and within sites of similar climates we compared to litter chemistry and among the parameters was the initial concentration of Mn. Lodgepole pine needle litter from the stands used was rich in Mn (Chap. 4), and in a comparative study between Scots pine and lodgepole pine needle litter, we may comment on that initial Mn concentration in the litter samples collected in paired stands was significantly higher for lodgepole pine litter.

Using the Berg and Ekbohm (1991) study as a background, we may take a further step and isolate a litter chemistry factor. So, extending our example to all available data in a comparison between the two species, we obtained a significant relationship (type X^a; $n = 16$; $R^2 = 0.548$; $p < 0.001$) between initial litter Mn concentration and limit value (Fig. 10.1).

If we accept the suggested causality (Sects. 2.5.2; 6.3.2) and consider Mn concentration to have a stimulating effect on litter decomposition in late stages, we may regard this effect as a continuum over species with the concentration in newly shed litter depending on e.g. species, soil conditions, and climate. With concentrations thus crossing borders between species, the continuum in Mn concentration in this example (Fig. 10.1) would regulate the level in limit value, from 100 % (no residue) to 68 % (32 % left). We discuss similarities within a genus further (below). It is thus possible that chemistry parameters should be compared within a limited group of litter or within a genus. Still, we may distinguish chemistry parameters as the causal factors.

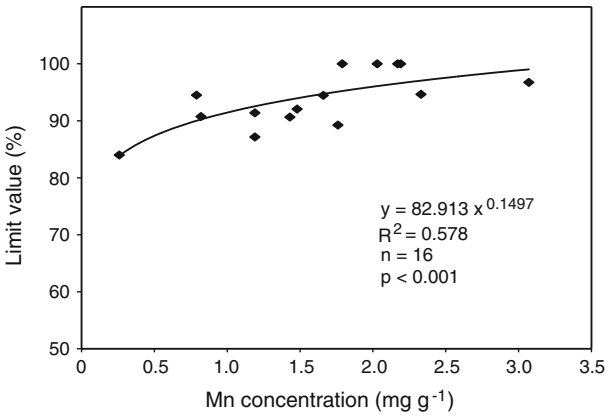

Fig. 10.1 Limit values for lodgepole pine and Scots pine needle litter plotted versus the initial concentration of Mn. Data in part from Berg and Ekbohm (1993; 1991) and from Berg et al. (2003)

10.3.2 Litter Chemical Properties: Specific Factors for Foliar Litter

10.3.2.1 What's in a Name? Can a Species Name Rather Hide than Reveal Causality?

Mn concentrations. We used the above example to argue in favor of litter chemistry to litter species as a determining factor for decomposition pattern. If we consider Mn concentration to have a causality, we may regard it as a continuum of concentrations with the concentration in newly shed litter depending on e.g. species, soil conditions, and climate and with variation in concentrations crossing borders between species. We may develop this using six species of pine (*Pinus*) litter over a transcontinental climate gradient.

Using local pine needle litter in a more than 4,000 km long climate gradient from north Scandinavia to northeast Libya, Berg et al. (2010) eliminated 9 factors out of 10 in common for all sites and incubated litter and obtained Mn as the single factor determining limit values (Sect. 2.6.3; Fig. 2.8). They estimated the limit value for each decomposition study and related these to all 10 factors in a backward elimination procedure. MAT ranged from c 0.7 to 17.1 °C and MAP from 410 to 1,070 mm. Manganese concentration in the pine litter is inversely related to MAT at the site of collection and incubation and concentrations ranged from 0.03 to 3.08 mg g^{-1} (Chap. 4). Being the dominant factor, Mn concentration alone decided the type of model for pine litter and with Mn concentrations above c 3.08 mg g^{-1}, and a linear relationship between limit value and Mn concentration a complete decomposition was suggested.

Their database for pine (*Pinus*) litter encompassed 56 separate studies on decomposition of pine needle litter, spanning Scots pine, lodgepole pine, Aleppo pine, stone pine, and white pine, mainly incubated at the site of collection. Studies were of sufficient duration to allow estimates of limit values of decomposition. They used a linear mixed model with regression effects to relate limit values to potential explanatory variables, namely the sites' long-term MAT, MAP, and substrate chemistry factors. The latter encompassed initial concentrations of water solubles, AUR, N, P, K, Ca, Mg, and Mn. Using backward elimination, they determined significant explanatory variables and found that limit values for litters decomposing at its site of origin were related mainly and positively to initial litter concentration of Mn. In other words, litter with higher Mn concentrations reached a limit value at a higher accumulated mass loss, likely because Mn is an essential component of the lignolytic enzyme MnP and most likely necessary for degrading litter in the late stage of decomposition (Sects. 2.5.2, 3.3.3).

The higher the initial Mn concentration, the lesser of a slowly decomposing fraction was formed; alternatively, the further the AUR fraction was degraded. We have given the limit values in Fig. 2.8 and the inverted ones in Fig. 10.2 to show the 'stable' residue (100-limit value).

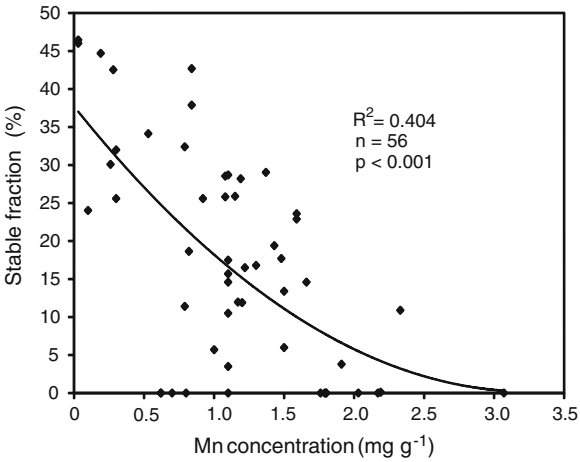

Fig. 10.2 Relationship between stable litter fraction (100-limit value) and initial litter Mn concentration (pine spp.) (cf Fig. 2.8). In their study of factors regulating limit values for pine needle litter (5 *Pinus* species), Berg et al. (2010) found Mn to be the sole regulating factor. Using their data, we fitted a negative exponential function. $R^2 = 0.404$; $n = 56$; $p < 0.001$). Data from Berg et al. (2010)

In Sect. 4.4.2, we commented on that for needle litter of *Pinus,* Mn concentration was negatively related to MAT at the site of growth. We may thus conclude that for this genus, the remaining fraction in principle would be indirectly related to site MAT with a larger remaining fraction at higher MAT due to the relationship between MAT and Mn concentration. In Fig. 10.2, we have used all available data for pine spp, indicating a high variation in the slow 'stable' fraction namely from 0 to 46 %. The relationship was well described using a quadratic function (type $X^2 + X$).

N concentration. Since lignin and N in combination appear to develop a suppressing effect on litter decomposition, we speculate that for a foliar litter poor in N, it would be more reasonable to apply a single exponential to a higher accumulated mass loss than for a more N-rich litter.

So far, most observations (e.g., Aber and Melillo 1982; Berg and Ekbohm 1991; Kang et al. 2009) indicate that high concentrations of N give a high rate initially. This indicates—generally seen—that at least N and P are in a balanced proportion, which may differ among litter species (Güsewell and Verhoeven 2006).

Litters with high initial rate often have a high N concentration and appear to decrease in decomposition rate as soon as the late phase is reached when degradation of lignin/AUR starts (e.g., Fig. 9.1). So far, that effect has been reported for litter from boreal and temperate climates.

There is no general evaluation of limit values versus litter nutrients, and possibly, such an evaluation should be done for single genera or limited groups. As regards the late stage, there is no general evaluation of the influence of N versus that of Mn. Using available data, Berg (2000) obtained a negative relationship between limit values and initial N concentration (Fig. 6.12). Using the same database, litter with both N and Mn concentrations resulted in two highly significant relationships (Fig. 6.12a, b). With identical data sets, N concentration gave an R^2 of 0.175 and Mn 0.169. Using a multiple regression ($n = 127$) N and Mn gave an $R^2 = 0.272$, thus 'explaining' c 27 % of the limit value for available data encompassing 14 litter species (deciduous and coniferous).

Heavy metals. For non-polluted litter, there are extremely few studies on the dynamics of heavy metals. We may see (Fig. 5.8) that concentrations of e.g. Pb, Cu, and Fe increase with accumulated mass loss, and we thus cannot exclude these from having a possible role in the formation of a stable fraction.

10.3.3 Environmental Factors

Climate influences, direct, and indirect ones. We mentioned (Chap. 4) that concentrations of N and Mn in at least some foliar litter species are related to climate factors such as MAT or AET. As these nutrients also influence the decomposition pattern, they may create an indirect influence of climate. An example on this is given (Fig. 10.2), which shows a variation in stable fraction (100-limit value) related to litter Mn concentration, in its turn related to MAT (Chap. 4). Further potential influences are those of other compounds related to climate such as N and AUR/lignin (Chap. 4; Berg et al. 2013).

A direct effect of climate on decomposition pattern may be complicated to distinguish. However, a study using a unified litter with a constant chemical composition over incubation sites may help to illustrate such an effect. In their cross-continental study, Harmon et al. (2009) using unified litter types commented on that decomposition went further at warmer and wetter climates, which means that the limit value was higher and lesser residue left. They had a convincing climate range (MAT from −7 to 26.3 °C and MAP from 240 to 4,090 mm), and with unified litter preparations, the internal litter chemistry was constant. Unfortunately, they did not comment on any possible differences among their litter species, alternatively the litters' chemical composition.

In the study of Berg et al. (2003), using 7 litter types at two climatically different sites, 3 deciduous litters decomposed further (had higher limit values) at the warmer, wetter, and more nutrient-rich site. The coniferous litter species gave a less clear pattern. That study was carried out in two contrasting forest stands: one temperate with wet and warm climate, which additionally had a soil rich in N and other main nutrients (Berg et al. 2003). The second forest was a boreal system, with low temperatures, rather dry and in combination with a generally nutrient-poor soil. Although this study is too small to allow any conclusions, it may give a certain support to the observation of Harmon et al. (2009).

Soil properties. Generally, there are extremely few soil chemistry data available for evaluation of decomposition studies. We may expect though that nutrients in especially the upper soil layers may be taken up to the litter, for example N.

A changed concentration of a nutrient in litter may influence the decomposition pattern. We may take an example from a study in a fertilized experimental forest with Scots pine (Table 10.1). Unified brown and green Scots pine needles were incubated in paired plots, namely control and plots fertilized with N and P. After c. 10 years of treatment, the ground vegetation had changed from moss, bilberry, and heather to grass and low herbs. Brown, nutrient-poor needle litter had higher limit

values in the control plots (70.5–74.2 %), than in the fertilized ones (53.1–59.6 %). Whereas this effect was observed for nutrient-poor needles, there was no measurable effect on green and considerably more nutrient-rich needles (Table 10.1). When a similar experiment was made in a fertilized Norway spruce stand, there was no clear response among the decomposing litter preparations.

Anaerobicity. We have commented on (Chap. 3) that the degradation of lignin and lignin-like compounds is an oxygen-demanding process. This means that a limited supply of oxygen may hamper the degradation. Such an effect may be long term, e.g., in a waterlogged environment or temporary. A temporary effect may develop in a wet ground under a melting or zero-degree snow cover.

Litter at the limit value appears to be biologically relatively stable in undisturbed systems. With decomposition rates as low as 0.0001 to 0.00001 % per day, values of the same magnitude as those measured from humus of the same stand (Table 10.2), we can regard the litter as stable humus (e.g., mor humus). As such, it can build humus layers over millennia. There are, however, additional stabilizing mechanisms that could contribute to creating a humus layer. One such mechanism would be an increasing anaerobicity in the thickening humus layer. The thickness of the layer itself would cause difficulties for diffusion of oxygen, and the ability of humus and litter to hold water would cause anaerobic pockets to develop. Lack of oxygen could prevent complete metabolism by aerobic microorganisms, and instead of releasing carbon dioxide and water as final products, organic acids would be produced. An increase in the anaerobic microflora would produce similar compounds that could either inhibit or resist further degradation. Organic acids alone (e.g., acetic acid and benzoic acid) are well-known inhibitors of microbial activity and, combined with a lower pH, could reduce the rate of litter decomposition, thus enhancing the rate of humus accumulation.

Table 10.1 Limit values (Eq. 9.5) calculated for standardized Scots pine needle litter and Scots pine green needles incubated in paired stands (control and N, P-fertilized plots) in a nutrient-poor Scots pine forest (Norrliden Tamm, 1990). The incubated material in each comparison was identical and incubated for c. 4 years. Some substrate chemistry data are given. B. Berg unpubl

Concentration (mg g^{-1})								Asymptotic model (Eq. 9.5)	
								Limit value (%, +/−SE)	
Wsol	AUR	N	P	Ca	K	Mg	Mn	Control	Fertilized
Brown needle litter									
178.4	228.6	3.8	0.30	5.93	0.90	0.39	1.08	71.5 (7.7)	59.6 (2.4)
178.4	228.6	3.8	0.30	5.93	0.90	0.39	1.08	74.2 (11.7)	59.6 (6.1)
Green needles									
199.7	211.9	14.0	1.62	2.40	5.09	0.78	0.84	62.0 (4.3)	59.6 (2.4)
199.7	211.9	14.0	1.62	2.40	5.09	0.78	0.84	57.3 (2.5)	60.8 (3.6)

Wsol water solubles; *AUR acid unhydrolyzable residue*; *nd* not determined

Table 10.2 Compartments of different stability in decomposing Scots pine needle litter and humus in a Scots pine forest. The sizes of the compartments were estimated and the rate constants were based on respiration measurements. Standard deviation in parentheses. From Couteaux et al. 1998

Labile comp. (%)	K_L (% day^{-1})	Intermediate comp. (%)	K_{IN} (% day^{-1})	Recalcitrant comp. (%)	K_R (% day^{-1})
Needle litter incubated in litter layer for 16 months					
4.09 (0.39)	0.124	17.01 (2.41)	0.0087	78.52	<0.0001
Brown needle litter from forest floor					
4.67 (0.61)	0.124	21.91 (1.54)	0.0087	74.93	<0.0001
H-layer particles <2 mm					
0.00	0.124	9.80 (1.32)	0.0087	91.20	<0.0001

10.4 What is the Relevance of a Limit Value or a Complete Decomposition? Long-Term Stability at the Limit Value and in Humus: Low or No Decomposition?

10.4.1 Can We Use Limit Values to Estimate Organic Matter or Carbon Budgets?

The concept limit value as we have used it and the way it is calculated does not imply a complete stop in decomposition. The asymptotic standard error, often in the range from 0.9 to 11.1 (Berg and Ekbohm 1991), allows for a certain continued mass loss, and the estimated 'limit value' may thus indicate a fraction with an extremely low mass-loss rate (cf Table 10.2). The factors we have considered (above) just illustrate contributions to a lower rate or partial inhibition. We cannot exclude that under some conditions, there will be an absolute stop, though.

Numerous attempts have been made to measure decomposition of humus using respiration. However, respiration rates from decomposing litter (and humus) often are used directly as measured. In short-term experiments, this means that the total respiration rates from litter are determined by those components that decompose the fastest. In an attempt to overcome this, Couteaux et al. (1998), using Scots pine needle litter, divided the litter into three compartments with components of different degradability and called them 'labile', 'intermediate', and 'recalcitrant'. Using different approaches, they determined the sizes of these pools and the rate constants for decomposition. The dominant pool was the recalcitrant one, making up between 79 and 85 % of litter samples. The respiration rate for the recalcitrant fraction was lower than 0.0001 % day^{-1} (<3.6 % in 100 years) and for the labile one about 0.124 % day^{-1} (Table 10.2).

Further, we may see (Fig. 2.9) that respiration rates from the organic layer humus decreased with increasing N concentrations. Thus, a high N concentration may well support humus stability, at least within the measured range.

With the extremely low mass-loss rate observed by Couteaux et al. (1998), we may investigate whether the stable fraction of litter may be used to estimate carbon sequestration. The stable fraction given in percent is 100-limit value, and with litter fall, we may simply multiply annual litter fall and the stable fraction.

$$(\text{Annual litter fall}) \times (\text{stable fraction}) = \text{annual sequestration}$$

Using four stands at mainly two sites, Berg et al. (2001) and later Berg and Dise (2004a, b) estimated C buildup and compared the sequestration over close to 3000 years. To this purpose, they used data of Berg et al. (1995b) and Wardle et al. (1997)

Site data and history for a 120-year-old stand. A budget for humus was created for a Scots pine forest and validated using information from the same pine forest, for which there existed well-documented background data and site history (Berg et al. 1995b). There were extremely good data for litter fall, litter decomposition, limit values, and amounts of soil organic matter on the ground. An important fact is that a violent fire took place in the mid-1800s that burnt off the existing organic layer. The existing humus layer has been built up on the resulting ash layer from the litter fall of the existing stand.

A litter-fall model estimated litter fall for 120 years. Litter fall was measured for 7 and 10 years in each of two pine stands, which were 18 and 120 years old, respectively, at the start of the study. The stands were growing on the same soil and had the same climate and hydrology (Flower-Ellis 1985). The combined litter-fall measurements covered a period of 17 years and allowed two litter-fall models to be developed. Root litter was not considered, as the pine roots had been observed mainly in the mineral soil in this stand (H. Persson, pers. comm.), and only cowberry rhizomes and heather roots, which form a small fraction of the total root biomass, were found in the humus layer.

A budget was set up. Staaf and Berg (1977) determined that the amount of SOM was 1.54 kg m^{-2} in the combined A_{01}–A_{02} horizon. This value, based on ash-free matter, did not include distinguishable litter remains. The needle litter fall from Scots pine completely dominated the litter inflow. Based on eight determinations of the limit value, the needle litter left an estimated residual of about 11 % (Berg et al. 1995b). Using that as a basis, the litter inflow for each of 112 years was estimated (the litter formed in the last 8 years had not yet formed a stable humus). Addition over 112 years gave an estimate of the accumulated organic substance of 1.67 kg m^{-2}. This theoretical result differed by only 8 % from the observed level of 1.54 kg m^{-2} (Staaf and Berg 1977). Because the chemical composition of the litter can be important in determining the limit value, it is important to note that the foliar litter formed from the pines was chemically similar over different years (Table 4.5, Berg et al. 1993b). Furthermore, the main part of the litter from the shrubs on the site had a chemical composition (lignin and N) that was close to that of the pines (Berg and Staaf 1981).

Three budgets covering millennia. Berg et al. (2001) set up further budgets by using data from Wardle et al. (1997). Humus layers had developed on 51 islands and were divided into three groups depending on the year the growth had started. The age of the three groups of humus layers had been determined to be 2984, 2081, and 1106 years, using ^{14}C analysis of ash from the latest forest fire. Wardle et al. (1997) determined the amount of ash-free humus to be 49.0, 34.6, and 14.3 kg m^{-2}, respectively (Table 10.3).

A simple regression model for needle litter fall from the completely dominant species (Scots pine and Norway spruce), based on measurements in boreal stands (northern Scandinavia, between 52 and 67°N), was used to estimate litter fall for all three groups of stands. With the use of the average limit value for needle litter of Scots pine and Norway spruce in northern Sweden ($n = 18$), the remaining fraction was calculated, and the magnitude of the annual accumulation was estimated and summed over the different periods. The accumulation thus estimated for foliar litter was 41.2, 28.7, and 15.2 kg m^{-2}, respectively, for the 2984-, 2081-, and 1106-year-old humus layers. The first two values were 16 and 17 % lower than the observed values, whereas for the 1106-year-old humus, the estimate was 6 % too high. When using total litter fall, the estimates were generally too high with 46, 37.6, and 86.3 %, respectively, for the 2984-, 2081-, and 1106-year-old stands (Table 10.2). It is possible that the method used to estimate litter fall is susceptible to error, and this may in part explain the magnitude of the deviation. Only data for litter fall were used, while the root-litter component was not considered.

10.4.2 Humus in Scots Pine and Norway Spruce Stands, Stability versus Humus N Concentration

Although we may use the limit value to distinguish a 'stable fraction', this does not mean that this fraction is undegradable. Further, fractions of different size as illustrated in Fig. 10.2 may have been identified using limit values. Still, we must not assume that such fractions of different size have the same stability as the chemical composition in part should be different. We may assume that similar factors as those discussed above (concn. of N, Mn) may have an influence, though.

An experiment that may give some information was one using respiration rates from humus. Using humus samples from a gradient along Sweden, respiration rates were found to be negatively correlated with the N concentration of the decomposing humus (Bringmark and Bringmark 1991; L. Bringmark, pers comm.). Thus, respiration rates of humus samples kept under standard climatic conditions showed a significant negative relationship to humus N concentrations ($r = -0.650$; $n = 13$ $p < 0.05$) (Fig. 10.3). Nitrogen concentrations were in the range of 1.0–1.9 %. Such variation in N concentrations in humus is a natural phenomenon (cf Berg et al. 1999a) rather than a pollution-related one. In another study in which humus was collected from across Europe, from the Arctic Circle to

Table 10.3 Observed and estimated amount of humus of known age in north Swedish forests at ca. 66°N (Wardle et al. 1997) and in a Scots pine forest at the SWECON site Jädraås at 60°49′N (Berg et al. 2001)

	Northern Sweden—Islands			Jädraås
	<0.1 ha	0.1–1.0 ha	>1.0 ha	
Age (years)	2984	2081	1106	120[a]
Forest floor mass (kg m^{-2})	49.08	34.62	14.33	1.54
Increment (kg m^{-2} $year^{-1}$)	0.0164	0.0166	0.0130	0.0128[a]
Est. litter fall[b] (kg m^{-2})	0.08–0.14	0.08–0.14	0.08–0.14	–
Modeled litter fall 112 years (kg m^{-2})[a]	–	–	–	151.55
Est. limit value[c] (%)	87.8	87.6	90.4	92.1
Av. limit value[d] (%)	83.0	83.0	83.0	89.0[e]
Est. forest floor mass[f] (kg m^{-2})	41.2–72.1	28.7–47.2	15.2–26.7	1.67
Missing fraction[f] (needle litter basis) (%)	16	17	6	–
Excess fraction[f] (total litter basis) [%]	46	37.6	86.3	8.4
N storage (g m^{-2})[i]	761	460	163	15[h]
P storage[g] (g m^{-2})	39.1[g]	28.7[g]	9.2[g]	0.72[h]

[a] It was estimated that at this site, it would take 8 years before the litter could be considered to be humus and part of the F/H layer (Berg et al. 1995b)
[b] Litter fall for the three groups 'Northern Sweden—Islands' was estimated using available Scandinavian data for pine and spruce forests between 59°N (north of the line Oslo-Stockholm-Helsinki) and 67°N (Berg et al. 1999a, 2000). The lower value gives needle litter fall and the higher total litter fall
[c] This limit value estimated as 1-increment/needle litter fall
[d] Estimated from existing limit values ($n = 18$) for Scots pine and Norway spruce litter at sites in northern Sweden (Berg and Johansson 1998)
[e] Limit value for needle litter decomposition at site Jädraås (Berg et al. 1995b)
[f] Berg et al. (2001)
[g] D. Wardle (pers. comm.)
[h] Calculated from Berg et al. (2003)
[i] Wardle et al. (1995)
Given are also measured amounts of N and P

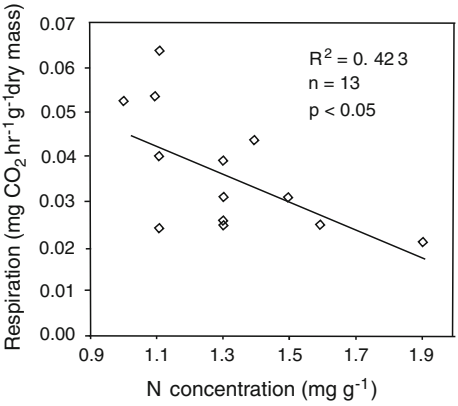

Fig. 10.3 A comparison of N concentration in humus (F and H layers) and CO_2 release rate from the same samples incubated under standard temperature and moisture conditions. Samples were taken in a gradient along Sweden (Bringmark and Bringmark, 1991; L. Bringmark pers. comm.). Figure from Berg and Matzner (1997)

the Mediterranean, a highly significant, negative relationship between respiration and N concentration was found (R. Laskowski, pers. comm.). Such results may index humus stability, although the humus layers may contain a mixture of organic compounds.

Chapter 11
Does Humus Accumulate and Where? What Factors May Influence?

11.1 Introduction

Neither C nor N was present in the original mineral soil that existed before plants evolved, but entered the ecosystem from the atmosphere. Both C and N are macronutrients and fulfill very different functions. Carbon makes up the skeleton of the macromolecules that create a storage matrix for N and other nutrients. Nitrogen is a major nutrient that must be stored in the ecosystem, to supply plants with an even flow of mineral N. Loss of N from the ecosystem would cause the vegetation on a given plot to move to an earlier successional stage due to N limitation, and the ecosystem may need N_2-fixing organisms to restore N to its prior level.

The mechanism by which the ecosystem stores C and N depends on the structure of the litter produced by a given plant, the degree to which that litter decomposes and the transformations it undergoes during decomposition. It would be reasonable to expect that each plant species would produce litter and litter remains that would store nutrients in concentrations high enough to allow the species to survive.

Nutrient elements can be added to an ecosystem through abiotic weathering, aerosol inputs from outside the system, or through fertilization. Ecosystems have the capacity to store at least some of these added nutrients.

The microbial decomposition of plant litter is a basic process in the functioning of ecosystems, not only for the general release of nutrients to plants, but also for the buildup of stable humus and the accompanying storage of nutrients.

Humus accumulates as the stand grows and ages (Ovington 1959; Forrest and Ovington 1970; Bormann and de Bell 1981; Schiffman and Johnson 1989). In these studies, the accumulation followed a nearly linear increase with stand age. However, a model formulated to describe the linear accumulation of humus with time may be general, but lacks causality.

If we define humus accumulation and carbon sequestration rates as the increase in the amount of humus/carbon per unit area, the rates may be estimated by a summation of the recalcitrant or resistant part of the decomposing litter (Sect. 10.4.1).

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7_11,

There is good support for the observation that a long-term net accumulation of humus takes place, even over millennia (Jenny 1980; Wardle et al. 1997). Such an accumulation can be predicted using the limit-value approach to humus accumulation at least for some undisturbed systems (Berg et al. 2001). The stable fraction is based on the concept of limit values (Chaps. 2 and 6) that gives the fraction of litter that decomposes extremely slowly. The level of the limit value is determined by causal factors, such as those discussed, namely concentrations of Mn, N, and AUR (Chaps. 2, 6, 10). In addition, we may have less investigated factors, one of which may be heavy metals in litter.

In Chap. 10, we discussed limit values (the stable fraction) and factors influencing the level of the limit value. We also showed that the limit value in combination with litter fall may be used to estimate carbon sequestration rates in forest stands. In the present chapter, we follow this path and investigate the growth of the humus layer. Depending on the specific measurement, we may find FH layers (the stabilized humus in the forest floor) or the FH layer plus litter (LFH). We may refer to Fig. 11.1 and call this a primary sequestration, the one that takes place on top of the mineral soil in the organic layer, for example a mor layer. We discuss this and influencing factors and intend to approach the complex of humus buildup (carbon sequestration) stepwise. Whereas we in this chapter focus on a small scale, we have devoted Chap. 12 to more large-scale and regional evaluations. This chapter aims to evaluate basic observations; what a storage mechanism for humus may mean in terms of amounts of humus stored . Of course, this is an extrapolation

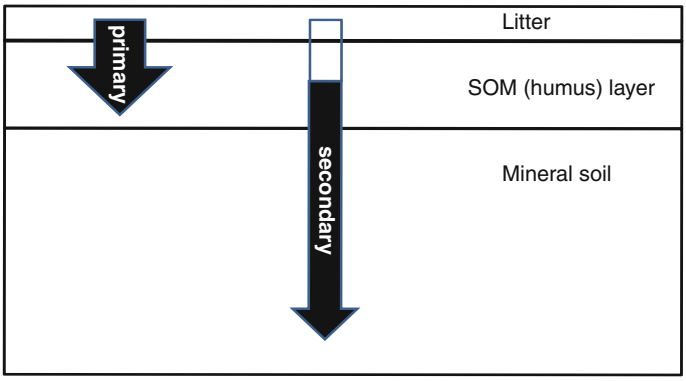

Fig. 11.1 Primary and secondary sequestration of carbon in humus and mineral soils. The arrow 'primary' indicates a transport of decomposing litter to the organic layers with more resistant/recalcitrant material and into a sink for material that is in a state of primary sequestration (long-term stable), for example a mor layer. The arrow 'secondary' indicates a transport of soluble organic material into the mineral soil. This secondary sequestration requires that material from upper layers is solubilized and transported with water to the mineral soil where it is sequestered. It is evident that root litter will contribute to the organic matter in the mineral soil. We have taken an example from a soil with clearly different layers. The layer(s) with primary sequestration in an organic layer are also called A_{01} and A_{02} or O_e and O_a or F and H. From Berg et al. (2008)

of existing, partially empirical, data and must be regarded as a prediction that needs to be validated.

In this chapter, we focus on studies carried out on types of forest soils in which more clear and accurate quantitative determinations can be made, which means a focus on boreal and temperate coniferous forests and mor soil. For forests in these climate types, there is a reasonable amount of available data. However, whenever data are available, we have compared the results from studies of other systems.

11.2 Amounts of Humus and Increase in Organic Layers. Is There a Steady State?

The accumulation of stabilized soil organic matter is the net result of a sequence of several subprocesses. The input through litter fall, in its turn dependent on site productivity, may be seen as a first step, followed by the decomposition processes, leaving a certain fraction as stabilized residue. Once this has been formed, a necessary request is the maintenance of the long-term stability of the litter fraction.

The two groups of processes, namely those resulting in accumulation and those in decomposition as well as several subprocesses, may be ruled by different conditions and have different optima. We may measure the net result as the amount of, for example, mor humus at a given point in time or over a period, thus obtaining a net change, for example an increase (sequestration) or a loss. One interpretation of a high sequestration rate is that the main processes, either all or most of them, have close to optimum conditions.

One strong driving variable to these processes ought to be the climate, and more than two centuries ago, de Saussure (1796) expressed the opinion that difference in climate was a primary influencing factor for the variable amounts in organic matter found on and in the soil. Among other scientists, Jenny (1930, 1941) found that the geography of soil carbon is controlled by temperature and moisture. Later, Meentemeyer et al. (1985), relating measured amounts of carbon to climate, found that stored soil carbon was related to actual evapotranspiration (AET) with an optimum at an AET of c. 390 mm. Their model also included site disturbance and annual soil moisture deficit. The model was valid for moderately drained sites but did not account for local effects.

Today, there are numerous estimates of soil carbon amounts, both global ones and for specific forest systems. The amounts of soil carbon stored in the upland boreal forest (the taiga) have been estimated to as much as 1,700 Pg (1,700 Mt), corresponding to c. 50 % of the global soil carbon and c. 18 times that in the boreal vegetation (DeLuca and Boisvenue 2012). Locally, amounts have been found to range between close to none and 245,000 kg ha^{-1} (Wardle et al. 1997).

Considering such a climate dependence as observed already by Meentemeyer et al. (1985), it would be obvious that there should be relationships not only between AET and standing amounts of soil carbon but also between climatic

factors and accumulation rate of C in stabilized SOM. We here refer to the net accumulation as the product of litter fall and the stable fraction of litter (primary sequestration, Fig. 11.1).

Accumulation or increases in stabilized SOM-C in, for example, humus layers have often been considered to continue until a steady state has been reached. The concept steady state has not been very clear in the context of soil carbon, although a general definition exists. Jenny (1980) discussed the concept and concluded that '…the soil organic matter regime is often viewed in short perspective as a steady-state system with inputs of C and N balancing their egress.' Suggestions have been forwarded about a regional steady state, for example for a whole country when including all possible influencing factors (Schulze et al. 1989). They suggested that the forested land of Sweden should be in a steady state as regards humus growth. However, such a statement may be difficult to confirm. Further, considering only the current humus layers, such a concept based on a whole region may need to allow rather wide fluctuations when we consider possible growth rates (Chap. 12) (e.g., Berg et al. 2009).

Organic layers may grow for millennia at least in limited areas or niches and be quite deep even in systems that are not waterlogged. Thus, Wardle et al. (1997) reported that a whole group of islands in Swedish Lapland, well protected from forest fires over a period of slightly less than 3,000 years, had developed mor humus layers to a depth of up to 150 cm. Berg et al. (1993, 2003) reported humus layers more than 1 m thick on Monte Taburno just east of Naples (Italy). Such layers have also been observed in NW Spain (B. Berg, pers. obs.). Also, in the Alps and Central European Mountains, the established concept 'Tangelhumus' (Rehfüss 1990; www.GeoDZ.com) means organic layers of up to 1 m depth. Thus, deep raw humus layers suggesting a long-term development may question the concept 'steady state' at least for coniferous forests over Europe. In the case reported by Wardle et al. (1997), growth had been continuous for close to 3,000 years (Fig. 11.2) and a highly significant relationship suggests a continued growth.

With such a growth over millennia, the concept steady state may become less interesting. We may consider the possibility that at least some ecosystems simply do not develop any kind of steady state unless factors such as wildfire may be a frequent regulating factor for humus growth. Of course, with a high wildfire frequency, for example at least every 50 years, a kind of steady state may develop, but will be broken with better fire prevention.

As regards the possible development of a steady state for some forest systems, we may consider this as being a balance between litter input, the degradability of litter, and the environmental influences on the sequestration process. Several factors influence the litter fall, litter chemical composition, and the stability of a potentially stable fraction as well as the multitude of litter species. Further, these may be combined with a variable and continuously changing environment, for example climate. One reasonable result is that we may expect several possibilities for humus layers to develop with developments following different patterns. Some seemingly extreme examples would be on the one hand more than meter-thick

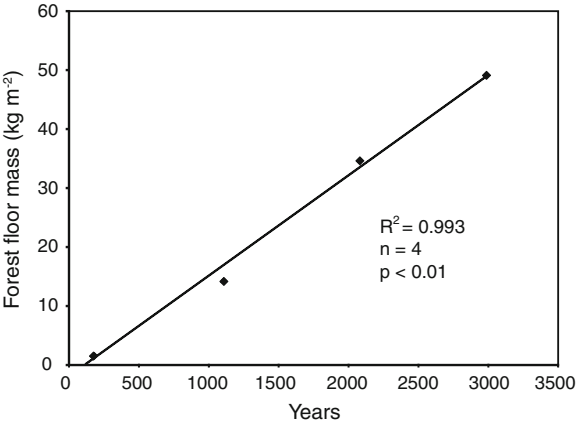

Fig. 11.2 A relationship ($R^2 = 0.993$; $n = 4$; $p < 0.01$) between the year for the latest forest fire and the accumulated humus carbon measured on isolated boreal islands. The islands were forested with Scots pine, Norway spruce, and birch spp. 50 islands were subdivided into groups according to age, with 2,984 years an average for 14 stands, 2,081 years an average for 24 stands, 1,106 years the average age for 12 stands. A 120-year-old Scots pine stand with 25 replicate samples was added. The age is that estimated since the humus layer growth started. Data from Wardle et al. (1997) and Berg and Staaf (1977)

humus layers (e.g., Tangelhumus) and on the other hand systems in which leaf litter residues never accumulate, but decompose so quickly that no organic layer is formed.

11.3 Accumulation of Stabilized Humus/Carbon in Organic Layers of Boreal and Temperate Forests

11.3.1 Accumulation with Stand Age

The purpose of this section is to show that there is a clear increase in organic-layer carbon with stand age. This has been observed by sampling both one stand over time and in chronosequences. In contrast, there are deciduous forest ecosystems that appear not to form any humus layer and just litter residues are found on the ground on top of the mineral soil after 1 year of decomposition. As mentioned above, any change in the amount of mor humus or mor humus C is the net result of several processes that both add and remove matter and we may consider any increase to be a net increase and any change a net change.

Observations in pine spp stands and chronosequences. It appears common, at least in boreal and temperate coniferous forest ecosystems that a net increase takes place in stabilized mor humus stored in distinguishable humus layers. Early

descriptions of this process are those of Ovington (1959) (Fig. 11.3) and a later one is that of Schiffman and Johnson (1989). Using chronosequences of Scots pine and loblolly pine stands, respectively, they demonstrated a rapid growth of both the FH layer and the total amount of dead organic matter in the forest floor. Measurements in a chronosequence of Scots pine in central Holland (Tietema 2004) gave a continuous increase with stand age and could be described by a linear relationship (Table 11.1).

An extreme event may be one at a Scots pine site in South Germany, where no change could be detected after 22 years although a nearby site showed an accumulation of 196 kg C kg ha^{-1} year^{-1} over 30 years (Prietzel et al. 2006).

Two stands with pine at warmer sites also showed an increase in the amount of sequestered humus with stand age. Thus, a stand with loblolly pine at a subtropical climate (southeast USA) showed a clear net increase over a period of 47 years (Table 11.1). A stand with Monterey pine (NSW, Australia) under a subtropical climate also increased the SOM-C mass in the forest floor, an increase that was linear *versus* stand age and with a rate of 1032 kg C ha^{-1} year^{-1} (Forrest and Ovington 1970).

Observations in stands with Douglas fir and Norway spruce as well as in gradients. Using a chronosequence of Douglas fir stands, Turner and Long (1975) found a linear increase in the forest floor carbon (Fig. 11.3b, Table 11.1). In a comparison over a geographic range from Central Germany to North Italy, across the alpine region, Thuille and Schulze (2006) could relate the growth of the SOM layer carbon stock in Norway spruce forests to stand age in spite of the wide range

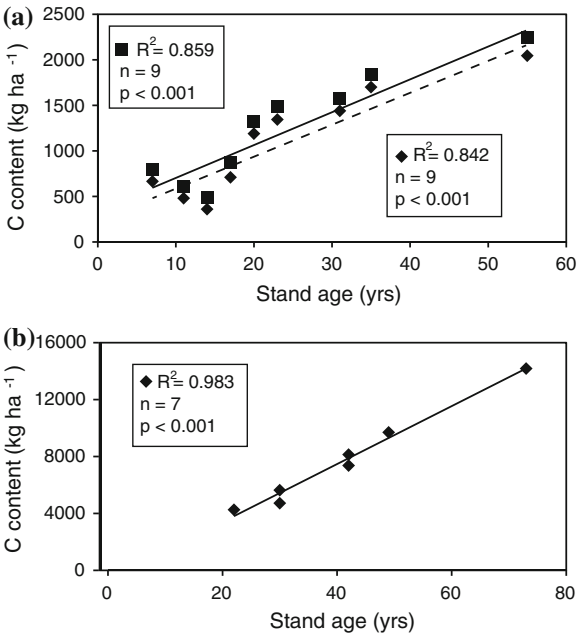

Fig. 11.3 **a** Accumulation of carbon in; (◆) the F + H layer of 9 Scots pine stands in a chronosequence with an age range from 7 to 55 years and (■) all dead organic matter in the forest floor. From Ovington (1959). **b** Accumulation of carbon in; (◆) the F + H layer of 9 Douglas fir stands in a chronosequence with an age range from 22 to 72 years. From Turner and Long (1975)

Table 11.1 A comparison of accumulation rates of SOM-C in forest floors in which the accumulation has been followed over time (stand age or in a chronosequence). The estimated increase rate in the measurement period is given as the slope of the linear function between accumulated amount and time

Species	Increase rate (Kg C ha^{-1} $year^{-1}$)	MAT	MAP	R^2	$p<$	Location Comment	Ref
Scots pine	380	9.5	517	0.859	0.001	England	(1)
Scots pine	537	9.8	827	0.627	0.001	Central Holland	(4)
Scots pine	196	5.8	615	**	0.05	South Germany	(8)
Scots pine	0	7.2	650	**	ns	South Germany	(8)
Monterey pine	1032	nd	1450	0.903	0.05	N So Wales Australia	(2)
Loblolly pine	237	12.8–15.6	1020	0.935	0.001	SE USA	(3)
Douglas fir	407	9.4	1440	0.982	0.001		(7)
Norway spruce	1106	5.3	1163	0.816	0.001	Central Germany	(5)
Norway spruce	360	7.7	600	0.887	0.01		(6)
Norway spruce	340*	5.8–6.8	815–1370	0.88	0.001*	Acid soils	(9)
Norway spruce	240*	4.1–7.5	661–1466	0.73	0.001*	Calcareous soil	(9)
Common oak	80	7.7	600	0.340	ns		(6)
Common beech	422	5.3	1163	0.609	0.05	Central Germany	(5)

* 6 chronosequences were investigated in the southern, central, and northern part of the Alps from Northern Italy to eastern Germany. P values estimated from data given in paper. ** Three samplings over 22 years. *ns* not significant. *nd* not determined

(1) Ovington (1959), (2) Forrest and Ovington (1970), (3) Schiffman and Johnson (1989), (4) estimated from Tietema (2004), (5) Berg (2004), Meesenburg et al. (1999), Maiwes et al. (2002), (6) Vesterdal, Ritter and Gundersen (2002). (7) Turner and Long (1975), (8) Prietzel et al. (2006). (9) Thuille and Schulze (2006)

in climate expressed as both MAT and MAP. This gradient had six sites with a range in MAT from 4.1 to 7.5 °C and MAP from 661 to 1466 mm. Further, each of the sites had a chronosequence with 4–6 stands plus an old control stand, in all 39 stands (both acid and calcareous soils). With the exception of the two oldest stands, the increase fitted a linear relationship very well (Fig. 11.4).

We may note that although an increase in SOM-C at a high rate appears normal, this kind of measurements is taken in well-documented forest stands that are managed. Management often includes a control on the number of stems per hectare and basal area. Such stands are thinned, which means that also litter fall is limited.

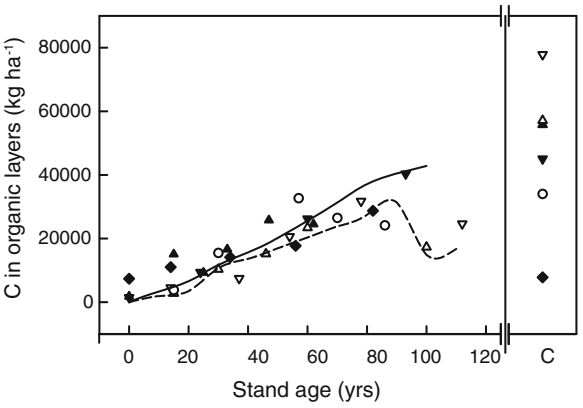

Fig. 11.4 Development of carbon stock in the organic layer of Norway spruce stands of different age in a gradient from east central Germany to north Italy. Black symbols show stands on acid bedrock, and open symbols show stands on calcareous bedrock. Redrawn from Thuille and Schulze (2006)

An exception is a stand of Norway spruce (Table 11.1) at Solling in Central Germany with an increase in the organic layer of 1106 kg C ha^{-1} $year^{-1}$. That stand was abnormally dense.

Some examples on deciduous forests. We have found two studies on deciduous species, namely on common oak (south Sweden) and common beech (Central Germany). The latter showed a significant linear increase in forest floor carbon with increasing stand age (Table 11.1).

11.4 Variation in Carbon Sequestration Rates among Tree Species and Soil Properties: Data for Northern Europe

11.4.1 Large-Scale Comparisons among Species Over Northern Europe

There is a limited number of studies useful for determining C sequestration rates in mor humus layers. Still, an inventory of existing data allows a certain synthesis as well as a few conclusions.

There is a clear variation in C sequestration rates in forest floors including both FH and LFH layers (Table 11.1), with the full range in measured values over the northern half of Europe, ranging from about 0 to 1,100 kg C ha^{-1} $year^{-1}$, the latter for a dense Norway spruce stand at Solling in Central Germany (Berg 2004).

In a first approach to analyze and distinguish a pattern, we combined two larger sets of data with in all 10 trials, one from England (Ovington 1954) encompassing three species trials and one from Denmark (Vesterdal and Raulund-Rasmussen 1998) encompassing 7 trials. The studies had very similar design and overlapping tree species. A brief overview to the main experiment; Vesterdal and Raulund-

Rasmussen (1998) used a tree trial experiment started 30 years earlier. That experiment investigated growth and humus formation of c. 16 tree species at 14 locations over Denmark. Each plot had a monoculture and measured at least 0.25 ha. All tree species on all locations were planted in the same year (Holmgaard and Bang 1977). One difference between sites was the type of soil and its richness in weatherable nutrients. Denmark is a rather flat land, and all sites were located within a circle with a radius of less than 150 km, which means that the climatic differences were minimal. The climate, expressed as MAT and MAP, ranged between 7.5 and 8.4 °C, and 610 and 890 mm, respectively. The mineral soil was bare at time for planting, meaning that the humus layer on top of the mineral soil had accumulated after the stands were planted. Further, all the organic material accumulated had formed a clearly distinguishable layer on top of the mineral soil. Thus, samples of the O horizon in a set of stands could be compared. Further, the similarities in the design of the experiment and in climate between stands allow data to be evaluated statistically as a block experiment. The experiment of Ovington (1959) had a very similar design with overlapping tree species and genera.

At all 10 sites, the forest floor was sampled once in stands of known age. SOM was sampled, and live plants plus branches were removed from the sampled material, which leaves foliar litter plus FH layer material for those stands in which a clear mor/moder humus layer was formed. In both studies, ash or C was determined and subtracted from the mor humus. We estimated the amount of carbon by assuming 50 % C in the organic matter of Ovington's study. Further, the amounts given by the authors were divided using stand age to give the annual C sequestration. Because of the similarities in climate, approach, and method as well as in tree species and genera in monocultures, we have combined data and compared values for the genera *Pinus, Picea, Pseudotsuga, Abies,* as well as *Quercus* and *Fagus.* In the evaluation, we used ANOVA.

The obtained dataset encompassed 75 values showing a large variation with a range in sequestration rates from 24 to 696 kg C ha^{-1} $year^{-1}$ (Fig. 11.5). Within the group 'coniferous' ($n = 53$), the sequestration rates ranged from 63 to 696 kg C ha^{-1} $year^{-1}$ and within 'deciduous' ($n = 22$), from 24 to 642 kg C ha^{-1} $year^{-1}$.

We may see that also at genus level, there is a large variation (Fig. 11.5, Table 11.2). Thus, the group pine spp encompassing 11 values for Scots pine, lodgepole pine, and Corsican pine had an average rate of 470 kg C ha^{-1} $year^{-1}$ and a range from 125 to 696 kg C ha^{-1} $year^{-1}$. The largest group was that for spruce species with 17 values, encompassing Norway spruce, Sitka spruce, and Serbian spruce. The mean value was 364 kg C ha^{-1} $year^{-1}$ and the range 151 to 693 kg C ha^{-1} $year^{-1}$. For *Pseudotsuga* and *Abies*, there was just one species in each group namely Douglas fir and Grand fir with averages of 266 and 189 kg C ha^{-1} $year^{-1}$, respectively, and ranges from 65 to 531 and 63 to 498 kg C ha^{-1} $year^{-1}$, respectively.

The averages for common beech and oak species were 277 and 90 kg C ha^{-1} $year^{-1}$, respectively, with ranges from 86 to 642 and 24 to 273 kg C ha^{-1} $year^{-1}$, respectively. We may see that the deciduous genera have clearly lower

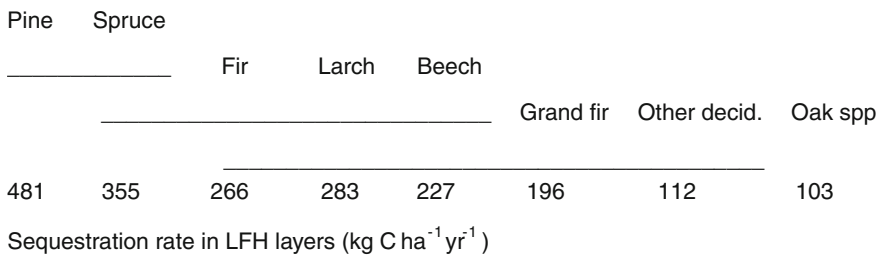

Fig. 11.5 Carbon sequestration data from 3 tree species trials in England (Ovington 1954) and 7 in Denmark (Vesterdal and Raulund-Rasmussen 1998). Each study gave a very carefully determined amount of soil organic matter on top of the mineral soil in monocultural stands. Data were combined to show the variation among genera. The full line underlining genera indicates accumulation rates that are not significantly different. Ash was subtracted, and we assumed 50 % C in the organic matter of Ovington's study (cf Table 11.3)

Table 11.2 Average sequestration rates for carbon bound in organic (L+F+H) layers in some monocultural planted forest stands. Measurements were made as one-time inventories of ash-free humus

Genus	Species	Average rate (kg C ha^{-1} $year^{-1}$)	S.D.	*n*
Coniferous genera				
Pinus	Lodgepole, Scots, Corsican	470	167.1	11
Picea	Norway, Sitka, Serbian	364	176.1	17
Pseudotsuga	Douglas fir	266	153.7	10
Abies	Grand fir	189	151.7	9
Larix, Thuja, Tsuga, Chamaecyparis		255	57.5	6
Deciduous genera				
Fagus	Common beech	227	203.9	8
Quercus	Common, red, sessile	90	77.6	11
Alnus, Betula, Castanea	Gray alder, white birch, chestnut	90	27.3	3
Main groups				
All coniferous		326	183.6	53
All deciduous		140	150.2	22

We have combined available data for some main genera from forest stands in Denmark and England (Vesterdal and Raulund-Rasmussen 1998; Ovington 1954) and estimated average rates from time for planting. All Danish stands were 30 years of age, and the age of the English ones ranged from 17 to 46. See also Fig. 11.5
S.D. Standard deviation

sequestration rates than the coniferous ones. In fact, the value for the group 'deciduous' is significantly lower than that for 'coniferous' ($p < 0.0001$; *t*-test; Table 11.3).

It is evident that in such a comparison, both the litter production, which is related to growth rate of trees (determining litter fall), and the stable fraction (100-limit value; Chap. 10) are variable. In these and similar comparisons, such factors

Table 11.3 Significant differences (p values) in SOM-C sequestration rates. Differences in LFH layers between different genera, as well as the main groups coniferous and deciduous. cf Fig. 11.5

	Spruce spp.	Douglas fir	Grand fir	Common beech	All decid.
Pine spp	0.068	0.006	0.0003	0.007	
Spruce	–	0.086	0.012		
All conif.					<0.0001

The average values from Table 11.2 were compared using t-test

as stand density and management are assumed to be similar enough to allow a combination of data.

A further study may support this result. Berg (2004) using data from Maiwes et al. (2001) and Meesenburg et al. (1999) compared the increase in forest floor C with time and estimated rates of 1100 and 320 kg C ha^{-1} $year^{-1}$ for Norway spruce and common beech, respectively. The stands (Central Germany) were paired, confirming a difference between species on the same soil. In that case, the Norway spruce stand was extremely dense, which may explain the very high rate.

11.4.2 Accumulation of SOM-C with Climate: Coniferous Forests in Gradients

There are gravimetric studies on C sequestration rates in SOM of coniferous forests, both in single stands and in chronosequences of mainly Scots pine, lodgepole pine, Norway spruce, and Sitka spruce. The rates vary considerably, and values between 0 and 1,100 kg C ha^{-1} $year^{-1}$ have been measured within the group 'coniferous.' Although there are few studies, they allow some conclusions that may be of guidance for further work.

The data originate from northern to south Sweden, Denmark, central Netherlands, central Italy, the UK, east Canada, and south Italy. In all cases, we compared SOM-C in an organic layer. Wood on the forest floor was excluded. In this relationship, we used information for the main coniferous genera, viz. spruce, mainly Norway spruce and pine spp. For the extensive experiments of Vesterdal and Raulund-Rasmussen (1998), we used average values for the two temperature (MAT) regimes given by them.

We found increasing sequestration rates with increasing MAT (Fig. 11.6). Although pine spp. has an almost significantly higher sequestration rate than spruce within a climatically homogeneous area ($p = 0.068$; Table 11.3; Sect. 11.4.1), we found that over this gradient, there was a clearly significant ($p < 0.01$) relationship between C sequestration rate and MAT when combining coniferous species.

A further example is presented and discussed in Sect. 12.5.6. Using a long-term (41 year) forest floor inventory covering the forested land of Sweden, Berg et al. (2009) found a highly significant positive relationship between temperature sum

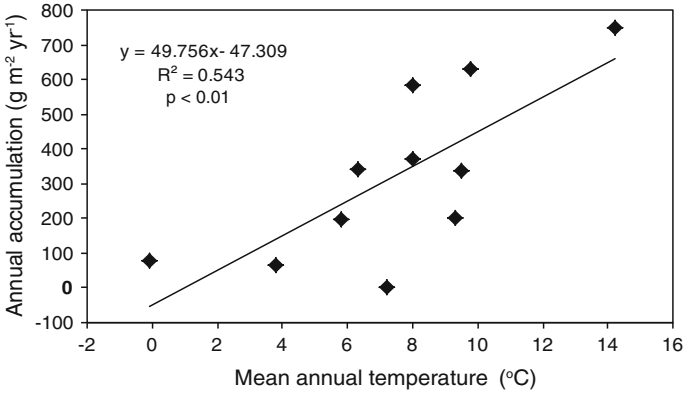

Fig. 11.6 Carbon sequestration rates in humus layers (kg C ha^{-1} $year^{-1}$ in coniferous forest stands ranging from north Scandinavia to south Italy, MAT range c. 0.1 to 11 °C. Available data originated both from chronosequences and from stands with controlled growth of an organic layer (one sampling). Scots pine, lodgepole pine, black pine, Monterey pine, Norway spruce, Sitka spruce, and Douglas fir. Available data for single stands and chronosequences from Tietema (2004), Berg and Staaf (1977), De Marco et al. (2012), Wardle et al. (1998), Vesterdal and Raulund-Rasmussen (1998), Ovington (1959), Turner and Long (1975), Sogn et al. (1999)

and carbon sequestration rate (measured humus accumulation). Temperature sum is defined as the sum of daily mean temperature exceeding +5 °C and calculated from latitude and altitude (www-markinfo.slu.se; Odin et al. 1983). They divided the country into 25 × 25 km grid cells and related humus depth to temperature sum. Using all plots with both Scots pine and Norway spruce, they found a positive linear relationship with the temperature sum ($R^2 = 0.29$, $n = 548$, $p < 0.0001$).

As discussed above, the SOM-C sequestration rate may be estimated from litter fall and the size of the stable litter fraction. Litter fall may be related to MAT, and at least for pine spp the stable fraction has been related indirectly to MAT. Although a relationship like that in Fig. 11.6 is empirical and needs further resolution, we may expect that at least short-term accumulation may have a causal relationship with MAT.

11.5 Some Factors Related to Mineral Soil may Influence Organic Layer C Sequestration

Soil factors include both physical and chemical properties. Texture is perhaps the most important physical property of soil because it influences nutrient and water dynamics, porosity and permeability, as well as surface area. Chemical properties include pH, cation exchange capacity, and organic matter content, all of which can influence the mobility of nutrients and the composition of the microbial community.

11.5.1 Soil Texture and Mineral Soil Nutrients

An experiment that may give a new view on the effect of nutrients and/or mineral soil structure on the long-term decomposition process as well as on storage or sequestration of organic matter on top of the mineral soil was that made by Vesterdal and Raulund-Rasmussen (1998) (cf above).

With 10 replicates per stand, Vesterdal and Raulund-Rasmussen (1998) measured the amount of LFH layer (and carbon) accumulated at 7 sites. Using 7 tree species, namely lodgepole pine, Norway spruce, Sitka spruce, Douglas fir, Grand fir, common oak, and common beech, they found clear differences among sites both as regards the chemical composition of the remaining organic material (humus) and as regards the amounts of sequestered carbon on top of the mineral soil.

They found an effect related to site (Fig. 11.7b). Taking the average values of all tree species for each site, they obtained average amounts that were significantly different. Carbon content in the O horizon was negatively correlated with mineral soil pH and to soil clay content; the coarser the soil structure is, the more was stored. Thus, carbon content in the humus layer was related to properties of the underlying mineral soil. The amount decreased with increasing concentrations of clay and silt and increased with increasing concentrations of coarse sand.

They related concentrations of extractable (plant available) mineral nutrients, originating from the mineral soil to the amounts of carbon sequestered. Amounts of carbon on top of the mineral soil decreased with increasing concentrations of extractable P, Ca, K, and Mg. They concluded that soil texture, Ca, and P concentrations appeared to be the most important variables for the amounts of C in the forest floor. When comparing concentrations of P with forest floor mass, clearly negative relationships were seen between the amount of carbon sequestered in the O horizon and mineral soil concentration of extractable P (Fig. 11.8).

Lodgepole pine forests stored the highest amounts and significantly more than the two spruce species and seemed not to be influenced by available Ca or P in the mineral soil. Although the stored amounts were generally lower at higher concentrations of Ca and P (Fig. 11.8), there was a tendency to order among species mainly like in Fig. 11.7. Lodgepole pine allowed significantly more carbon to be stored than common beech, which in its turn stored more carbon than common oak. Douglas fir and Grand fir were in between.

11.5.2 Organic Layers' Natural Nutrient Availability

Of the single species, lodgepole pine had formed an O horizon that was beyond comparison more nutrient poor than those of the other species. In general, Grand fir, common oak, and common beech had the most nutrient-rich organic layers (Table 11.4). Worth noticing is that lodgepole pine had the most C accumulated in the forest floor and the three latter species, the least.

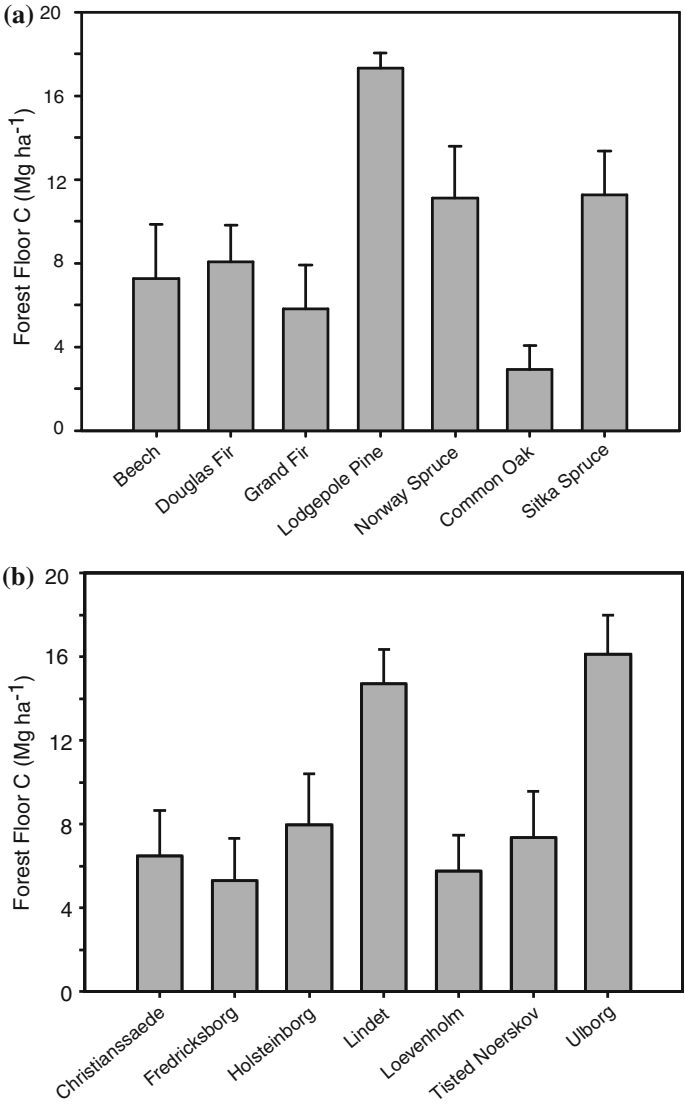

Fig. 11.7 The average amount of carbon in humus layers formed in stands of seven monocultures of different tree species. The same tree species were planted at seven different sites with soils of different richness. The figure gives average amount of carbon stored in humus. **a** Average values for tree species over the seven sites. **b** Average values for all tree species within each site. The figure thus suggests an effect of both tree species and site. Bars with the same letter indicate no significant difference at $p < 0.05$. Abbreviations: O. common oak, B. common beech, DF. Douglas fir, SS. Sitka spruce, NS. Norway spruce, LP. lodgepole pine. From Vesterdal and Raulund-Rasmussen (1998)

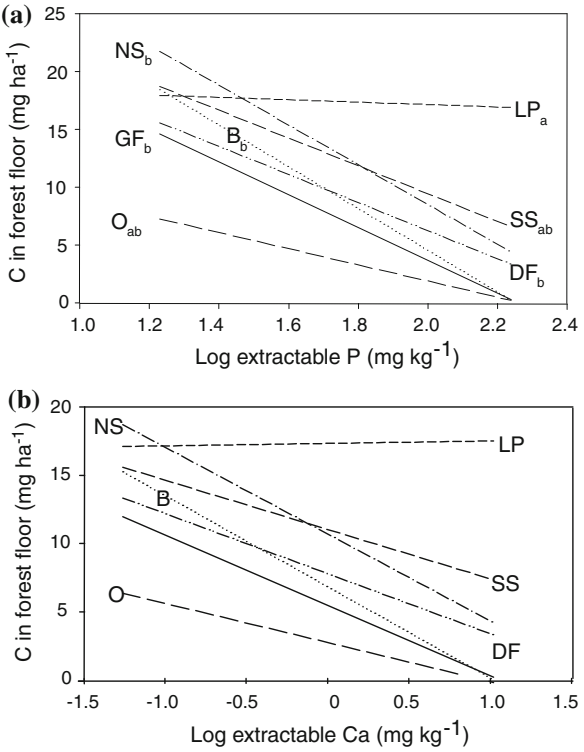

Fig. 11.8 **a** Linear relationships between average concentrations of extractable P in the mineral soil (0–50 cm) and amounts of carbon in the forest floor for seven tree species. Lines with the same lowercase letters do not have significantly different slopes ($p < 0.05$). **b** Linear relationships between average concentrations of extractable Ca in the mineral soil (0–50 cm) and amounts of carbon in the forest floor for seven tree species. From Vesterdal and Raulund-Rasmussen (1998)

Table 11.4 Average values for soil nutrients as related to the organic fraction of the forest floor, formed under seven tree species in a tree trial experiment on different soils and very similar climate

Tree species	C/N	C/P	C/Ca	C/K	C/Mg
Lodgepole pine	35.2	674	264	805	753
Sitka spruce	28.7	530	94	533	648
Norway spruce	26.4	462	77	412	480
Douglas fir	31.4	434	114	462	546
Grand fir	26.8	465	58	438	482
Common beech	26.8	465	48	337	396
Common oak	27.5	440	55	315	398

From Vesterdal and Raulund-Rasmussen (1998)

Although nitrogen is a nutrient that often is limiting, it is one that originates from the air, like carbon. Like carbon, it is taken up by fixation processes through plants, except for the N deposited in the natural background deposition. Still, an index for a soil's ability to store carbon would also be an index for its ability to store nitrogen as these two compounds are sequestered and stored together, let be in different proportions as dependent on species (Table 11.4).

The finding of Vesterdal and Raulund-Rasmussen (1998) relates to a period that may correspond to a certain stand age (30 years). Assuming that soil properties affect the soil microorganisms, such effects may decrease as a humus layer develops and the immediate environment for the microorganisms change. Although this may take some time, it may mean that we cannot exclude the possibility to find well-developed humus layers under deciduous stands also on rich soils.

11.6 Humus Layer Stability versus its Turnover

A relative stability or a slow decomposition is, in general terms, a condition for the accumulation of humus. We discussed (Sect. 10.2) the relative stability of the organic matter at the limit value.

Berg and McClaugherty (2003, 2008) discussed four main classes of humus turnover or disturbed stability. First, there is humus decomposition in completely undisturbed humus. Further, there is decomposition associated with elevated microbial activity, one being caused by a strongly activated mycorrhizae, a third due to mechanical disturbances caused by soil manipulation and drainage leading to radically higher decomposition rates. Finally, high rates of humus turnover have been observed in humus subjected to very high N inflows.

We have not found any studies of humus decomposition or stability relating to causal factors in really undisturbed soil systems. However, Berg and Matzner (1997) reported a study on respiration rates from humus cores, incubated in the laboratory under standard temperature and moisture conditions. Humus samples with differing N concentrations showed very different respiration rates that were negatively related to concentration of N in humus (Fig. 10.3). If we consider the respiration rate as measure on stability/instability of the humus fraction, we may conclude that the stability increases with increasing N levels; still, our conclusion is limited to the set of measured data.

11.7 Carbon in the Mineral Soil

The amounts of carbon in mineral soil in the boreal forest are estimated to be up to 60 times that in the organic layers although there is a high variation among sites. Further, it is considerably more stable to degradation (DeLuca and Boisvenue 2012).

11.7.1 Does the Amount of Organic Matter in the Mineral Soil Change?

The storage or sequestration of carbon in the mineral soil appears to follow another pathway than that in an organic layer. Berg et al. (2008) suggested the term

'secondary sequestration' (Fig. 11.1). Later, De Marco et al. (2012) presented an example of two forest stands, one with black pine and the other with black locust where the former mainly formed a clear humus layer on top of the mineral soil and the black locust stand appeared to have a higher fraction stored in the mineral soil. The sequestration patterns thus were different, supporting different pathways. This may illustrate that one species/genus may cause sequestration in an organic layer and another may produce organic matter that is less stored on top of the mineral soil, but possibly, in part degraded and solubilized components are precipitated in the mineral soil.

Investigations have been made as regards changes in the C amounts in mineral soil with time, and even long-term investigations give about no measurable change. In a temperate mixed deciduous forest (MAT c. 12 °C), Kiser and Johnson (2009) did not see any large-scale change in amount over a period of c. 30 years. Working in a watershed in Tennessee (USA), they had identified 8 soil types, and when taking an average, no increase was found. However, subdividing their data according to soil type gave new information. They found significant changes in carbon concentration and amount in the top 10 cm of the mineral soil. Their data show that even within a limited area of 94 hectares, there may appear significant both increases and decreases.

Another study (Johnson et al. 2007) from a watershed in the same region gave variable results. Over 30 years, there was an increase in the upper 0–15 cm of the mineral soil in most cases and a high variability.

11.7.2 Organic Matter Mixed into the Mineral Soil

One of the first long-term studies to examine the effects of soil properties on decomposition was that by Jenkinson (1977). He examined the decomposition of ^{14}C-labeled ryegrass in a variety of soils. In these soils, clay content ranged from 5 to 21 %, pH from 3.7 to 8.1 and organic C from 0.97 to 4.57 %. He found that neither organic matter content nor pH had much impact, except that decay was initially slower in the most acidic (pH 3.7) soil. On the other hand, soil texture was an important factor, with more litter-derived C retained in soils with higher clay content. Similarly, the total soil organic matter levels were less in sandy soils (14 %) than in soils with more clay (up to 29 %). This suggests that mineral soils with clay are able to hold onto more biologically degradable SOM than are sandier soils. Several mechanisms could account for the influence of soil texture on decomposition.

Because soil texture is so closely related to soil water dynamics, Scott et al. (1996) undertook a study to examine the effects of both soil texture and soil water pressure. They made artificial soils by blending soils collected from the field. Their soils had sand contents of 40, 55, and 73 %. In each of these soils, they regulated water at −0.012, −0.033, and −0.30 MPa. This combination of treatments yielded a continuum of water content that they described with a single variable, percentage

water-filled pore space. Soil texture had no effect on the decomposition of wheat litter. However, there was an interaction between soil texture and water pressure, such that the effect of water pressure was negligible in the sandy soil and was greatest in the loam soils. Also, noteworthy was that the effects of soil texture and water pressure on litter decomposition were very much less than their effects on the decomposition of the older C that was already in the soil.

We conclude that soil texture is more important for long-term organic matter dynamics than for initial phases of decay. Not surprisingly, finer-textured soils will interact with water more than coarser-textured ones. As a result, water levels generally influence decay relatively little on sandy soils, but have a significant effect on loams or finer-textured soils.

11.7.3 Is There any Effect of Disturbance?

There appears to be different dynamics of humus (carbon) in different soil layers, and to illustrate this, we have selected a study carried out in stands of Norway spruce and common oak (Vesterdal et al. 2002). Using the same stands, the authors followed the concentration of carbon in the organic layer and in three layers of mineral soil, namely at 0–5, 5–15 and 15–25 cm. In the studied case, the concentration of newly stabilized carbon increased in the organic layer (Fig. 11.9) over a period of 29 years and in the top mineral soil (Fig. 11.10). However, in the two lower layers (5–15 and 15–25 cm), a decrease was statistically significant and in the magnitude of 250–290 kg carbon per hectare and year, respectively, for each of these two lower layers. The mineral soil had been plowed before the stands were planted and that the concentration of carbon in the mineral soil is decreasing is very likely a consequence of that. That a disturbance of soil activates the soil microorganisms is well known to soil microbiologists, and Fig. 11.10 gives a

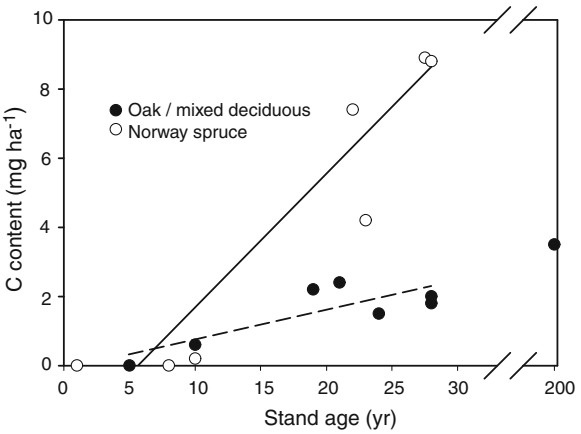

Fig. 11.9 Absolute amount of soil carbon in the organic layers in chronosequences of Norway spruce (○) and common oak (●) up to 29 years of age. All studies were carried out on the same soil and under the same climate. Redrawn from Vesterdal et al. (2002)

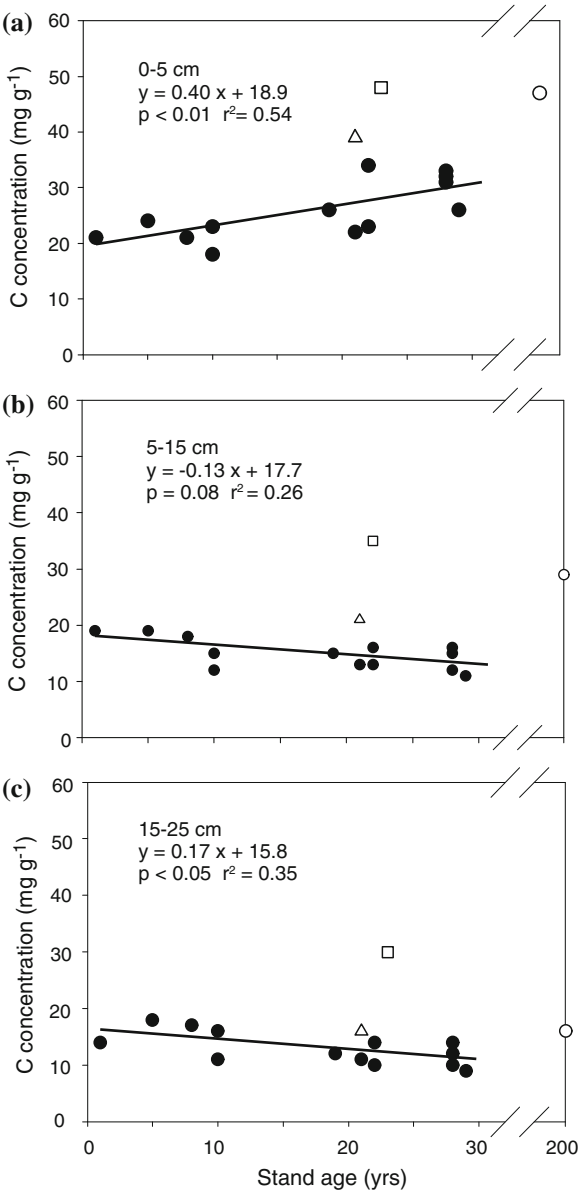

Fig. 11.10 Carbon concentration in three mineral soil layers in a chronosequence of Norway spruce (●) and an adjacent c. 200-year-old mixed deciduous plantation (○). One adjacent Norway spruce stand (□) was excluded from the regression. Permanent pasture (△)

quantification of this effect, resulting in a clear decrease in carbon concentration over at least 28 years since the disturbance. We have selected this study to illustrate this kind of effect, which also is likely after, for example, ditching or site preparation of a forest soil, allowing air (oxygen) to penetrate deeper soil layers.

We do not know the limitations of this effect, and the question remains whether a similar decrease in carbon in deeper soil layers is found after such disturbances as a clear-cut or after a forest fire. A consequence may be that there is a new formation of stable matter, whereas for old organic matter that has been disturbed, a degradation may take place.

Chapter 12
Estimating Carbon Sequestration Rates on a Regional Scale

12.1 Long-Term Accumulation of Carbon in Organic Layers (O Horizon): General Comments

In Chaps. 10 and 11, we discussed the fraction of litter that we considered stable and the buildup of a humus layer. Further, we discussed the accumulation of humus and its stability in single plots and in single stands. In our examples, we used the stable fraction (100-limit value) for one litter type, namely foliar litter, to calculate the amount of humus in a given stand. It is evident that humus layers are built up from different litter components, not only the foliar litter from the trees, although this litter component is a dominant one. Ideally, we should have used limit values for a whole set of litter components, at least the major ones and added stable fractions for litter components such as leaf litters from the ground vegetation, from moss, from other tree litter components such as cones and woody material, for example twigs. We can make the list longer. For a proper quantification, this is evident. Unfortunately, the available information to do this is lacking. The only litter component for which there exists reasonable information is the foliar one from trees, both as regards litter production and as regards the decomposition process. We have discussed the possible formation of stable humus from other litter components, and we cannot exclude that, for example, woody litter may produce just a small fraction. Litter production from, for example, moss is not really quantified and decomposition experiments lacking. Litter production from roots is also too little known, and decomposition experiments have so far not given unequivocal results in undisturbed systems.

The fact that we could reconstruct quantitative accumulation of mor humus for a period of close to 3,000 years (Sect. 11.2) using limit values and remaining stable fractions for foliar litter does not exclude the possibility that, at least in boreal coniferous systems, the foliar litter component is a major one as regards formation of humus in an organic layer.

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7_12,

Most decomposition studies are made on a short-term basis and give information with a short-term perspective, namely a few years. Sequestration of carbon is a process that is a result of the decomposition process, but should be observed and ideally studied over periods of centuries, millennia, or at least decades. In Chap. 11, we followed the C sequestration for smaller areas such as stands and short gradients, studied with a corresponding methodology, namely direct sampling and gravimetric determination. In this chapter, we have taken a further step and estimate the buildup of humus over a region. Further, we compare the results of an upscaling to a region to those of single stands. The specific region we use for the case study is the forested area of Sweden, and the stands for comparison are located over Scandinavia and Northern Europe.

When organic matter accumulates in boreal and temperate forest soils, two main fractions can be distinguished, functionally and spatially distinct and different. One fraction forms a more or less distinct organic layer, and the other is found in the mineral soil. These main fractions are best separated in mor humus and considerably less in mull. Focusing on our regional case study, the organic layer on top of the mineral soil (O horizon) is mainly a mor humus layer, which has facilitated or made the quantification of amounts over time possible.

The organic layer fraction may be built up rather quickly but is vulnerable to forest fires. With a natural fire frequency, sometimes as high as one every 50–60 years, organic layers at drier sites rarely have reached a mass of any magnitude. However, today's efficient prevention of wild fires has resulted in a significant general increase in the mass of the O horizon, and in smaller, isolated plots that have not been reached by fire, an accumulation over millennia may be found (cf. Wardle et al. 1997).

There appears to be very different mechanisms for the sequestration in an organic layer and in the mineral soil. These two main layers have different properties and different protection, and we may need to specify what we refer to. The organic layer on top of the mineral soil (e.g., a mor layer) is where the 'primary' sequestration takes place (Glossary, Appendix I), namely the accumulation of the stable fraction of litter. The carbon sequestered in the mineral soil is transported either in soluble form or as aggregates and precipitated in the mineral soil. Further, decomposing root litter gives an addition. It appears natural to call this a secondary sequestration (Berg et al. 2008). We have defined these concepts (Glossary, see also Fig. 11.1).

An often-expressed a priori assumption in ecosystem studies is that the system either is in or approaching a 'steady state,' a notion that has been effectively challenged by Botkin (1990). This is especially true as regards the amount of carbon or other materials found in the system, and this assumption deserves to be questioned. We have already discussed this (Sect. 11.2), and in this chapter, we develop the discussion to a region.

12.2 Influences on Carbon Sequestration Rates in Forested Land: Regional Level

12.2.1 Undisturbed Sites and Anthropogenic Influence

Some factors influencing the C sequestration rates over a region are evident, such as variation in climate, soil nutrients promoting tree growth, tree species, forest management, and N deposition, and we will discuss them briefly.

We discussed the concept of stable residue earlier (e.g., Sects. 2.6.3, 6.4) and that litter chemical composition influences the size of the stable fraction as defined by the limit value. When applied to single stands on relatively nutrient-poor soil, it has been possible to relate foliar litter fall and stable residue to humus accumulation rates with acceptable precision (Sect. 10.4.1). However, over a region, the number of factors that may influence the sequestration rate increases, variation in climate being a prominent one with warmer and wetter climates, giving, for example, a higher production of litter. Further on, climate also has an effect on litter chemical composition (Chap. 4). Also, tree species may vary with climate and with soil type, resulting in litter inputs of different magnitudes and of different chemical compositions.

Climate. Over a region, climate influences tree growth rate and litter fall (Liu et al. 2004; Berg and Meentemeyer 2002) and litter chemical composition both within species (Figs. 4.1, 4.3, 4.6) (Berg et al. 1995) and over species (Liu et al. 2006), normally resulting in higher concentrations of at least N with increasing MAT or AET. Decreasing concentrations of Mn have been observed with increasing AET and MAT (Berg et al. 1995, 2010). Further, AUR concentration appears to be positively related to that of N at least for some litter species (Fig. 4.2) (Berg et al. 2013).

Tree species. Different species produce foliar litter at different rates and have different substrate qualities, that is, different concentrations of Mn and N, which should affect limit values and the sequestered amounts of C (Sect. 10.3.2; Fig. 10.2) and could be expected as a significant factor over larger areas.

Soil nutrients and substrate quality. Over a region, the availability of nutrients may vary, both as regards N and as regards weathered nutrients. The bedrock may form a patchwork of properties as regards the mineral soil, which influences the availability of different nutrients through their concentrations and by pH. A soil richer in nutrients can promote a higher tree growth rate and thus a higher litter fall. Natural soil properties may vary violently even within small areas and create very different intensities in litter fall. Also, substrate quality will be influenced. We have discussed and focused on the effects of mainly N and Mn on the limit value and the stable fraction.

Anthropogenic factors. As regards forest management practices, they may vary and be different over a larger region. Ditching, site preparation, fertilization, clear-cutting, and other harvest policies can influence SOM accumulation. As far as we can tell, most forest management will clearly disturb the sequestration of soil carbon for evident reasons.

Site preparation may be done in different ways, and in some cases, the mineral soil is actually plowed just before planting the trees. The purpose is to activate the soil microorganisms and support a decomposition of organic matter and thus improves the nutrient supply. Such activation may have a long-lasting effect. In one study, an inventory of amounts of soil carbon in three soil layers was made in a chronosequence up to 29 years after site preparation. In the layer 0–5 cm, both the concentrations and amount of carbon increased, whereas in the layers 5–15 and 15–25 cm, both concentrations and amount decreased in the whole period. The top layer received a new inflow of carbon from decomposing litter, whereas the deeper layers did not (Fig. 11.10) (Vesterdal et al. 2002).

Clear felling means not only an interruption of the litter input but an additional disturbance of the upper soil layers including the absent root uptake of nutrients. Part of the decomposition process, namely that of newly shed litter, is removed, which results in an increase in soil pH and no addition of stable litter residue. Further, concentrations of available soil nutrients increase as well as the level of soil water. The absence of a growing forest and its influence on the soil, for example through the absence of root exudates, may change the properties of the remaining humus and influence its stability.

Nitrogen deposition/pollution may have a large-scale fertilization effect, possibly resulting in increased tree growth and litter production and an ensuing effect on SOM accumulation.

Afforestation and reforestation may mean an introduction of forest on land that has been agricultural; thus, on soil that may have been plowed, fertilized, and had crops over so long a time, the soil microflora may have been completely exchanged. It is possible that the soil simply has developed entirely new properties that may enhance or prevent decomposition of forest litter.

Although these factors are likely to be important, we have limited possibilities to discuss and quantify their effects here and will focus on the effects in natural and mainly undisturbed or less disturbed forests.

12.2.2 General Consideration as Regards a Database for Regional Modeling

For the upscaling of data to a region, we need forest information that is related to specific and identifiable geographical points and the information mentioned above may be part of such a database. The information should be organized into grid cells

of a useful size such as those normally found in, for example, a national grid net. The grid cells could have different size depending on circumstances, for example 1 or 100 km^2. The total information associated with each cell can vary, but examples on information useful to our purpose would be tree species, stand age, some measure of stand density, the fraction of each cell covered by forest, and possibly soil data. It may be necessary to add information, for example estimated litter fall or climate factors.

Our case studies to estimate humus buildup and carbon sequestration will be different in character, and the databases thus will be different. Because much of the data utilized for each case study is unique, the databases will be discussed separately.

12.3 Two Case Studies

We present two very different case studies for the same region. The first one demonstrates carbon sequestration using data on *actual increases in humus depth as measured over* 41 years (Sect. 12.4). In the later section, we use the concept of *stable residue* (*limit values*) in decomposing litter and discuss an approach that can explain a potential buildup (Sect. 12.6).

Direct measurements of humus depth. In this case study, we present a method to evaluate direct measurements of humus depth over time, an approach that includes the effects of forest management and disturbance. The average measured accumulation rate is thus a net rate including the site-specific effects of wild fires, climate change, and forest management, such as site preparation.

Humus depth was thus measured at a high number of plots (tracts) over time, transformed to an area using Kriging for grid-net units and related to time for each such unit. In a last step, a transformation to amount of carbon was undertaken.

Stable residue. The discussion about a stable residue (limit-value) approach includes quantitative litter fall and litter quality as factors that influence the buildup of the O horizon. Effects of wild fires, forest management or other disturbances, and possible effects of mineral soil properties are not included. The calculations are based on foliar litter fall in mature stands and do not include the clear-cut phase. We may consider this a theoretical approach based on the assumption that all sequestration takes place in an organic layer (primary sequestration; Fig. 11.1).

As our estimates are based only on foliar litter, they would be expected to underestimate accumulation. In all cases, the estimated accumulation should be considered as order-of-magnitude estimates and serve to illustrate the potential for carbon sequestration in a particular forest as contrasted with the actual accumu-

lation. However, we will offer some validation data to support the reasonableness of the estimates. We call this accumulation 'potential,' because the calculations cannot at this level include all possible effects of forest management and other disturbances and thus rather would give the potential accumulation.

12.4 Case Study for a Region: Direct Measurements of Humus Depth

12.4.1 Background

The amount of humus in, for example, a mor layer or in an O horizon may vary considerably also within a relatively small area, often making it difficult or even impossible to determine the amount with any accuracy or to follow a change in amount over time. Well-defined profiles as found in mor humus developed on sediment soil may give a relatively good basis for such determinations, whereas humus developed on till soil or perhaps on a slope will create a more difficult situation or even an impossible one.

With a high enough number of measurements over a long time, this kind of problem may be overcome, at least to some degree. In contrast to small-scale measurements (Chap. 11), the methods to cover a larger area may be different, and for example, a high number of repeated humus depth measurements may make it possible to cover a whole region.

In 1961, long-term measurements started in Swedish forested land: simple registrations of humus depth that were combined with chemical analyses of humus samples and determination of bulk density. In 2002, more than 800,000 single measurements had been made rather evenly distributed over a 41-year period and an evaluation was initiated. These values will serve as the foundation for our case study.

In this region, covered by the case study, there were just two tree species that dominated, namely Scots pine and Norway spruce, often in monocultures. In the database, the dominant species as determined by basal area was given for each of the measurement spots. Berg et al. (2009) also included a third type of forest called 'all species,' which includes all possible combinations of species, including, for example birch spp. This type also provided the rate that is representative as an average for the whole country. When presenting general representative data, the numbers for this 'all species' alternative are used.

12.4.2 General Design of the Humus Inventory

Annual direct measurements of humus depth were taken over a period of 41 years. The absolutely most common type of humus layer is the mor, and a clear O

horizon was distinguished in all the cases used. Below, we discuss humus accumulation and carbon sequestration taking place in the humus layer on top of the mineral soil (primary sequestration).

In a first evaluation of humus accumulation rates, Berg et al. (2009) limited the analysis to podzols. A total of more than 800,000 single determinations of depth were made, resulting in a total of 127,139 average values for humus depth, each value being an average of at least five simple measurements. Of these, Berg et al. (2009) used 82,513 values for podzols.

The measurements of humus layers in this approach were taken in four separate inventories in the periods 1961–1972, 1973–1975, 1983–1987, and 1993–2002 (data on http://www-markinfo.slu.se). The sample plots were chosen randomly within a predetermined sampling pattern, and each year, 10–20% of the plots were sampled. Humus depth was measured, and at the same spot, a sample of the O horizon was taken and used for carbon analysis and bulk density determinations.

The measurements were taken in forests that were, and still are, subject to forest management practices such as site preparation, which has been ongoing since the 1960s. Newly planted stands were included, encompassing afforestation of agricultural land. No data were collected on mires, and the humus on practically all plots can be classed as mor.

12.4.3 Scaling up from Field Measurements on Humus Depth in Plots to C Sequestered on Country Level: Overview

The 82,513 measurement values distributed over the country were converted to values for grid cells in the national grid net by using Kriging interpolation. Thus, the measured depths were converted to average values for amounts of sequestered carbon in grid cells with a dimension of 25 × 25 km (Fig. 12.1). The calculation for each grid cell can be described in three steps. First, the increase in humus depth was determined over the 41-year period (e.g., Fig. 12.2). Second, the bulk density of humus given as amount of carbon per mm and hectare was calculated over time. In a third step, using bulk density and carbon sequestration, the increase in amount of carbon was calculated and given as kg per hectare and year. This sequence is given in Fig. 12.4a, b, c.

Humus-layer thickness. The thickness of the humus layer in each 25 × 25 km grid cell was calculated for each year as a weighted average using humus depth from all sampling plots located within a circle with a radius of 55 km (Fig. 12.1). The rates for increase in humus thickness (humus accumulation rates; given as mm per year) were then calculated for each of the 25 × 25 km grid cells by using a linear relationship between time and the thickness of the humus layer (Fig. 12.2). For the whole country, Berg et al. (2009) obtained 460, 505 and 548 such linear relationships for stands dominated by (1) Norway spruce, (2) Scots pine, and (3)

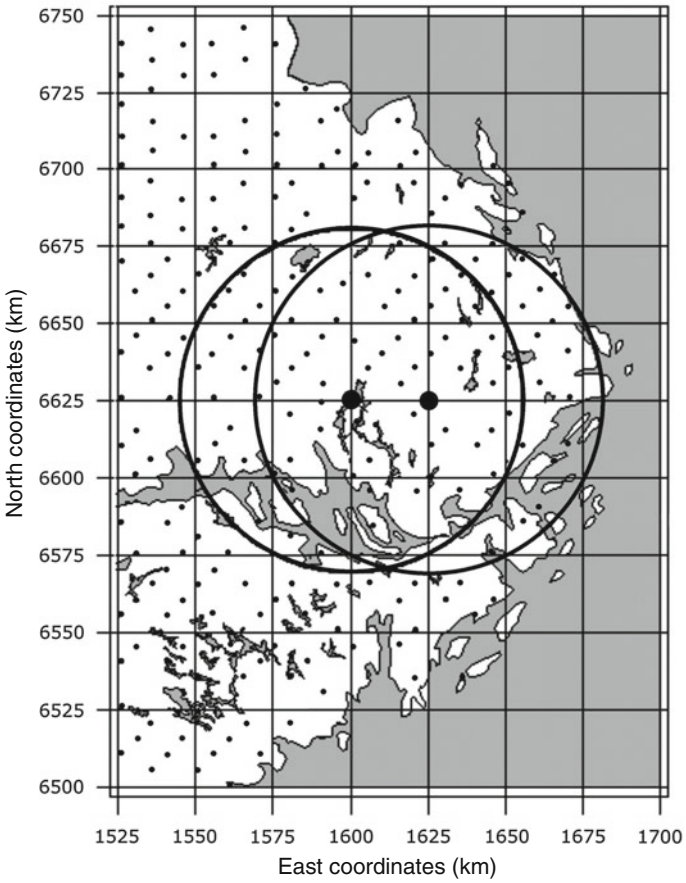

Fig. 12.1 Illustration of the use of the national Swedish coordinate system with intersection set at a distance of 25 km. Each intersection is the center of a circle with a radius of 55 km (marked with full line). All sampling plots located within such a given circular area were used for calculating the humus depth at the intersection, viz. the center of the circle. This spot was considered to be the center of a new quadrat (25 × 25 km) and represents the humus depth for that one. The calculated thickness of the humus layer in each intersection is a weighted mean using humus depth from all sampling plots located within the circle. Gray areas represent lakes and the Baltic. The black spots at uniform distances indicate sampling plots clustered together in tracts. From Berg et al. (2009)

stands without species dominance, 'all species' (Table 12.1). In this approach, only three groups were used, the third group, 'all species,' reflecting an average value over all species combinations.

Humus depth converted to carbon. Using bulk density for humus in each sampling plot (tract) as well as C analysis, they converted the annual increase in humus depth to increase in sequestered carbon. This was done separately for each of the grid cells.

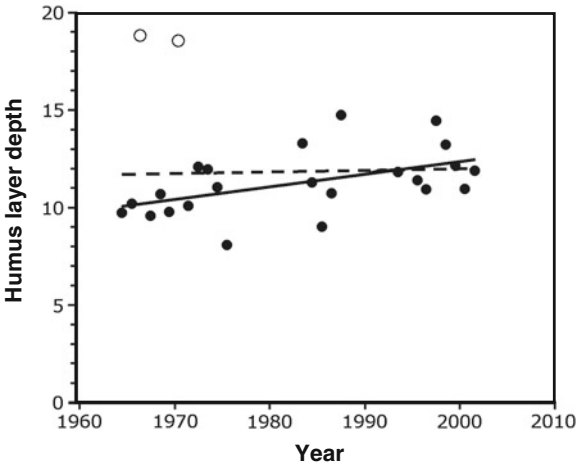

Fig. 12.2 An example of linear relationship at an intersection (cf Fig. 12.1) with humus-layer thickness related to time for both retained observations (*solid line*) and all observations, including those with too extreme studentized deleted residuals (*open circles, dashed line*). From Berg et al. (2009)

12.4.4 Changes in Organic Layer Thickness over Time

12.4.4.1 Overview to the Whole Case Study Region

The country was divided into three main zones based on temperature sum (Fig. 12.4), namely one with temperature sum >1,249 degree days called zone High and one with temperature sum between 850 and 1,249 degree days called zone Medium. Finally, zone Low was defined as those areas with a temperature sum of <850 degree days. These zones as well as their names may refer to tree growth and litter fall as well as humus growth, but the values for temperature sums were taken arbitrarily.

Humus-layer growth rate. Berg et al. (2009) obtained a clear demonstration of humus-layer growth rates by comparing data for the three main climatically different zones 'Low,' 'Medium,' and 'High' (Fig. 12.3). Using non-parallel lines for these zones, they illustrated that the humus layers were thicker in the southern third of the country with 7.19 cm (zone High) and 6.40 cm in zone Medium as compared to zone Low with 5.27 cm already before the measurements started. This initial thickness in humus layers is significantly different among the three zones.

All values from all four inventories are shown in Fig. 12.3, giving highly significant linear relationships with time, each zone having a linear relationship. Berg et al. (2009) assumed non-parallel lines in their model and obtained three linear relationships with the slope for zone High significantly steeper than for zones Low and Medium, which were not significantly different. The model was highly significant ($p < 0.0001$; F-test; $n = 83$) with $R^2 = 0.819$.

For 'all species,' the mean annual increase in humus-layer thickness is shown for the three zones based on temperature sum and differing in both climate and tree species composition (Fig. 12.4a). Zone High has a dominance of Norway spruce

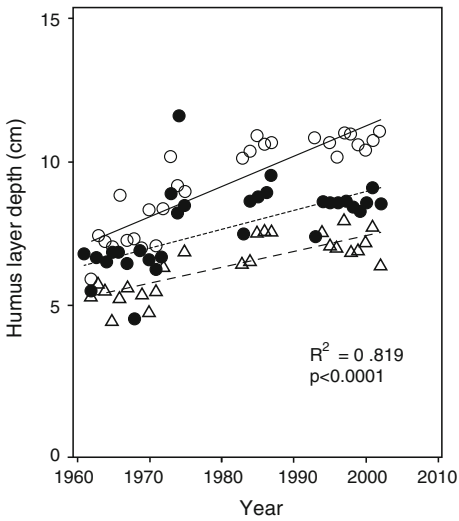

Fig. 12.3 Linear relationships for humus depth against time using non-parallel lines. Mean values for humus depth for each zone (*High, Medium,* and *Low*) are calculated on an annual basis, with each value being mean of 62–3,626 recorded average values. The slope coefficients are 1.05 mm (O——) for zone High, (● - - - -) 0.65 mm for zone Medium, (Δ - - - -), and 0.57 mm for zone Low. The *F*-test against non-parallel lines showed a significant result ($p = 0.0041$). From Berg et al. (2009)

and deciduous trees, zone Medium has Norway spruce and Scots pine without dominance, and zone Low has a dominance of Scots pine.

The estimated slope of 1.05 mm year^{-1} for zone High was significantly different from the estimates 0.65 mm year^{-1} of zone Medium ($p = 0.01$) and 0.57 mm year^{-1} of zone Low ($p = 0.002$). The difference between Medium and Low was not significant ($p = 0.60$).

There was a clear indication that this pattern is maintained over time. Thus, in zone High, the humus layers had increased to an average value of 11.39 cm in the last inventory (covering 41 years), which is significantly higher than in the first inventory (7.19 cm). In zone Medium, the increase was significant in the same 41-year period with an increase from 6.40 to 9.00 cm. Also, in zone Low, the increase was significant with an increase from 5.27 to 7.56 cm (Fig. 12.3). Based on this information, we can conclude that the measured humus-layer thickness has increased in general over large parts of Sweden in the studied period. The growth rates of the humus layer in the 41-year period ranged from c. 0.1 mm year^{-1} to $>$ 1.6 mm year^{-1} among the 25 $\times$ 25 km grid cells. The pattern is patchy, but there is a general tendency to higher growth rates in the warmer zone as compared to the more northern with a lower temperature sum.

Areas with a decrease in humus-layer thickness were found in zones Medium and High (spruce) and for pine in the northernmost part of zone Low.

12.4.4.2 A General Tendency for Organic Layers to Increase with Time

In addition to the distribution of significant ($p < 0.05$) and non-significant relationships, Fig. 12.5 also gives areas without forest, indicated by white. Thus, in the

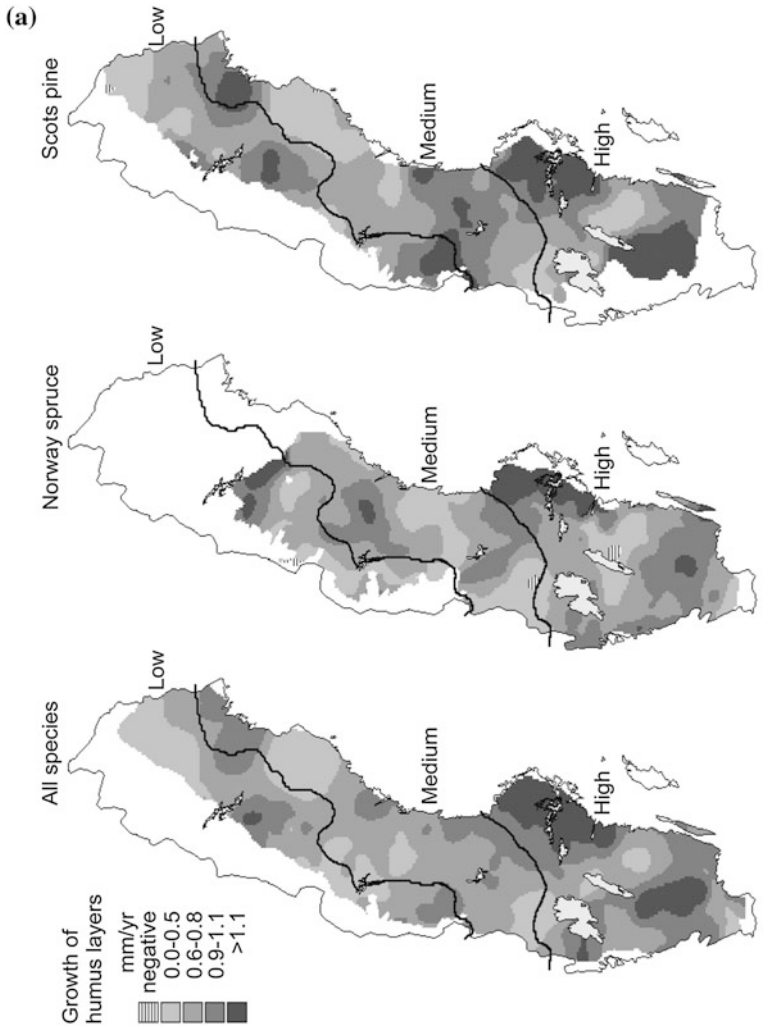

Fig. 12.4 The forested land was divided into three zones based on temperature sum, namely a zone with temperature sum >1,249 degree days called zone High, one with a temperature sum between 850 and 1,249 degree days and called zone Medium. Finally, zone Low was defined as those areas with a temperature sum of <850 degree days. There was also a subdivision of the area based on tree species. The map denoted 'all species' gives data for Norway spruce, Scots pine, and deciduous forests in mixed or in monocultural stands, while the maps denoted 'Norway spruce' or 'Scots pine' show areas where these species dominate. **a** Annual rate of increase in the humus layer. **b** Amount of carbon per mm humus layer and hectare (calculated from bulk density and C concentration). **c** Annual rate of carbon sequestration in the humus layer in Swedish forests in the period 1961–2002. (cf. Fig. 12.8). From Berg et al. (2009)

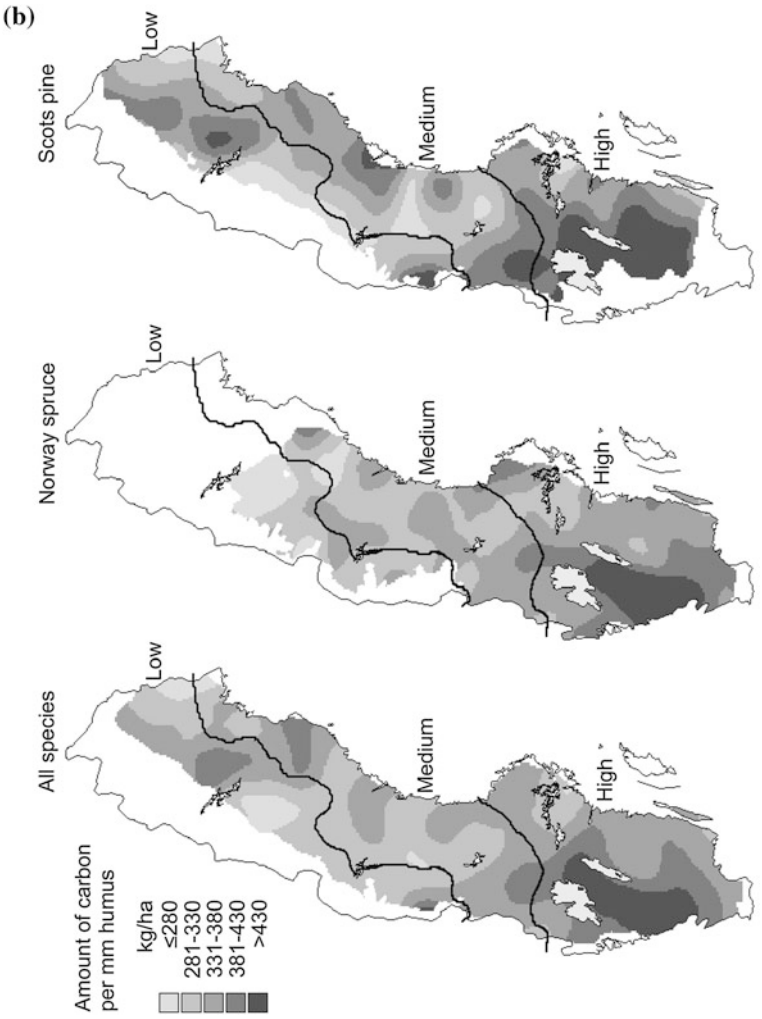

Fig. 12.4 continued

northwestern part is a mountain range with land classed as not forested. On low-nutrient soil in northern Sweden, there is too little Norway spruce planted to allow a separate evaluation. Likewise in the southwest, on richer soil and a wetter climate, Norway spruce dominates and very little Scots pine is growing.

There is a general tendency for the average thickness of the organic layer to increase with time. The areas with statistically significant increases in humus depth (cf Fig. 12.2) are distributed all over the country (Fig. 12.5). Within a dominant part of the country, the linear relationships, in some cases corrected by removing outliers, are statistically significant (Table 12.1, Fig. 12.5), providing evidence of a change in the humus-layer thickness.

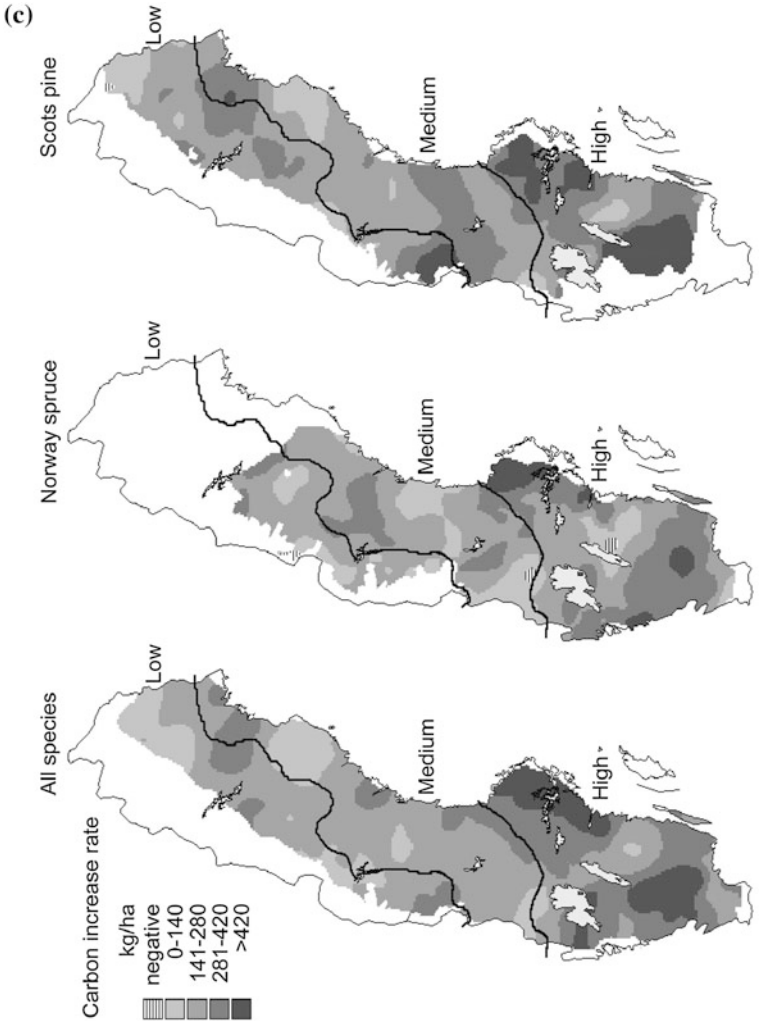

Fig. 12.4 continued

The three main areas with non-significant relationships in zone High (Fig. 12.5; all species) have long-term agricultural traditions, but since the 1960s, an extensive and ongoing afforestation is taking place. In zones Low and Medium, the relatively slow forest growth results in low litter fall and a low humus—accumulation rate that may explain the non-significant accumulation rates in these zones (Fig. 12.5). The 'all species' forest represents the whole forested area investigated, meaning that all combinations of species were evaluated together.

Table 12.1 Number of linear relationships for humus depth versus time for Scots pine and Norway spruce–dominated forests (basal area) plus forests encompassing all combinations of tree species

	Number of intersections (% in parenthesis)			C sequestration rate (kg ha^{-1} year^{-1})			
Tree species	Total	Significant	Non-significant	Mean	SD	Min	Max
All species	548 (100 %)	461 (84 %)	87 (16 %)	251	113	16	690
Positive relationships	548	461	87				
Negative relationships	0	0	0				
Spruce-dominated[a]	460 (100 %)	291 (63 %)	169 (37 %)	239	130	104	1,226
Positive relationships	456	291	165				
Negative relationships	4	0	4				
Pine-dominated[b]	505 (100 %)	422 (84 %)	83 (16 %)	283	158	34	1,187
Positive relationships	503	422	81				
Negative relationships	2	0	2				

The average C sequestration rate for each type is given. Cf. Fig. 12.4. From Berg et al. (2009).
[a] >70 % Norway spruce by basal area.
[b] >70 % Scots pine by basal area.

12.4.4.3 Humus-Layer Growth Rates Appear to be a Patchwork

The areas with high growth rates of the humus layers are found in Scots pine forests, whereas the humus layer of Norway spruce–dominated stands grows more slowly. We can compare this to the observation of Berg and Meentemeyer (2001) as recalculated by Akselsson et al. (2005) that foliar litter fall as a function of MAT is higher in Norway spruce forests (Table 12.2).

Scots pine. For pine-dominated forests, Berg et al. (2009) obtained a range of rates for humus-layer increase ranging from approx. 0.1 mm year^{-1}, mainly in the northern parts of the country, to 1.6 mm in the southeastern parts of zone Medium and northeastern parts of zone High (Fig. 12.4a). Pine forests in the central parts of zone High also had a humus layer with a growth rate above 1.1 mm year^{-1}. Areas with values in the range 0.9–1.1 mm year^{-1} were distributed all over the country. The relatively large white areas (Fig. 12.4a) indicate too few Scots pine-dominated stands to allow an evaluation, as pine is less common in coastal and maritime areas in the western parts of zone High. The small area with negative relationships in the northernmost part of zone Low (Fig. 12.4a) corresponds to the two intersections given for pine in Table 12.1.

Norway spruce. For forests dominated by Norway spruce, a range of annual humus-layer increase rates were seen ranging from a few negative values to a minor group with rates >1.1 mm year^{-1}, the higher rates applying for smaller areas. Like for pine, high rates were seen in the in the northeastern part of zone High (Fig. 12.4a), a former agricultural area. A small area with decreasing humus-layer thickness was found in the central parts of zone High, and a small area on the border between zones High and Medium, in all 4 intersections. The large white areas are due to a too low frequency of spruce forests to allow an evaluation.

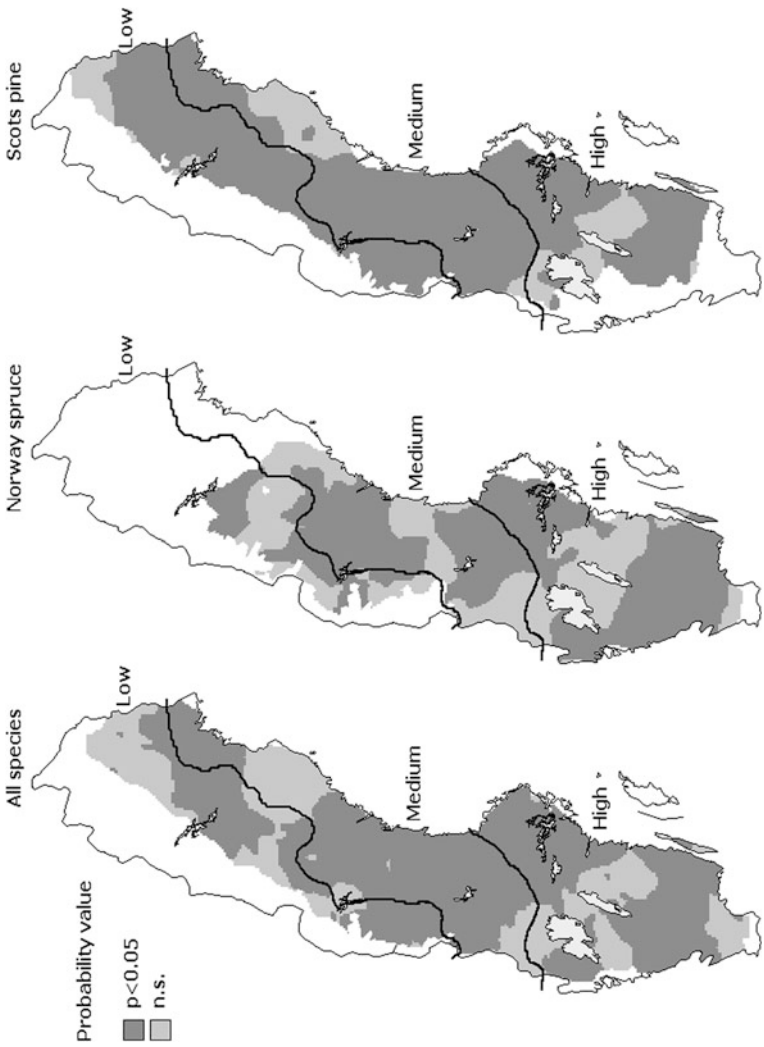

Fig. 12.5 Significant rates of increase in humus layer thickness ($p < 0.05$) as measured over 40 years. No decrease was statistically significant. The map denoted 'all species' gives data for Norway spruce, Scots pine, and deciduous forests in mixed or in monocultural stands, while the maps denoted 'Norway spruce' or 'Scots pine' show areas where one of these species dominate. (cf Table 12.1)

12.4.5 Calculations of Carbon Bulk Density in the Humus Layer

In the conversion of humus-layer growth (mm $year^{-1}$) to C accumulation rate (kg C ha^{-1} $year^{-1}$), bulk density and C analysis were used to calculate 'carbon bulk density' (kg C mm^{-1} humus ha^{-1}). For this purpose, Berg et al. (2009) used the bulk density and carbon analysis made at each sampling point and transformed the bulk density determined for humus to carbon density.

The carbon density varies over the country with a factor of 2 (Fig. 12.4b). The values for humus density used were in all cases based on local samples, and a clear variation was seen with species all over the country, with the highest density found in zone High.

12.4.6 Calculated Carbon Sequestration Rates and Some Patterns

12.4.6.1 General Comments to the Whole Case Study Region

In a third step, the humus growth rate (mm $year^{-1}$) was converted to increase in amount of carbon (kg C ha^{-1} $year^{-1}$) by simple multiplication with carbon bulk density (kg mm^{-1} $ha^{-1)}$ (Fig. 12.4c). Berg et al. (2009) thus converted the rate of increase in humus-layer depth to annual increase in C storage (C sequestration) (Fig. 12.4c). They obtained significant relationships (*t*-test; $p < 0.05$) for C sequestration rates, ranging mainly between 140 and 420 kg C ha^{-1} $year^{-1}$.

General patterns in high and low rates. The maximum rates for spruce-dominated and pine-dominated areas as well as for 'all species' were determined using the 25 × 25 km grid cells (Fig. 12.1; Table 12.1) and found to be 1,226, 1,187 and 690 kg C ha^{-1} $year^{-1}$, respectively. The average rate for the 'all species' group was 251 kg C ha^{-1} $year^{-1}$ (SD = 113). This is also the rate that is representative as an average for the whole country.

Areas with low sequestration rates (lower than 140 kg C ha^{-1} $year^{-1}$) were almost exclusively found in zones Low and Medium (Fig. 12.4c). The main part of zone High had C sequestration rates above 281 kg C ha^{-1} $year^{-1}$, including an area with rates above 420 kg C ha^{-1} $year^{-1}$ and only two small areas with rates below 140 kg C ha^{-1} $year^{-1}$. Again, the white zones indicate too few sampling plots to allow calculation of the sequestration rates.

Areas with high sequestration rates were larger in pine-dominated forests than in spruce-dominated ones. Pine-dominated forests in the northeastern and central parts of zone High had a very high sequestration rate of more than 420 kg C ha^{-1} $year^{-1}$.

Spruce-dominated forests showed a very different distribution as compared to pine-dominated forests, and there was only one main area with sequestration rates

higher than 420 kg C ha^{-1} $year^{-1}$, located in the northeastern part of zone High. Two areas indicated a decrease, and a number of small areas had rates lower than 140 kg C ha^{-1} $year^{-1}$ (Fig. 12.4c).

In areas that had a significant humus accumulation rate (Fig. 12.5), the carbon sequestration rate ranged from less than 140 kg C ha^{-1} $year^{-1}$ to more than 420 kg C ha^{-1} $year^{-1}$. The maximum C sequestration rate in the same group was 696 kg ha^{-1} $year^{-1}$.

Relationship between net sequestration rate and temperature. The rate of C sequestration for 'all species' forests did not show any evident pattern over the country, although there was a positive linear relationship with the temperature sum ($R^2 = 0.29$; $n = 548$; $p < 0.0001$). The range in MAT for this region was c. −1.7–7.4 °C.

12.4.6.2 Carbon Sequestration Rates: Scots Pine versus Norway Spruce Forests

In the forested area studied, the two coniferous species, Scots pine and Norway spruce, dominate and we may evaluate the ecosystems as defined by this dominance. The average rates were 239 kg C ha^{-1} $year^{-1}$ (SD = 130) for Norway spruce-dominated forests and 283 kg C ha^{-1} $year^{-1}$ (SD = 158) for Scots pine-dominated forests.

Pine-dominated forests in the southern part of zone High showed a very high increase rate for stored carbon with >420 kg C ha^{-1} $year^{-1}$. Also, in pine forests in the northeastern parts of zone High, the increase rate was high, ranging from 281 to above 420 kg C ha^{-1} $year^{-1}$. The maximum C sequestration rates obtained were 1,226 and 1,187 kg ha^{-1} $year^{-1}$ for the forests dominated by spruce and pine, respectively.

Direct comparison of sequestration rates—Scots pine versus Norway spruce. It appears that Scots pine forests on the average can sequester more C in humus layers than those with Norway spruce. Berg et al. (2009) made a special comparison of carbon sequestration rates for the humus layer in pine-dominated forests as compared to spruce-dominated forests. A condition was that each 25 × 25 km grid cell used in the comparison (the same intersection; cf Fig. 12.1) must have both groups represented. They thus used only those 25 × 25 km grid cells in which plots with both kinds of domination were found and obtained 348 areas that fulfilled this condition. In these cells, the difference in C sequestration rate in the humus layers in Scots pine and Norway spruce forests was on average 71 kg C ha^{-1} $year^{-1}$ (SD = 161; $p < 0.0001$; paired t-test). The stands were located under similar climate conditions (temperature sum).

This comparison was made using only zones within which both forest types were represented by a sufficient number of plots to allow a comparison. Scots pine stands were located on soils typical for planting pine and Norway spruce on soils on which spruce normally is planted. The values calculated by Berg et al. (2009) thus represent sequestration rates under actual conditions integrating climate and

soil properties but do not show the capacity of the pine or spruce ecosystem as such.

It is worth emphasizing that the values for ecosystems represented by single tree species, namely Scots pine and Norway spruce ecosystems, give very different values, namely 283 and 239 kg C ha^{-1} $year^{-1}$ when determined for the whole forested area (Table 12.1). These two latter values are not average values for the species as such over the country but rather representative for two types of ecosystems and as such they may give some guidance to studies on the capacity of different humus layers to sequester carbon. The typical Scots pine system has a more open canopy, and the inflowing light allows rich ground vegetation that normally covers the ground completely. This may be, for example, mosses, heather, cowberry and bilberry or herbs, and grasses. In Norway spruce ecosystems, we normally find such dense canopies that the sparse light reaching the ground may support considerably less ground vegetation. In earlier chapters, we have discussed the possible humus contributions from woody litter components from the trees and from roots. We cannot exclude that the difference in ground vegetation may explain part of the difference between these two systems, especially as both have about similar amounts of woody components and Norway spruce in addition has a somewhat higher foliar litter fall.

If this reasoning holds, we may speculate that if such woody components as branches give very small inputs to the sequestered carbon, then this may be a similar contribution for both spruce and pine forests. The 239 kg C per hectare and year sequestered in Norway spruce forests may be realistic to compare to the average value of 180 kg C ha^{-1} $year^{-1}$ as estimated by the limit-value approach based on needle litter fall only (below; Sect. 12.6).

12.4.7 Possible Sources of Error in Estimates of C Sequestration Rates

The present case study was made in forests that were and still are subject to management, including clear felling, site preparation, and ditching. This method to determine sequestration rates, in contrast to the theoretical limit-value approach, includes both inputs and losses and can thus be considered to give a net sequestration.

This means that the direct measurement approach registered a net increase in humus and carbon. Management practices such as site preparation and ditching initiate and stimulate microbial activity and increase humus decomposition and have been in practice since 1960s. In spite of this, there is a general annual increase in the humus layers of at least 0.57 mm (zone Low) and up to as much as 1.05 mm per year in zone High (Fig. 12.4a). Considering that there appears to be an effect of forest management on humus-layer thickness, the actual growth rate

should be considered a net rate and probably an underestimate of the potential accumulation.

A technical error source in this method is also afforestation of old farmland. A certain plot that is registered as farmland is not included in the measurement system until it is planted. Directly after plantation, it is classified as forested land and humus-layer thickness are determined. With a minimum layer to be recorded, its contribution to the average for, for example, a 25 × 25 km grid cell thus results in a lower total increase. With several newly planted plots, this can cause a significant decrease (in average value) although all humus layers actually grow. Often, such farmland is planted with spruce which may explain the higher number of non-significant relationships for spruce.

12.5 Carbon Sequestration in Mineral Soil. Observations on a Regional Scale

12.5.1 Different Sequestration Patterns?

Sequestration in the mineral soil appears to go more slowly than the more readily measurable one in the organic layers, and on a regional scale, we have rather found inventories of amounts than indications of rates of change. It is not our intention to review the sequestration process in mineral soil, and we just intend to illustrate the connection between the primary and the secondary sequestration. We give a case study for the forested land of Sweden and may therefore directly compare the accumulation in the humus layer to that in the mineral soil.

The carbon bound in mineral soil has been suggested to be more protected than that in a humus layer. For example, mechanical disturbance and fire will primarily affect the organic layer. Still, there appears to be influences that may affect the carbon in the mineral soil, too. A recent report (Stendahl et al. 2010) adds useful information to our case study and appears to demonstrate that the primary and secondary sequestration may be related to tree species, and we have included these as an illustration.

We commented (above, Sect. 12.4.6) that the measured amounts of C in humus layers were significantly higher in pine-dominated forests as compared to those dominated by spruce.

New regional measurements on amounts in mineral soil in stands dominated by pine or spruce (Stendahl et al. 2010) over Sweden indicate a significantly higher storage in the mineral soil under spruce than pine ($p < 0.001$). Some parts of the sequestration pattern were similar and thus increased the amount of sequestered C with temperature sum (Fig. 12.6). This appeared to be most noticeable for pine. However, in both cases, the amount stored to 100 cm depth (O horizon plus mineral soil) increased with temperature sum. Stendahl et al. (2010) divided the sampling sites according to temperature sum and found that for each single group,

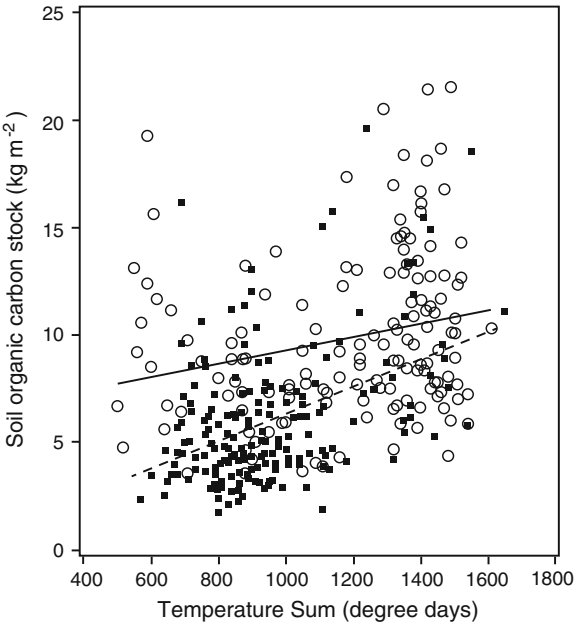

Fig. 12.6 Linear relationship between soil organic carbon (SOC) stock in the 0–100 cm soil layer and temperature sum for Scots pine plots (■ —) and Norway spruce plots (o —). The difference in slope was significant ($R^2 = 0.319$; $p < 0.001$). Figure from Stendahl et al. (2010)

spruce had higher sequestered amounts when both humus layer and mineral soil were considered (Fig. 12.7).

We thus cannot exclude that primary and secondary sequestration may be related to tree species. We have discussed this earlier (Sect. 11.7.1) for two systems (De Marco et al. (2010), namely with black pine and black locust. A simple reasoning thus gives that with Scots pine stands sequestering most in the humus layer and Norway spruce stands less, a higher total sequestration in spruce forests means a higher sequestration in the mineral soil.

12.5.1.1 Carbon Dioxide Budgets and a Case Study

For a limited area in zone High where Berg et al. (2009) measured high sequestration rates (Fig. 12.4c), it has been reported that the soil is a C source, as judged from net ecosystem exchange measurements of CO_2 in 1995–1997 (Valentini et al. 2000). With an estimated C sequestration in the humus layer of more than 420 kg C ha^{-1} $year^{-1}$ for the area, losses of more than 1,000 kg C ha^{-1} $year^{-1}$ from the mineral soil should occur to explain the source strength by Valentini et al. (2000). The authors attributed this unexpected loss of soil C to past soil drainage in the footprint area of their measurements. However, in a later study by Lindroth et al.

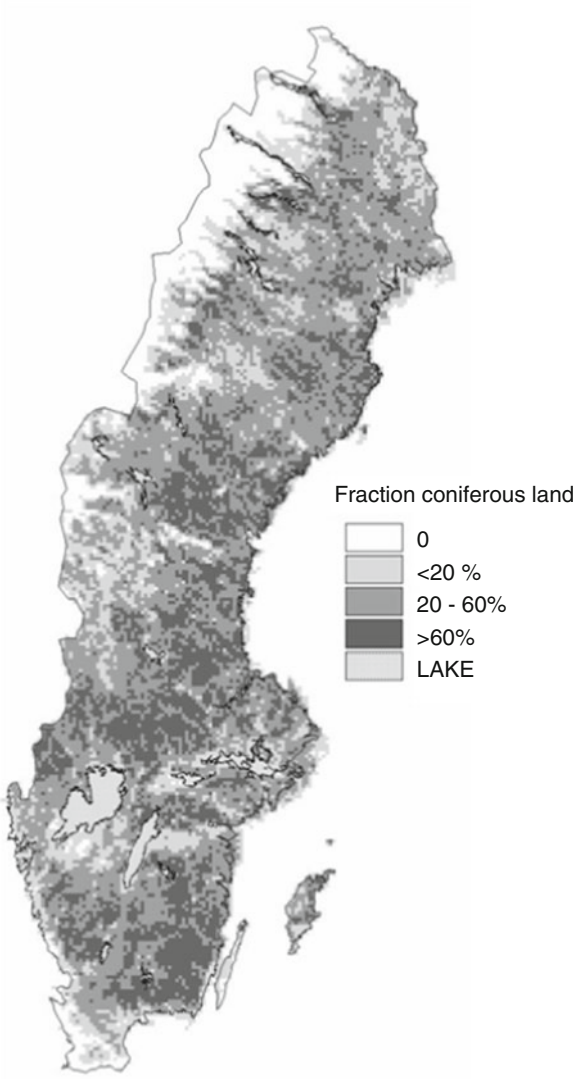

Fig. 12.7 Output from the geographical database giving the fraction of coniferous forest in Sweden with a resolution of 5 × 5 km. The basis for this geographical database is an IRS WIFS satellite image interpretation of the forested land (Mahlander et al. 2004). The satellite data have a resolution of 180 × 180 m, and the resolution of the database is 5 × 5 km. Thus, for each 5 × 5 km grid, the fractions of different land use classes are given as extracted from the satellite image. The database originates from Department of Forest Soils, Swed Univ Agr Sci., Uppsala. Figure from Akselsson et al. (2005)

(2008), using the same technique, this finding of a net loss from the soil (whole soil column) was repeated in Norway spruce stands at three further locations: two in our zone Medium and one in zone High. The obtained average net losses were c. 1,000 kg ha^{-1} $year^{-1}$ (96–125 g m^{-2} $year^{-1}$; Lindroth et al. 2008) and consistent over two measurement years (2001–2002). The results of Berg et al. (2009) for the humus layer in the corresponding areas were 140–280 kg C ha^{-1} $year^{-1}$ sequestered. Unless the soil has been disturbed at these investigated sites, resulting in an increased C mineralization, a possible conclusion would be that there is a heavy loss of carbon from the mineral soil. Lindroth et al. (2008) speculated that

anomalously warm years were the reason for these unexpected losses, which appears to be in contrast to our finding of a positive relationship between temperature sum and C sequestration rate. However, the investigated plots were rather small. The authors give a radius of 100 m, which means a plot surface of 3.14 ha. With construction work and thus heavy soil disturbance plus active soil sampling work, at least part of the heavy carbon loss may be explained.

These contrasting differences in short-term and long-term results and methodologies underline the need for more detailed knowledge on SOM dynamics and stabilization and the need for comparison of several methods and approaches on the same locations.

12.6 Remaining Stable Fraction: A Theory and a Possible Regional Approach

12.6.1 Short Background

This section suggests an approach to estimate humus buildup or carbon sequestration by applying the concept of stable residue. We have used this approach before for a single site (Sect. 10.4; Table 10.3). Like for the case study above, we discuss just primary sequestration (Fig. 11.1). We describe the database that was used by Akselsson et al. (2005) and the expansion to a regional scale, the calculations of humus and carbon as well as the potential sequestration rates. After that, we discuss the effect of tree species on C sequestration rates and finally sources of error.

12.6.2 Geographical Database

In the database, all forested land is divided into (1) grid cells of the size 5 × 5 km, (2) forest classes, namely coniferous, deciduous and mixed forests, and clear-felled areas. An example of the information is given in Fig. 12.8, showing the fraction of coniferous forest in each 5 × 5 km grid cell. For each such cell, the fraction of different land use classes is given as extracted from a satellite image.

On the level of grid cell, there is also information about tree species. In the present case, the principal coniferous species were Scots pine and Norway spruce as well as two birch spp. as the dominant deciduous species. The fractions of Norway spruce and Scots pine in coniferous forests are known for each grid cell, as well as the fractions of birch and other deciduous trees in deciduous forests. The species that are lumped together and called ‘other deciduous’ are mainly common oak and common beech. For mixed (coniferous-deciduous) forests, the fractions of coniferous and deciduous are included in the database. The information on species

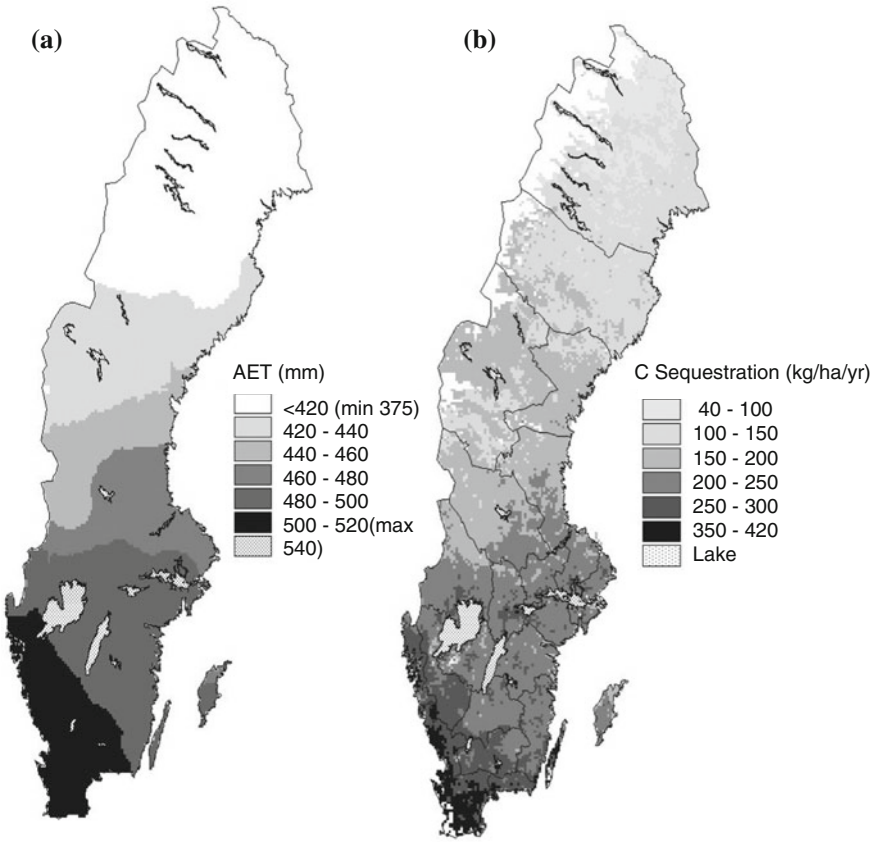

Fig. 12.8 **a** AET in Sweden, given as values for grid cells the size of 5 × 5 km. AET was calculated using the Thornthwaite and Mather (1957) water balance procedures and interpolated according to Kriging to cover 17,000 grid cells. **b** Carbon sequestration rates (kg C ha^{-1} $year^{-1}$) in the organic layers of forest soils in Sweden according to the limit-value approach. Values were calculated for the same 5 × 5 km grid cells as the AET climate index. Figure from Akselsson et al. (2005)

originates from the Swedish National Forest Inventory, and data from 15,318 specific sites were interpolated by Kriging. In this way, data based on specific sites were used to estimate values for all grid cells, giving each cell its fraction of coniferous and deciduous trees. Based on this, fractions of spruce, pine, birch, and 'other deciduous trees' were calculated for each grid and used for the further calculations.

Akselsson et al. (2005) used the climate variable actual evapotranspiration (AET), which is the sum of evaporation and transpiration in an ecosystem. Being a combined measure of heat and soil water, AET has shown to be a good predictor of various plant processes (Meentemeyer et al. 1982), for example litter fall, which is used in this study. An approximation of the field capacity of 300 mm for the root

zone in the whole country is in accordance with previous work (e.g., Meentemeyer 1978; Meentemeyer et al. 1982; Dyer 1990) and makes it possible to use this climate variable on a regional basis. The first step for estimating AET for the grids was to calculate AET for 95 sites located all over Sweden that had detailed climatic data. Kriging interpolation to the 5 × 5 km grid cells was then performed based on these 95 sites, and the resulting values for AET were included in the geographical database. It may deserve to be pointed out that AET may have a wider generality as a climate variable than, for example MAT. In the case with Scandinavia and Northern Europe, however, MAT may fulfill the same purpose, as heat is limiting in this area (Berg and Meentemeyer 2002).

12.6.3 Expanding to a Regional Scale

To convert data for stable fractions of litter to a regional scale, Akselsson et al. (2005) used the linear relationships between foliar litter fall and AET. Three relationships were used, namely one for Scots pine, one for Norway spruce, and one in common for all deciduous species (Table 12.2). That was the factor they used for scaling up. It allowed for the estimation of litter input rates of each species or species group into each cell. In this step, MAT may be used as the litter fall in Northern Europe is linear to MAT (Table 12.2) and even gives a better linear model than AET. Beginning with litter fall and species composition, the limit-value (or stable residue) approach described earlier (cf. Sect. 10.4) can be applied to estimate potential carbon sequestration rates (below).

Table 12.2 Litter fall (kg ha^{-1} year^{-1}) as a function of AET (mm) for different tree species as well as groups of species in the forested land of Sweden

Tree species	Litter fall function				Source
	Intercept	Slope	R^2	n	
Norway spruce	−3,646.4 (642.1)	+12.09 (12.1)	0.47	13	(1)
Scots pine	−3,593.7 (508.6)	+11.03 (2.0)	0.48	35	(1)
Downy and silver birch	−785.5 (51.3)	+5.81 (1.8)	0.79		(2)
Other deciduous	−785.5 (51.3)	5.81 (1.8)	0.79		(2)

Standard error is given within parentheses. From Akselsson et al. (2005). Recalculated from Berg and Meentemeyer (2001).
[1] Berg and Meentemeyer (2001).
[2] Meentemeyer et al. (1982).

12.6.4 Calculation of the Buildup of Humus and Carbon

The annual foliar litter fall for each species group (Scots pine, Norway spruce, birch spp., and 'other deciduous') in a given 5 × 5 km grid cell was estimated separately using the equations based on AET (Table 12.2). The fraction of litter that would remain as stable matter was calculated as (100-limit value)/100 for each species and multiplied by the estimated litter fall. This gives the annual SOM buildup (cf. Berg et al. 2001) (Sect. 10.4) for each group of tree species. The values for SOM from all groups of species were added to give the average SOM buildup in each grid cell. In this first approach, Akselsson et al. (2005) used the same limit value for the dominant tree species, namely Norway spruce, Scots pine, and birch species. They took the general average value of 78.1% (a stable fraction of 0.239 for pine and spruce litter) and 63.8% for 'other deciduous' (stable fraction of 0.362).

The sequestration of carbon was calculated by multiplying the derived SOM buildup by the fraction of carbon in the foliar litter, and Akselsson et al. (2005) assumed a constant C fraction of 0.5. This simplification should be allowed since the calculations were based on falling foliar litter, in their case with a minimum of ash (less than 2% initially). The result is the C sequestration rate (kg C ha^{-1} $year^{-1}$) in the organic forest soil layers.

12.6.5 Potential Carbon Sequestration Rates

Potential C sequestration rates in the organic layers in forest soils in Sweden range from 40 to 410 kg ha^{-1} $year^{-1}$ with an average of 180 kg ha^{-1} $year^{-1}$ (Fig. 12.8b), as based on the limit-value concept. The general gradient gives decreasing C sequestration rates from the southwestern to the northern part of the country, mainly following the variation in AET (Fig. 12.8 a). In the southernmost and the southwestern parts, the C sequestration rates range between 300 and 410 kg ha^{-1} $year^{-1}$, in mid-Sweden, the levels are mainly between 150 and 200 kg C ha^{-1} $year^{-1}$, and in the northern parts, the sequestration is lower than 100 kg ha^{-1} $year^{-1}$ with a minimum of 40 kg ha^{-1} $year^{-1}$ at and north of the Arctic Circle. The annual C sequestration for the whole country is estimated to 4.8×10^6 t to be compared to 6.7×10^6 t as calculated from direct measurements in our first case study (Sect 12.4; Berg et al. 2009).

The general patterns of AET distribution and C sequestration rates are similar (Fig. 12.8). The AET ranges from 375 mm in the northern part of Sweden to 540 mm in the southwestern part with higher temperature and more precipitation. Because litter fall was related to AET and Akselsson et al. (2005) used a single average limit value for the three main tree species, AET has a major effect on carbon sequestration rates and this pattern should be expected. The approach of Akselsson et al. (2005) was based on foliar litter fall from mature stands and on limit values for

decomposition of the foliar litter fraction. The rates given by them are thus only potential rates for the foliar litter fraction, without considering the effect of wild fires, site preparation, or other forest management practices. Further, the methods do not consider effects of non-foliar litters or stand age but give the potential growth rate for sequestered carbon from foliar litter only. Such a potential may have a value for determination of the capacity of the forest system as regards C sequestration.

12.6.6 The Effect of Tree Species on Carbon Sequestration Rates in the Humus Layer

Foliar litter fall is higher in Norway spruce than in Scots pine forests according to litter fall measurements (Table 12.2). In the present approach, this results in a higher annual mean C sequestration in Norway spruce than in Scots pine forests with 200 kg C ha^{-1} as compared to 150 kg ha^{-1}. The mean C sequestration rate in birch forests is the same as for pine, but the gradient over Sweden is more emphasized in pine forests (Fig. 12.9) with a wider range (60–260 kg ha^{-1}

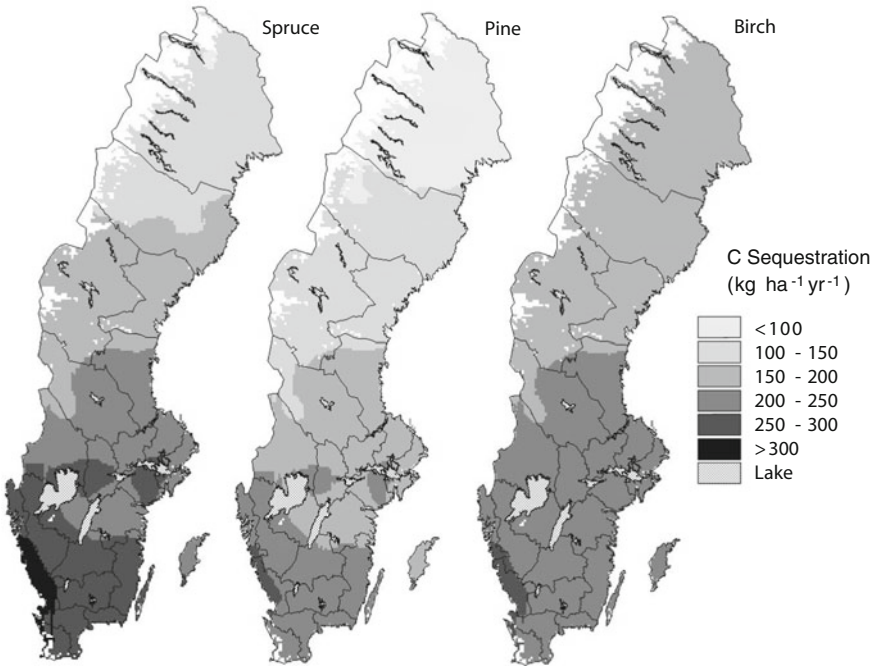

Fig. 12.9 Annual carbon sequestration rates in monocultural stands of Norway spruce, Scots pine, and birch spp. in different regions of Sweden. The sequestration rates were calculated using the limit-value method. Figure from Akselsson et al. (2005)

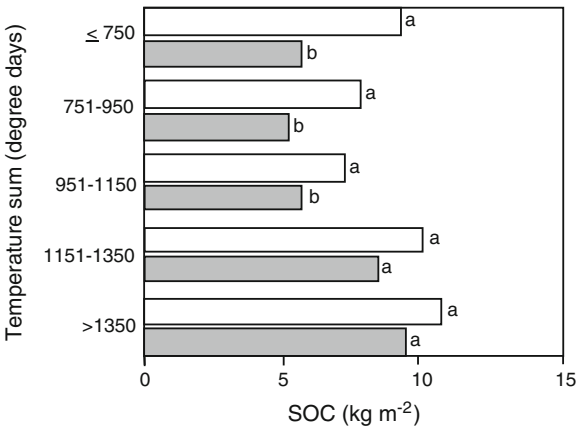

Fig. 12.10 Mean soil organic carbon (SOC) stock in the 0–100 cm mineral soil layer in plots of pure Norway spruce (*white bars*) and Scots pine (*shaded bars*) in different temperature sum regions in Sweden. Different letters indicate significant differences between plots with different tree species within each region ($p < 0.05$). Figure from Stendahl et al. (2010)

year^{-1}) than for birch (150–260 kg ha^{-1} year^{-1}). We may compare our first case study in which the C sequestration in humus layers was lower in spruce than in pine forests. Although the potential sequestration for spruce is higher than for pine, the actual amount in the humus layer is smaller, which may support different mechanisms for sequestration.

The litter class with 'other deciduous trees,' viz. common beech and common oak, is limited to the southernmost part of Sweden. It has the highest fraction of stable matter, 0.36 (average limit value 64 %), which leads to a higher C sequestration rate (about 400 kg ha^{-1} year^{-1}), than for Norway spruce, Scots pine, and birch litter, all with a stable fraction of 0.22. This effect can be seen in parts of southernmost Sweden (Fig. 12.9) where forests of common beech and common oak make up a significant fraction of the forested area, comprising up to 22 % of the stand biomass.

12.6.7 Sources of Error in the Limit-Value Approach

So far only foliar litter has been included in the calculations, and the potential rates of Akselsson et al. (2005) are thus potential rates for foliar litter only. Woody litter appears to have different decomposition kinetics, which at present makes it difficult to estimate its long-term contribution to C sequestration, which possibly is small. Further, for the different root and rhizome litter types, we still lack sufficient long-term basic information from decomposition studies to apply the limit-value concept. This also applies to moss, the litter formation of which is little known as is any limit value for decomposition.

There are further evident error sources. Akselsson et al. (2005) used foliar litter fall as a reasonable first approach, and the litter input is a primary error source, both as regards source and as regards rate. Their data for calculating litter fall were those available, which originated from mature stands. Smaller inputs following a

clear-cut as well as the lower litter fall in the younger stands were not considered. The foliar litter fall is of course only one of the several fractions of the total litter fall, and in mature boreal stands of Scots pine and Norway spruce, foliar litter may encompass c. 70 % of the total litter fall in contrast to c. 100 % in very young stands (Mälkönen 1974). On the other hand, as pointed out by Flower-Ellis (1985) (see also Berg and Laskowski 2005), there are extremely few data on real total litter fall. The traditional litter trap for foliar litter is methodologically unsuitable to give correct recordings for 'total' litter fall, which means foliar litter plus, for example branch, twig, bark, and cone or acorn litter. This means that available data in the literature for 'total litter fall' in many cases simply may be incorrect and probably understated. Further, a general assumption on litterfall data is that the forest is relatively homogeneous, namely that it either has a naturally regulated high density or when comparing forests, the management is similar. For example, litterfall data are normally given as kg per hectare, and normally, tree density is not given but assumed to be similar among compared plots. A measure based on, for example, basal area which would reflect the biomass of the trees possibly could improve this.

Further, the input of root litter is very little known from a quantitative point of view as are the inputs of moss, grass, and shrub litter. The more open Scots pine forests support a higher growth of mosses and shrubs as compared to the more closed and darker Norway spruce forests. A calculation based on only foliar litter fall from the trees would thus underestimate the carbon sequestration in Scots pine forests as compared to Norway spruce. Further, in their approach, Akselsson et al. (2005) assumed that all the species sequestered C primarily in a humus layer.

The limit values reflect a relatively stable fraction of the foliar litter, but we simply know very little about the formation of stable material from woody litter and from fruits (e.g., cones and acorns) as well as of root litter. Available information suggests that at least for some tree species, the decomposition of woody litter may have a different pattern as compared to foliar litter. For litter from finer roots, different observations suggest that very small remains are left after decomposition under natural conditions.

In addition, effects of mineral soil Ca and P concentrations (Sect. 11.5) on long-term storage of humus in the O horizon were not considered in the approach taken by Akselsson et al. (2005) but could have a clear impact on the actual carbon sequestration rate.

12.7 Carbon Sequestration Rates in the Case Studies Compared to Quantitative Measurements in Single Stands and Chronosequences as well as among them

We have presented measurements taken in the organic layer, and they indicate a clear increase in spite of management practices. We have compared the rates calculated in the two case studies with more detailed and more long-term

Table 12.3 Comparison of measured sequestration rates for carbon as measured for specific stands in chronosequences or in other separate detailed and long-term investigations on podzolic soils. Only organic layers were considered

Location	Sequestration rate (kg C ha^{-1} $year^{-1}$)	Tree species	Source
Central Swedish Lapland	153	Mixed stands	(1, 5)
Central Sweden[a]	128	Scots pine	(1, 6)
South Finland	47	Norway spruce/Scots pine	(8)
Southwest Sweden	650	Norway spruce	(12)
Denmark	170–530	Different species	(2)
Denmark (Jutland)	350	Norway spruce	(11)
Denmark (Jutland)	80	Common oak	(11)
Scotland (UK)	353	Conifers	(10)
Wales (UK)	400	Sitka spruce	(9)
England (UK)	721	Scots pine	(13)
Central Netherlands	537	Scots pine	(3)
Central Germany	1,100	Norway spruce	(4)
Central Germany	320	Common beech	(4)
Central Germany and the Alpine region[b]	190–470	Norway spruce	(7)

[a] Extremely nutrient-poor stand.

[b] Six stands of Norway spruce.

1. Berg et al. (2001), 2. Vesterdahl and Raulund-Rasmussen (1998), 3. Estimated from Tietema (2004), 4. Berg (2004) as recalculated from Meesenburg et al. (1999) and Maiwes et al. (2001), 5. Wardle et al. (1997), 6. Staaf and Berg (1977), 7. Thuille and Schulze (2006), 8. Peltoniemi et al. (2004), 9. Gundersen et al. (2006) 10. Billet et al. (1990), 11. Vesterdal (2003). 12. Vesterdal (2006). 13. Ovington (1959).

measurements for Sweden and the other Nordic countries that are reasonable to use for a comparison (Tables 12.3, 12.4). The detailed measurements are taken at single sites, and we compare them with the calculated rates for the corresponding region.

The site measurements were taken by resampling of humus layers over several decades or inferred from studies of chronosequences of stands including some afforestation sites where the organic layers were built since planting of the stand. For natural, unmanaged stands (mixed species) in Swedish Lapland (Wardle et al. 1997), the mean rate (153 kg C ha^{-1} $year^{-1}$) was similar to that estimated for the surrounding investigated area with a range of 141–280 kg C ha^{-1} $year^{-1}$, 'all species' group. For the same area, the case study using stable residue obtained a rate of 100–150 kg C ha^{-1} $year^{-1}$ (Table 12.4). For central Sweden, the measured rate in a very nutrient-poor Scots pine forest (128 kg C ha^{-1} $year^{-1}$) was close to the range estimated for pine forest in that area (<141 kg C ha^{-1} $year^{-1}$). The stable residue approach gave a range of 150–200 kg C ha^{-1} $year^{-1}$ (Table 12.4).

For southernmost Sweden, we compared our estimated values with measurements taken in southern Sweden and in the areas at the same latitude and with a

Table 12.4 Comparison of measured carbon sequestration rates (humus layers) in a case study and a limit-value approach for the forested land of Sweden and detailed local studies

Location	Measured other studies (kg C/ha/year)	Stable residue approach	Direct humus determinations
General comparison			
Central Swedish Lapland	153	100–150	141–280
Central Sweden	128	150–200	<141
Southwestern Sweden	650	250–420	280–420
East Denmark	170–530	250–420	141–280
Average values			
Whole country	nd	180	251
Scots pine ecosystems	nd	150	283
Norway spruce ecosystems	nd	200	239

Table from Berg et al. (2009). nd stands for not determined.

similar climate in Denmark and found that the estimated values of Berg et al. (2009), viz. 141 to more than 420 kg C ha^{-1} $year^{-1}$, were in the same range as the measured 170–530 (east Denmark) and 650 kg C ha^{-1} $year^{-1}$ in south Sweden (Table 12.4). The stable remains approach gave a range from 250 to 420 kg C ha^{-1} $year^{-1}$.

Carbon sequestration rates for southern Germany and the Alpine region at sites with temperature and precipitation ranges similar to those found in south Sweden and a few sites in Scotland and Wales are reported to range between 200 and 500 kg C ha^{-1} $year^{-1}$ and are thus comparable with our values (Table 12.3). At one Scots pine site in south Germany, no change could be detected after 22 years although a nearby site showed an accumulation of 200 kg C kg ha^{-1} $year^{-1}$ over 30 years (Prietzel et al. 2006).

Measurements in a chronosequence of Scots pine in central Holland gave a sequestration rate of approximately 540 kg C kg ha^{-1} $year^{-1}$, thus somewhat higher than the highest values found by us for east-central Sweden. In central Germany, rates of 1,100 and 320 kg C ha^{-1} $year^{-1}$ have been found for Norway spruce and common beech stands, respectively (Table 12.3), indicating a difference between species on the same soil.

Appendix I
Glossary

Short definitions of phrases and terms used in the book.

Accumulated Mass Loss
The total amount of mass lost from a decomposing substrate, usually expressed as a percentage of initial mass.

Acid Unhydrolyzable Residue (AUR)
The solid residue after acid hydrolysis of plant litter. The term AUR is used for gravimetric determinations according to different methods and may encompass, native lignin plus several other compounds, for example, waxes. When degradation has started also recombination products may be registered. Still, numerous analyses have been made and AUR concentration has shown to be a useful index for substrate chemistry.

Aerobic
Oxygen demanding. The term as used here refers to microbial processes which demand the presence of oxygen.

Allophane
A soil dominated by amorphous (noncrystalline) clay-sized aluminosilicates. These are frequently found in highly weathered volcanic deposits.

Ammonium/Ammonia Fixation
Fixed NH_3 is the NH_3 that is retained by the soil organic matter or decomposing plant litter after intensive extraction and leaching with either diluted mineral acid or neutral salt solutions (Nömmik and Vahtras 1982). Not to be confused with dinitrogen fixation.

Anaerobic
Does not demand oxygen. The term as used here refers to microbial processes that can proceed without the presence of the oxygen.

Annual Mass Loss
(see Period mass loss).

AUR
Please see 'Acid Unhydrolyzable Residue' (above).

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Biomass
(1) Organic matter present as live microbial tissue. (2) The mass of organic material produced by living organisms, including both living and non-living tissue.

Breakdown
This term is used here to indicate '… a reduction in particle size of the organic resource' (Swift et al. 1979) or **comminution.** A similar effect is brought about by abiotic factors such as freezing and thawing, or wetting and drying cycles.

Constant Fractional Rate
Refers to decay rate according to first-order kinetics (e.g., radioactive decay) in which the decomposition of material proceeds at a constant rate for all periods of the process, until the original material has been completely used up.

Continentality
For our purpose, 'continentality' refers to the effects of climate, that is, temperature and precipitation. Thus when comparing temperature and precipitation along a transect from the sea toward inland, the annual average precipitation decreases and the mean annual temperature decreases. The temperature amplitudes increase both over the day and over the year, for example, between July and January.

Decomposition
We have used the word 'decomposition' or 'mass loss' as the loss of mass from plant litter due to microbial decomposition or leaching of water-soluble substances. Decomposition can also be defined as litter CO_2 release plus leaching of compounds. Breakdown (above) is not included in the concept.

Fulvic Acid
Colored material, which remains in solution after removal (Stevenson 1982; Waksman 1936) of humic acid by acidification.

Humic Acid
The dark-colored organic material which can be extracted from (Stevenson 1982; Waksman 1936) soil by various reagents and which is insoluble in dilute acid.

Humic Substances
A series of relatively high molecular weight, brown- to black-colored (Stevenson 1982; Waksman 1936) substances formed by secondary synthesis reactions. The term is used as a generic name to describe the colored material, or its fractions, obtained on the basis of solubility characteristics. These materials are a distinctive characteristic of the soil (or sediment) environment, in that they are dissimilar to the biopolymers of microorganisms and higher plants (including lignin).

Humin
The alkali-insoluble fraction of soil organic matter or humus (Stevenson 1982; Waksman 1936).

Humus
Sum total of the stable organic substances in the soil, not including undecayed animal and plant tissues, partially decomposed material and the soil biomass (Stevenson 1982; Waksman 1936).

Leaching
The loss of nutrients and incompletely decomposed organic compounds (This vol.) from the intact remains of decomposing litter, due to the action of water.

LH Factor
Litter-to-humus factor. The remaining stable fraction of the litter when decomposition has reached the limit value (see below), namely (100-limit value)/100 (Berg et al. 2001).

Lignin
Native lignin. See, for example, Fig. 3.3.

Limit Value
Calculated value for the extent of decomposition of a given litter type, at which the decomposition rate approaches zero. Limit value may be given as accumulated mass loss (%) or as a fraction.

Litter
The same as litter residue (cf. newly shed litter).

Litter CO_2 Release
The mineralization of carbon from litter. Gives mass loss from litter minus leaching of compounds. See also the 'decomposition.'

Litter Residue
Undecayed plant and animal tissues, and their partial decomposition products (Stevenson 1982; Waksman 1936).

Newly Shed Litter
Plant litter that has been shed so recently that the decomposition processes have not yet started. The concept is confused by the presence of 'newly shed litter' which starts decomposing when still attached to the plant.

Non-humic Compounds
Compounds belonging to known classes of litter chemical compounds, such as amino acids, carbohydrates, fats, waxes, resins, organic acids. Humus probably contains most, if not all, of the biochemical compounds synthesized by living organisms (Stevenson 1982; Waksman 1936).

Period Mass Loss
Fraction of litter lost in a defined period, often one year. For calculation, see Appendix II. May be expressed as a fraction or a percentage.

Potential Accumulation
Also potential sequestration of carbon. The accumulation that we will estimate is called potential, because the calculations cannot at this level include possible effects of forest management and disturbance (e.g., wildfire), thus tending to overestimate accumulation.

Potential Humus
A theoretical concept and refers to the fraction of litter that can be calculated to become humus. We have also used the term LH factor.

Sequestration
We have used the term for long-term storage of mainly C and N, and occasionally other nutrients in stabilized residue. The use follows the definition given by Webster's Dictionary (Gove 1996) and refers to the fact that the compounds are bound and removed from the biological activities in their system, unless the system is subject to such changes that it may be considered altered. Our use differs from that currently used by plant physiologists, namely that a compound (e.g., C) bound into live plant tissue is sequestered. The binding of, for example, CO_2 to plant tissue is one of the several steps in the process of sequestration and only part of the C taken up by plants is sequestered, the rest being released as CO_2 during decomposition.

Sequestration Rate
We have used this term for the net increase (per unit time) in C and N in humus (SOM).

Soil Organic Matter
or SOM, The same definition as for the humus (Stevenson 1982; Waksman 1936).

Steady State
A term sometimes used also about humus layers. We have not found any real definition of the term directed to humus but only a suggestion to an application for a specific boreal region of country size. Thus Schulze et al. (1989) suggested that today's humus layers, accumulated after the last glaciation, reflect a steady state, namely the amount that has accumulated considering all possible influencing factors, including fire and anthropogenic influences. A problem with such a definition is of course that when, for example, forest fires are suppressed, like today, the basic conditions for the definition are changed. On a smaller geographical scale, for example, a stand level, it would not be useful. In this book, we have avoided to use the term 'steady state' for humus. The reason is that we have not found any evidence for the validity of such a concept. We cannot exclude, though, that in ecosystems with developing humus layers, steady states do exist.

Appendix II
Comments to Design of Litter-bag Experiments and Some Calculations

Introductory Comments

It is overly evident that each litter-bag experiment may have its own design as given by the scientist. Still, there are some basics that need to be considered; (1) properties of the sampled litter such as contents of ash and water, (2) requests on the number of replicate samples as well as on the design of the plot for incubation.

It may be commented upon that decomposition experiments carried out in a laboratory tend to give different results as compared to such that are carried out in the field and the comments below refer to field experiments. It is clear and evident that not all work on litter decomposition can be carried out in the field although the borderline between field and laboratory experiments is not always clear.

We have preferred to make some general comments, based on our experience and hope that they may be of help. In the discussion below, we assume a long-term descriptive experiment, with samplings as far as it is possible to measure the decomposition.

The Litter You Collect for Incubation

Foliar litter from different trees (of the same species) may have differences in chemical composition at litter fall even when growing on the same soil. To have a representative sample of the stand, it may be necessary to sample from a number of trees, say, 10–20. For some tree species, litter fall occurs regularly, for example, in the autumn or at a dry summer period and a high amount can be obtained in a short time. One way to collect litter is to let it fall onto spread-out tarpaulins or to shake the limbs carefully. Some species/genera, for example, spruce (*Picea*) shed a large part of the needle litter more irregularly and a possibility is to collect from younger trees or from natural litter fall on spread-out tarpaulins. To collect litter from the bare forest floor should be avoided.

Preparation of Samples for Incubation (Litter Bags) from the Sampled Litter

Litter that has been sampled normally contains water. Even if it may feel and look dry, it can contain water to a rather high concentration (normally well above 10 %). Unless this water is considered, it will be registered as litter mass loss in the first determination of mass loss and may create a considerable error.

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When investigating this, we found that needle litter that had been drying at room temperature in the laboratory (with low humidity) for a week after collection normally held between 6 and 11 % water with a clear and high variation among samples. Water was determined as loss of mass at 85 °C for 24 h.

We found that a main problem was to obtain an even water level over the sampled litter and managed to obtain homogeneity among samples often after a drying period of about a month, sometimes a bit shorter time. Our 'quality index' was the variation in water concentration among 20 random samples. Normally the final water concentration sank to about 5 or 6 % and the accepted variation was +/−0.5 %-units, a variation that was possible to reach—at least for a limited number of litters—in our case c. 12 species. As weighing of litter for litter bags may take several days, the dried and homogeneously dry litter should be kept in a closed plastic bag/sack or in a tight glass jar.

A final comment may be that the drying temperature for water determination should be the same as for determination of litter mass loss.

A Representative Plot for the Incubation

We may first ask; 'representative of what?' Such a question and further ones are motivated for a field experiment. Should the plot represent the system, for example, a whole forest system or just part of it? A certain plant community within the forest? The average climate in the forest?

Having decided this, i.e. what the study should represent we may need to consider how we implement it. For incubating the litter, we may choose a number of spots taken randomly within our stand. Let us assume that we consider a set of individual spots over the plot according to a random selection. A next question may be—is there any kind of spot that must be excluded and why? Or is there any other disturbance? A lack of homogeneity?

It is difficult if not impossible to cover all reasonable possibilities in a short text, so let us take an extreme example. Let us take a situation with a lack of homogeneity. We assume a forest with dense tree canopies almost reaching the ground, for example, canopies of spruce (*Picea*) or fir (*Abies* or *Pseudotsuga*), alternatively dense bushes. Under the canopy projection and outside of it temperature and rainfall will be different, often enough illustrated by different plant species. May be a third or half of the plot area falls within the canopy projection and the rest outside of it, so we cannot neglect this as a potential problem. As far as we know the differences in temperature and moisture may be enough to give significantly different decomposition rates under and outside of the canopy projection. Another example is a gap, where a few trees have been left out. The gap will have more sunshine (and more rain) and a consequence is higher temperature and a quicker drying of the soil and litter, which also may give a considerable difference in rate.

One way to cover such an uneven structure is to have a high enough number of replicate spots for incubation of litter and take the spots randomly (see below). A high enough number of incubation spots may allow for the variation caused by, for example, vegetation. Another possibility is to have separate sets of litter bags under and outside of the canopy projection.

Plot Size

There are few studies, if any on this concept. Still, there is the question of a plot size big enough to represent the biotope or stand (cf. above) and the variation within it. A too small plot may ruin several years of work when data are to be evaluated. Thus, a plot measuring a few meters square generally would be too small. In most cases, a plot size of 50 × 50 m would be enough for boreal and temperate forests and their tree species.

The Number of Replicate Litter Bags in Each Sampling

It is evident that such a number may vary depending on the question the scientist will ask and the frequency of samplings and we cannot give any fixed number. There is simply no clear rule and very few studies on, for example, number of replicates versus sampling frequency. We keep to the assumption of an experiment in which the scientist wants to make a basic description of a not-yet-studied litter species and wants as low a variation as possible among samples, just to have as homogeneous a material as possible for each step in the decomposition process.

Below we give values for standard error (StE) for different values on accumulated mass loss for a decomposition experiment on Scots pine in a boreal forest over a period of c. 5 years. We used 20 replicate samples with 3–4 samplings per year;

Acc. m.l.(%) 0, 15.6, 22.4, 29.9, 38.5, 45.6, 47.5, 54.1, 58.1, 62.5, 66.0, 67.4

StE 0, 0.27, 0.33, 0.68, 0.82, 0.94, 1.73, 1.78, 1.62, 1.36, 1.51, 1.80,

To give a minimum number of replicates is not really meaningful. In a study on leaf litter of common beech, Hristovski et al. (201X) collected 3 replicate samples every week, thus a rather high frequency. The results allowed calculations of decomposition kinetics with good precision.

The variation in accumulated mass loss around an average value should increase from a low one at a small accumulated mass loss and peak at c. 50 % accumulated mass loss to decrease again. Statistical tables may give the number of replicates needed to give significant difference between two given values for accumulated mass loss. However, there appear to be several factors influencing and in an experiment using Norway spruce needle litter comparing the standard deviation, 100 replicate samples did not give any lower standard error than 20 replicates (B. Berg unpubl).

Empirical findings related to analytical work on data have indicated that with a number of 15–25 replicate samples and a sampling intensity giving about 5 %-units increase in accumulated mass loss between samplings we may have a continuously increasing value for accumulated mass loss, which has a value for calculating mass-loss rate in a certain period (e.g., annual mass loss) or else analyzing decomposition dynamics over periods. In other words, the risk for a variation that gives a decrease in accumulated mass loss between two samplings should be low.

Ash in Litter

Ash, meaning the residue after heating a litter sample to, for example, 500 °C for 2 h may have a content of different origin, one being the original mineral nutrients in the litter (e.g., P, Ca, K, Mg, Mn) as well as heavy metals, which together may create the concept internal ash. Available data for Scots pine give a range from 12 to 24 mg g^{-1} over 14 years of samplings of newly shed litter and among 5 stands with Norway spruce sampled for 2 years the average value was 83 mg g^{-1}. Silver birch had concentrations of 84 and 57 mg g^{-1} as highest and lowest, respectively, and available values for trembling aspen give a range from 93 to 47 mg g^{-1}.

Another source for ash may be fine mineral particles from the soil when litter (external ash) is incubated in contact with mineral soil or is covered by excrements from burrowing animals, for example, worms (lumbricides).

Some litter species appear to have considerably more internal ash than other ones when shed. An amount of 3–4 % units is not uncommon and may influence calculations of litter mass loss, especially if external ash has penetrated the litter. It may also happen that parts of the internal ash are concentrated in the decomposition process. In an extreme example, the ash concentration increased from 5.3 to 15.6 % for litter incubated on a clayey soil (Wessen and Berg 1986). In another one, Hristovski et al. (201X) determining carbon instead of ash found a change in litter carbon concentration from 41 to 28 %, thus non-carbon compounds (ash) had increased by a factor of 1.5.

Ash may influence not only the mass-loss determination but the analysis of gravimetric lignin (AUR; see the Glossary). With a main part of the ash not being soluble in strong acid, it will be recorded as AUR and may influence its concentration with several % units.

Some Possible Treatments of Data That may be Related to Experimental Design

This section gives a few examples, based on our experience.

Descriptive Studies Several studies are descriptive in the sense that they give accumulated mass loss and chemical changes, for example, in organic compounds and/or in nutrients and heavy metals. Such a study may be used for comparison, for example, when different litter species are compared and rates in periods/year may be of interest.

Calculation of Period Mass Loss/Annual Mass Loss If you want to analyze your data in detail, say investigate what happens in the course of decomposition from incubation to an accumulated mass loss of, say 70 or 80 %, it is essential to have very regular sampling intervals. For annual mass loss, you may have intervals of 365 days between samplings, even if you have samplings several times in a year. An alternative may be to have samplings, for example, every month or any other regular interval.

When calculating mass loss in such a period, say from end of year 1 to end of year 2 (2nd year of incubation), you should consider this period as a separate unit. You use for example the value for remaining amount at the end of year 1 as a start

value for estimating the second-year mass loss and the remaining amount at the end of year 2 as end value. The lost amount is the remaining amount at the end of year 1 minus the remaining amount at the end of year 2. That amount was lost in this period and you relate that amount to the initial amount of the period (remaining amount at the end of the year 1). Thus, divide with the amount after 1 year and obtain the fraction lost. The fraction you obtain is multiplied by 100 and period mass loss in % is given. This kind of calculation is dependent on the quality of the individual mass-loss values in each sampling, namely the number of replicate samples and their variation. It is thus of great value to have well defined values for accumulated mass loss.

Appendix III
Short Overview to Some Common Analytical Methods of Organic Compounds in Litter with Focus on Lignin

III.1 Introduction

The traditional gravimetric analysis for lignin and other litter compounds is today being replaced by newer methods. Both the traditional and the new approaches are applied and used in plant litter research, and we make a comparison of what information they may provide us with as regards lignin. With the present fast development of analytical techniques, we may just comment of the situation in 2013.

What many of us refer to as traditional analytical methods for lignin determination were originally rather intended as standardized analyses for specific purposes and not for research and as such some methods may rather give an index than the quantity of a real chemical compound. For example was the sulfuric-acid lignin (Klason lignin; Tappi T222 om-98) intended as an industrial analysis for lignin in wood material, not for the chemically more complex foliar litter and even less for the litter's different decomposition stages. Van Soest lignin (Van Soest 1963) was intended for determination of digestibility of fodder. Just applying these methods to fresh and partly decomposed plant litter may result in suboptimal results, unless specific method studies have been carried out. Considering the variety and complexity in chemistry of plant litter, we may face the possibility of less reliable results when applying a method tested for one purpose onto, for example, decomposing litter of several species not investigated before. Nevertheless, these methods have provided us with new information and theories, which have been based on the outcome of their use.

There is a good number of studies based on 'gravimetric lignin' such as Klason lignin, Effland lignin as well as Van Soest lignin. A further method is the CuO oxidation (e.g., Hedges and Ertel 1982) based on hydrolysis of the lignin, followed by chromatography of the products.

We may mention and name several methods and their modifications. However, that goes beyond the purpose of this appendix. We have selected three main methods, commonly found in research on forest litter and discuss these briefly.

The term lignin for gravimetric lignin may today be misleading. To apply a new terminology, we may call the analyzed fraction not lignin but Acid Unhydrolyzable Residue (AUR), which in fact is a correct term and may refer

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to and cover different analytical methods of gravimetric determination. In short, AUR and lignin are not the same compound but AUR covers a whole group of different compounds, one of which is native lignin.

When we in this book use the term 'lignin,' it refers to native lignin as based on ^{13}C-NMR. We have known for a long time that AUR from plant litter contains ash which must be analyzed for separately. There are also further organic compounds, originating from both the newly shed litter and from recombination products developed in the decomposition process, which appear to be included in the gravimetric fraction. Some examples are waxes, tannins, and cutin.

Although many of us know these methods (Klason, Effland, Van Soest) as 'lignin determinations,' the analytical process may provide us with not only AUR, but we may add further analytical steps and determine, for example, different specific components in extracts and in hydrolysis products (e.g., Berg et al. 1982a). We intend to discuss this in just general terms.

The purpose of this appendix is to give basic information about the procedures for a few common analytical methods and about some of the information we may expect from three main approaches. This information is supportive for the discussion, especially in Chaps. 2, 4, and 6.

III.2 Methods for AUR, Lignin, and Carbohydrates

III.2.1 Gravimetric Lignin

Examples on gravimetric lignin determinations are, for example, Klason lignin (Tappi standard method T222 om-98), Effland lignin (Effland 1977) and Van Soest lignin or acid-detergent lignin (ADL) (Van Soest 1963), and we give some detail for the Klason lignin.

In a first step, soluble substances are removed by extraction; after that follows an hydrolysis, resulting in solid residue and a solution with hydrolysis products, for example, glucose from cellulose and other monosaccharide sugars from hemicelluloses. The solid residue is simply unhydrolyzed organic compounds plus ash. After the original articles were published, numerous papers have been published with modification and adaptation to different plant species. For a few practical details on Klason lignin, see Preston et al. (2009a); Berg et al. (1982a).

A method like Klason lignin originally intended for fresh wood includes not only native lignin in the solid residue but also some specific compounds from the foliar litter, for example, waxes, tannins, and cutin, that are not acid hydrolyzable. Further, applying the method onto partly decomposed litter means that new products formed during the decomposition process are included in the non-hydrolyzable portion (e.g., Preston et al. 2009a, b). The first step, viz. extractions of the sample are intended to remove compounds, for example, proteins that

otherwise may interfere and react with the hydrolysis process. In partly decomposed litter, such reactions may have taken place resulting in new, often unspecific compounds.

In the Klason lignin analysis, a first extraction is made of a well-ground sample with water and the extract contains water-soluble substances, mainly low-molecular ones that may be further analyzed, for example, using chromatographic methods. A next extraction is done with an organic solvent, for example, ethanol or acetone, removing among other compounds more high-molecular fatty acids and some phenolics. It is possible to use further or alternative solvents to obtain different fractions of soluble substances (e.g., Berg et al. 1982a). After the extractions, the hydrolysis is made in steps.

The dried residues are hydrolyzed (12 M H_2SO_4) at room temperature for 2 h and after that diluted to 0.358 M and refluxed for 6 h. The unhydrolyzed residue is determined gravimetrically. The acid solution now containing simple mono-sugars and may be used for determination of the monosaccharide building units of cellulose and hemicelluloses, for example, by gas chromatography. When the residue is dried and weighed, an ash determination is made (e.g., 600 °C for 2 h).

Ideally, after this analysis one may know (1) the ash-free AUR (gravimetric lignin), (2) the amounts and relative composition of cellulose and the different hemicelluloses, and (3) at least the main groups of soluble substances, for example, water solubles or ethanol solubles. Further, we will know how these groups change in amount with decomposition of the litter.

III.2.2 CuO Oxidation

Cupric-oxide oxidation, described by, for example, Hedges and Ertel (1982) and modified by among others Kögel and Bochter (1985), is a technique widely used for characterization and quantification of lignin in plants, sediments, and soil organic matter (Kögel 1986). It means a relatively mild oxidation and yields a suite of single-ring phenolic compounds, which indicate not only the origin of the lignin but also its degradation state (Thevenot et al. 2010).

After drying the sample, for example, at 40 °C and grinding, the analysis may start. Different approaches exist and we give an example. The proportions of sample and oxidation liquid are critical. Thus, 50 mg dry mass of sample may be mixed and oxidized with 250 mg of powdered CuO, 50 mg of $Fe(NH_4)_2(SO_4)_2.6H_2O$ and 10 ml of 2 M NaOH. This oxidation should be carried out under an N_2 atmosphere for 2.5 h at 170 °C. After cooling, the oxidation products are purified using a combination of washing, centrifugation, and acidification (with 6 M HCl). The separation and the quantification of the oxidation products may be carried out using, for example, high-pressure liquid chromatography, HPLC (Waters 1,525 binary HPLC pump). An alternative is given by Klotzbücher et al. (2011a, b).

The hydrolysis products from lignin belong to three groups, vanillyl (V), syringyl (S), and cinnamyl (C) compounds (Kögel 1986). The vanillyl compounds are vanillic acid and vanillin, the syringyl compounds are syringic acid and syringe aldehyde. Finally, the cinnamyl compounds are *p*-coumaric acid and ferulic acid. The sum of these phenolic compounds (V + S + C) is an index of the lignin concentration. The ratio between vanillic acid and vanillin can be used as an indicator for the degradation level of the litter lignin (Otto and Simpson 2006).

Ideally, after this analysis, we may know the content of native lignin in litter at different decomposition stages.

III.2.3 ^{13}C-NMR Analysis of Lignin and Carbohydrates

NMR or ^{13}C-NMR is normally run on whole, finely ground samples, so the analysis is not destructive. The samples are scanned in a spectrometer using a spectrum of different frequencies. Different carbon bonds in the molecules respond to the different frequencies and this response is recorded and shown as, for example, a peak in a diagram, with the surface giving a quantitative measure of the relative amount of that bond in the sample. To this purpose it is practical to identify carbon atoms e.g. by giving them numbers in, for example, lignin or carbohydrate subunits (Figs. AIII.1, AIII.2b. Thus, a specific bond, for example, a C–O bond in a carbohydrate, say, that to carbon 1 in cellulose (Fig. AIII.1) is recorded in one and the same peak as that from the same bond in another carbohydrate, for example, mannose in the hemicellulose mannan or in galactose building up galactan. So, the method records the relative amount of C bonds of a given type, not specific molecules, and in many cases, irrespective of in what compound that bond is found. This also means that a complex molecule like native lignin (Fig. AIII.2a) and its subunits with several types of carbon bonds respond to different frequencies and is recorded in the different provisional groups that have been adopted (Table AIII.1). We may thus find bonds originating from lignin in the group phenolic-C (the phenolic C–O bond), in aromatic-C (the aromatic C–C bond) as well as in methoxy-C giving the –O–CH_3 bond in the methoxyl group attached to the aromatic ring (Table AIII.1).

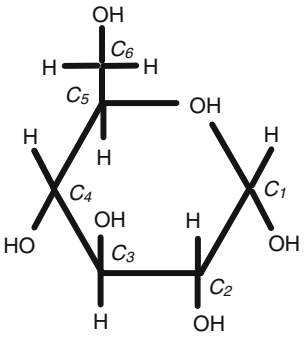

Fig. AIII.1 Glucose is the building unit of cellulose. The numbers of the carbon atoms are given. We may note the O–alkyl–C (no 4) and the di–O–alkyl–C (no 1)

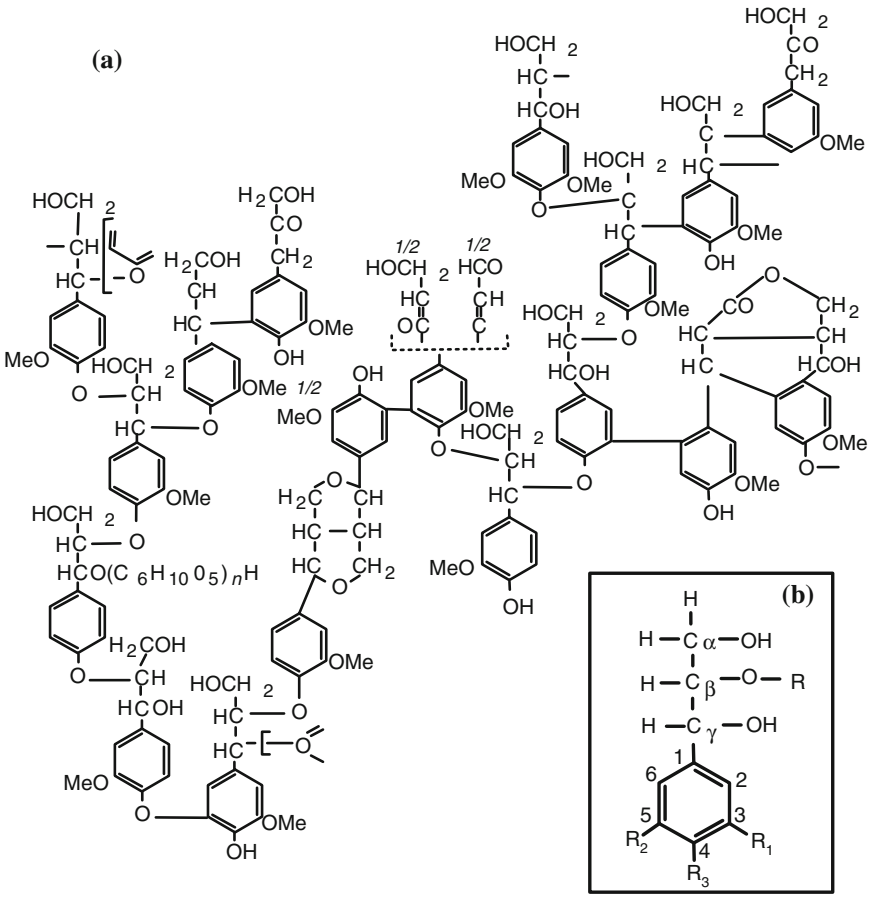

Fig. AIII.2 **a** Molecule of native lignin (Norway spruce). **b** Numbering and denomination of specific C atoms in a building unit of lignin

This method allows us to follow the changes in amount of specific bonds, which not necessarily reflect specific compounds. In the case of lignin, we may follow the change in concentration of different bonds such as methoxy-C, aromatic-C, phenolic-C, and alkyl-C (Table AIII.1). Using this information we may calculate a more correct concentration of native lignin (as compared to the gravimetric one).

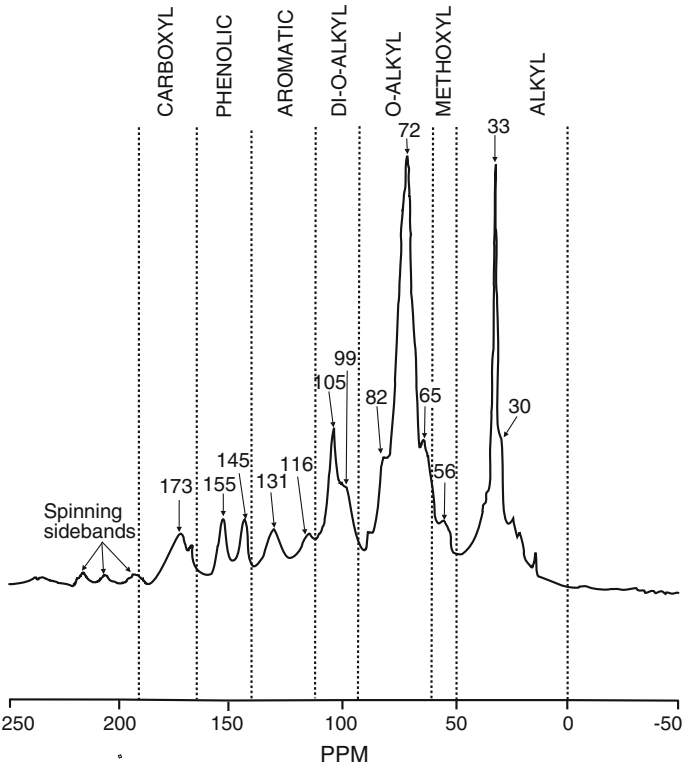

Fig. AIII.3 **a** ^{13}C-NMR spectrum of trembling aspen leaf litter. We may see the frequency regions used to identify different bonds. Cf Table AIII.1. From Preston et al. (2009b)

III.3 What Information may the Different Approaches Give?

The above question has been asked before and we quote from an article by Jung et al. (1997)

> Klason lignin values are typically two to four times greater for grasses than the sulfuric ADL estimates are for lignin concentrations of the same samples. Klason lignin values are approximately 30 % higher than ADL values in legumes. The reason for the differences between grasses and legumes in lignin yield caused by method of analysis is not known, but presumably relates to structural characteristics of the lignins in these two forage classes.

Hatfield et al. (1994) concluded that 'Klason lignin is a more accurate estimate of plant cell-wall lignin content than is ADL.'

It thus appears that the method selected is critical to the outcome. Further, of the hydrolytic methods, it appears that Klason lignin may be to prefer as the hydrolyzate allows determination of carbohydrate composition. Still the method records compounds other than true lignin and Preston et al. (2009a, b) give a list of

Table AIII.1 An overview of standard chemical shift regions for a set of different carbon bonds using 25 MHz CPMAS NMR.

Bond name	Shift region (ppm)	Registers mainly C in bonds of the type
Alkyl	0–50	$–CH_2–$ long-chain $–CH_2–$ carbon, also C in acetate of some hemicelluloses
Methoxyl	50–60	$–O–CH_3$ methoxyl group in lignin (on carbon 5 in Fig. AIII.2b)
O–alkyl	60–93	$–O–CH_2–$ cellulose, hemicellulose, for example, carbon 2, 3 and 6 in cellulose, the aliphatic side chain on carbon 2 in lignin (see number on glucose unit in Fig. AIII.1)
Di–O–alkyl	93–112	$–O–CH_2–O–$ cellulose, hemicelluloses, for example, carbon 1 and 4 in cellulose (see glucose unit in Fig. AIII.1)
Aromatic	112–140	aromatic-C (Carbon Nos 1–6 in lignin unit; Fig. AIII.2b), guaiacyl lignin, condensed tannins, phenolic compounds
Phenolic	140–165	guaiacyl lignin, condensed tannins, phenolic compounds. Carbon No 3,4 or 5 when R is an –OH group (Fig. AIII.2b)
Carboxyl	165–190	carboxylic acids, amides, esters

Shift regions may vary among studies and different litter types and species may give different responses. We offer this as a general example and the table should not be used for analytical purposes. Cf Fig. AIII.3. Data taken from Preston et al. (2009b)

compounds that may be included (tannins, cutins, and surface waxes), which even may be a larger proportion of the litter than the phenylpropane-based lignin, produced by higher plants.

AUR as determined using different methods and often negatively related to mass-loss rate. It may give an index of litter recalcitrance, which however, may have a limited generality. As such it may even be specific for each litter species or genus and the initial chemical properties of the initial litter. Considering new information and resolution of the AUR complex (Klason lignin), we must state that at present we do not know what compounds that cause the index function.

The CuO method and the ^{13}C-NMR (^{13}C-TMAH) approach may give native lignin for litter in different decomposition stages.

III.3.1 Comments on Information We Can Reach at Present

With the fast development of new techniques we may just comment on the situation in the year 2013.

1. *Klason lignin* may give AUR. The preceding extraction and the hydrolysis allows us to have AUR concentration plus detailed information about different high-molecular carbohydrates as well as compounds in different groups of soluble compounds. The extractions preceding the hydrolysis may be used for identification of low-molecular compounds. It has been claimed that this method may give AUR values that are close to native lignin in fresh and not yet decomposed samples (C Preston pers. comm.).

2. The CuO oxidation may give a set of compounds that are building units of native lignin, which may be quantified into lignin. Such values may result in AUR/lignin values that clearly differ from those determined as, for example, Klason lignin.
3. The ^{13}C-NMR analysis may give detailed information about frequencies of concentrations of specific bonds in different compounds.
4. Like for other analytical methods ^{13}C-NMR fractions may give concentrations of a given C-bond in litter as well as remaining amount, the latter based on remaining amount of total C.

Appendix IV
Scientific Names of Vascular Plants

We have listed here the vascular plant species mentioned in the text. Where the same species has different common names in American and European English, we have given both, indicated with (A) and (E), respectively, followed by the Latin/botanical name. Different dictionaries give different common names for the same species, and our purpose here has been to give the correct common names as they were used here, rather than to list the most widely accepted. Plants are divided into two groups: gymnosperms and angiosperms. Within each group, species and genera are arranged alphabetically by the American common name.

IV.1 Gymnosperms

Firs

Douglas-fir (A, E) *(Pseudotsuga menziesii* Mirb. Franco.) (=*Pseudotsuga douglasii*)
European silver fir (A), common silver fir (E) (*Abies alba*) (=*Abies pechinata* D.C.)
Pacific silver fir (A, E) (*Abies amabilis* Douglas ex J. Forbes)
Subalpine fir (A) (*Abies lasiocarpa* (Hook.) Nutt.)

Hemlocks

Eastern hemlock (A), Canadian hemlock (E), (*Tsuga canadensis* (L.) Carr.)
Western hemlock (A, E), (*Tsuga heterophylla* (Raf.) Sarg.)

Pines

Aleppo pine (*Pinus halepensis* Mill)
Austrian pine (A, E), Black pine (A) (*Pinus nigra* Arnold)
Chinese pine (*Pinus tabulaeformis*)
Chir pine (*Pinus roxburghii)*
Corsican pine (A, E), (*Pinus nigra* var. *maritima*)
Eastern white pine, White pine (A), Weymoth pine (E) (*Pinus strobus* L.)
Jack pine (A, E) (*Pinus banksiana* Lamb.)
Korean pine, Korean nut pine (*Pinus koraensis*)

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Limber pine (A, E) (*Pinus flexilis* James)
Loblolly pine (A, E) (*Pinus taeda* L.)
Lodgepole pine (A, E) (*Pinus contorta* var. *latifolia* Engelm.)
Lodgepole pine (A), shore pine (E) (*Pinus contorta* var *contorta*)
Maritime pine (E) *(Pinus pinaster* Ait.)
Monterey pine, Radiata pine, Insignias pine, Cambria pine (*Pinus radiata*)
Ponderosa pine (A), Western yellow pine (E) (*Pinus ponderosa* Laws.)
Red pine (A), Norway pine (A, E) (*Pinus resinosa* Aiton)
Scots or Scotch pine (A, E) (*Pinus sylvestris* L)
Stone pine, Umbrella pine (E) (*Pinus pinea* L.)
White pine or Eastern white pine (A, E) Weymouth pine (E) (*Pinus strobus* L.)

Spruces
Black spruce (*Picea mariana* [Mill]. BSP)
Glehns spruce, Sakhalin spruce (*Picea glehnii* (F.Schmidt) Mast
Norway spruce (A, E) (*Picea abies* (L.) Karst.) (=*Picea excelsa* Link.)
Red spruce (A, E) (*Picea rubens* Sarg.) (=P. rubra [DuRoi] Link)
Sitka spruce (A, E) (*Picea sitchensis* (Bong.) Carr)
White spruce (A, E) (*Picea glauca* (Moench.) Voss)

Some other species
Hinoki cypress (*Chamaecyparis obtusa* (Siebold & Zucc.) Endl.)
Japanese cedar, Sugi (*Cryptomeria japonica* (L.f. D. Don)
Tamarack, American larch, Hackmatack (*Larix laricina* (Du Roi) K. Koch)
Western red cedar, Pacific red cedar, Giant cedar (*Thuja plicata* Donn ex D. Don)

IV.2 Angiosperms

Alders
Red alder (A), Oregon alder (E) (*Alnus rubra* Bong.) (=*A.oregona* Nutt.)
Gray alder (A), Grey alder (E) (*Alnus incana* (L.) Moench)
Nepalese alder (A, E) (*Alnus nepalensis* D.Don)

Aspen
Bigtooth aspen (A, E) (*Populus grandidenta* Michx.)
Quaking aspen, Trembling aspen (A, E) (*Populus tremuloides* Michx.)

Beeches
American beech (A) (*Fagus grandifolia* Ehrh.)
European beech (A), Common beech (E) (*Fagus silvatica* L.)
Japanese beech (A, E) (*Fagus crenata* Bl.)

Birches
Black birch, Sweet birch (A) (*Betula lenta* L.)
Chinese birch, Korean birch (*Betula costata*)

European white birch (A); Common birch, Silver birch, Weeping birch, White birch (E) (*Betula pendula* Roth. = *B. verrucosa* Ehrh.)
Hairy birch (A), Downy birch (E) *(Betula pubescens* Ehrh.)
White birch, American white birch, Canoe birch (*Betula papyrifera* Marsh.)
Yellow birch (A) (*Betula alleghaniensis* Britt.) (=*B. lutea*)

Grasses

Perennial ryegrass, English ryegrass (A), Italian ryegrass (E) (*Lolium multiflorum* Lam.) (=*L. perenne* var. *multiflorum* (Lam.) Parnell)
Small six-weeks grass (A) (*Vulpia microstachys* (Nutt.) Munro)
Soft chess (A), Soft brome (A, E) (*Bromus hordaceus* L. = *B. mollis* L.)
Wild oats (A, E) (*Avena fatua* L.)

Maples

European maple (A), Norway maple (A, E) (*Acer platanoides* L.)
Red maple (A, E) (*Acer rubrum* L.)
Sugar maple (A, E) (*Acer saccharum* Marsh.)
Sycamore maple, Great maple, Sycamore, Scottish maple (*Acer pseudoplatanus* L.)

Oaks

Black oak (A) (*Quercus velutina* Lam.)
Chestnut oak (A), Basket oak (E) (*Quercus prinus* L.)
Common oak, Peduncular oak (E), English oak (A) (*Quercus robur* L.)
Durmast oak (E) (*Quercus petraea* (Mattuschka) Lieblein)
Eastern red oak, Northern red oak (A), red oak (E) (*Quercus rubra* L.) (*Q. rubra* du Roi) (*Qborealis* Michx. f.)
Pin oak (A), Hill's oak (*Quercus ellipsoidalis*)
Pyrenean oak (E) (*Quercus pyrenaeica* Willd.) (=*Q. toza* D.C.)
White oak (A), American white oak (E) (*Quercus alba* L.)
Japanese oak, Blue Japanese oak (*Quercus crispula* (Blume) (=*Quercus mongolica, subsp crispula* (Blume)), Japanese name Mizonara.

Other woody plants

Ash, Common ash, European ash (*Fraxinusexcelcior* L.)
Black cherry (A, E) (*Prunus serotina* Ehrh.)
Black locust (*Robinia pseudoacacia* L.)
European ash (A), Common ash (E) (*Fraxinus excelsior* L.)
European blueberry (A), Bilberry (E) (*Vaccinium myrtillus* L)
European mountain ash, Mountain ash (A), Rowan (E) (*Sorbus aucuparia* L.)
Filbert (A), Common hazel (E) (*Corylus avellana* L.)
Flowering dogwood (A), Cornel (E) (*Cornus florida* L.)
Heather (A, E) (*Calluna vulgaris* (L.) Hull)
Lime (*Tilia cordata)*
Lingonberry (A), Cowberry (E), (*Vaccinium vitis-idea* L.)
Sierra palm (A), Mountain palm (E) (*Prestoea montana* (R. Graham) Nichols.)
Tabonuco, Gommier, Candle tree (A, E) (*Dacryodes excelsa* Vahl)
Yellow poplar, Tulip poplar (A, E) (*Liriodendron tulipfera* L.)

References

Aber JD, Melillo JM (1982) Nitrogen immobilization in decaying hardwood leaf litter as a function of initial nitrogen and lignin content. Can J Bot 60:2263–2269

Aber JD, McClaugherty CA, Melillo JM (1984) Litter decomposition in Wisconsin forests—mass loss, organic-chemical constituents and nitrogen. Univ Wisc Res Bull R3284, University of Wisconsin, Madison

Aber JD, Melillo JM, McClaugherty CA (1990) Predicting long-term patterns of mass loss, nitrogen dynamics, and soil organic matter formation from initial fine litter chemistry in temperate forest ecosystems. Can J Bot 68:2201–2208

Aber JD, McDowell WH, Nadelhoffer KJ, Magill A, Bernston G, Kamakea M, McNulty SG, Currie W, Rustad L, Fernandez I (1998) Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. BioScience 48:921–934

Aerts R (1997) Climate, leaf litter chemistry and leaf-litter decomposition in terrestrial ecosystems—a triangular relationship. Oikos 79:439–449

Agee JK, Huff MH (1987) Fuel succession in western hemlock—Douglas-fir forest. Can J For Res 17:697–704

Ågren G, Bosatta E (1996) Quality: a bridge between theory and experiment in soil organic matter studies. Oikos 76:522–528

Ågren G, Hyvönen R (2003) Changes in carbon stores in Swedish forest soils due to increased biomass harvest and increased temperatures analysed with a semi-empirical model. Forest Ecol Managem 174:25–33

Akselsson C (2005) Regional nutrient budgets in forest soils in a policy perspective. Ph.D. thesis, department of chemical engineering, Lund University, Sweden

Akselsson C, Westling O (2005) Regionalized nitrogen budgets in forest soils for different deposition and forestry scenarios in Sweden. Global Ecol Biogeogr 14:85–95

Akselsson C, Berg B, Meentemeyer V, Westling O (2005) Carbon sequestration rates in organic layers in boreal and temperate forest soils—Sweden as a case study. Global Ecol Biogeogr 14:77–84

Alban DH, Pastor J (1993) Decomposition of aspen, spruce, and pine boles on two sites in Minnesota. Can J For Res 23:1744–1749

Anagnost SE (1998) Light microscopic diagnosis of wood decay. IAWA J 19:141–167

Ander P, Eriksson K-E (1977) Selective degradation of wood components by white-rot fungi. Physiol Plant 41:239–248

Ander P, Marzullo L (1997) Sugar oxidoreductases and veratryl alcohol oxidase as related to lignin degradation. J Biotech 53:115–131

Anderson JM, Macfadyen A (eds) (1976) The role of terrestrial and aquatic organisms in decomposition processes. Blackwell, Oxford, pp 474

Anonymous (1996) Forstliche Standortsaufnahme. Begriffe, Definitionen, Einteilungen, Kennzeichnungen, Erläuterungen, 5th edn. IHW, Eching. ISBN 3-930167-18-2 (in German)

B. Berg and C. McClaugherty, *Plant Litter*, DOI: 10.1007/978-3-642-38821-7,

Anonymous (2000) Skogliga konsekvensanalyser 1999. National Board of Forestry, Report 2:2000 (In Swedish). ISSN 1100-0295

Anonymous (2002) Atlas florae europaeae issued by the botanical museum of the finnish museum of natural history, Helsinki. Web site http://www.fmnh.helsinki.fi/map/-afe/E_afe.htm?pageid=571&language=English

Archibald F, Roy B (1992) Production of manganic chelates by laccase from the lignin-degrading fungus *Trametes (Coriolus) versicolor*. Appl Environ Microbiol 58:1496–1499

Armentano T, Loucks O (1990) Spatial patterns of S and N deposition in the midwestern hardwoods region. In: Loucks O (ed) Air pollutants and forest response: the ohio corridor study, Year 4 Annual Report. Miami University, Holcomb Research Institute, Oxford

Arnold von saknas I listan, Beier C, Eckersten H (1998) Modelling the effects of nitrogen addition on soil nitrogen status and nitrogen uptake in a Norway spruce stand in Denmark. Environm Pollut S1 409–414

Arthur MA, Fahey TJ (1990) Mass and nutrient content of decaying boles in an Engelmann spruce/subalpine fir forest, Rocky Mountain National Park, Colorado. Can J For Res 20:730–727

Arthur MA, Tritton LM, Fahey TJ (1993) Dead bole mass and nutrients remaining 23 years after clear-felling of a northern hardwood forest. Can J For Res 23:1298–1305

Axelsson G, Berg B (1988) Fixation of ammonia (^{15}N) to scots pine needle litter in different stages of decomposition. Scand J For Res 3:273–280

Axelsson B, Bråkenhielm S (1980) Investigation sites of the swedish coniferous forest project—biological and physiological features. In: Structure and function of northern coniferous forest. An ecosystem study. Ecol Bull (Stockh) 32:391–400

Bakken LR (1997) Cultural and nonculturable bacteria in soil. In: Van Elsas JD, Trevors JT, Wellington MH (eds) Modern soil microbiology. Dekker, New York, pp 47–62

Bal L (1973) Micromorphological analysis of soils. Soil survey papers of the Netherlands soil survey institute No 6, Wageningen

Ballard R, Will GM (1981) Accumulation of organic matter and mineral nutrients under a *Pinusradiate* stand. NZ J Forest Sci 11(2):145–151

Beatty SW, Stone EL (1986) The variety of soil micro-sites created by tree falls. Can J For Res 16:539–548

Bélaich JP, Tardif C, Bélaich A, Caudin C (1997) The cellulolytic system of *Clostridium cellulolyticum*. J Biotech 57:3–14

Bengtsson G (1992) Interactions between fungl, bacteria, and beech leaves in a stream microcosm. Oecologia 89:542–549

Berg B (1984) Decomposition of root litter and some factors regulating the process: long-term root litter decomposition in a scots pine forest. Soil Biol Biochem 16:609–617

Berg B (1988) Dynamics of nitrogen (^{15}N) in decomposing Scots pine (*Pinus silvestris* L.) needle litter. Long-term decomposition in a Scots pine forest VI. Can J Bot 66:1539–1546

Berg B (1998a) A maximum limit for foliar litter decomposition—a synthesis of data from forest systems. Dept For Ecol For Soil, Swed Univ Agric Sci. Rept 77:158

Berg B (1998b) Organic-matter quality and C/N ratio as controlling factors of RSOM turnover. In: refractory soil organic matter (RSOM): structure and stability. Bayreuth, 26–28 Apr 1998. Mitt Dtsch Bodenkundl Ges 87:79–91

Berg B (2000a) Initial rates and limit values for decomposition of Scots pine and Norway spruce needle litter—a synthesis for N-fertilized forest stands. Can J For Res 30:122–135

Berg B (2000b) Litter decomposition and organic matter turnover in northern forest soils. For Ecol Manage 133:13–22

Berg B (2004) Sequestration rates for C and N in humus at four N-polluted temperate fo est stands. In: Matzner E (ed) Biogeochemistry of forested catchments in a changing environment. A German case study. Ecological studies Vol 172. Springer, Berlin, pp 361–376

Berg B, Cortina J (1995) Nutrient dynamics in some decomposing leaf and needle litters in a Pinus sylvestris forest. Scand J For Res 10:1–11

Berg B, Dise N (2004a) Does a higher N content in plant litter give a higher N sequestration in soil organic matter? Water Air Soil Pollut Focus 4:343–358
Berg B, Dise N (2004b) Calculating the long-term stable nitrogen sink in northern Eurpean forests. Acta Oecologica 26:15–21
Berg B, Ekbohm G (1983) Nitrogen immobilization to decomposing needle litter at variable carbon—nitrogen ratios. Ecology 64:63–67
Berg B, Ekbohm G (1991) Litter mass loss rates and decomposition patterns in some needle and leaf litter types. Long-term decomposition in a Scots pine forest VII. Can J Bot 69:1449–1456
Berg B, Ekbohm G (1993) Decomposing needle litter in lodgepole pine (*Pinus contorta*) and Scots pine (*Pinus sylvestris*) monocultural systems. Is there a maximum mass loss? Scand J For Res 8:457–465
Berg B, Johansson M-B (1998) A maximum limit for foliar litter decomposition—a synthesis of data from forest systems. Dept Forest Ecology Forest Soils, Swed Univ Agric Sci Rep 77:158
Berg B, Lundmark J-E (1987) Decomposition of needle litter in lodgepole pine and Scots pine monocultures—a comparison. Scand J For Res 2:3–12
Berg B, Matzner E (1997) The effect of N deposition on the mineralization of C from plant litter and humus. Environ Rev 5:1–25
Berg B, McClaugherty C (1989) Nitrogen and phosphorus release from decomposing litter in relation to the disappearance of lignin. Can J Bot 67:1148–1156
Berg B, McClaugherty C (2008) Plant litter, decomposition, humus formation, carbon sequestration, 2nd edn. Springer, Heidelberg, p 338
Berg B, Meentemeyer V (2001) Litterfall in European pine and spruce forests as related to climate. Can J For Res 31:292–301
Berg B, Meentemeyer V (2002) Litter quality in a north European transect versus carbon storage potential. Plant Soil 242:83–92
Berg B, Staaf H (1980a) Decomposition rate and chemical changes in Scots pine needle litter. II. Influence of chemical composition. Ecol Bull (Stockh) 32:373–390
Berg B, Staaf H (1980) Leaching, accumulation and release of nitrogen from decomposing forest litter. Ecol Bull (Stockh) 32:163–178
Berg B, Staaf H (1981) Chemical composition of main plant litter components at Ivantjärnsheden—data from decomposition studies. Swed Conif For Proj Int Rept 104:10
Berg B, Staaf H (1983) The influence of slash removal on soil organic matter and nutrients in a Scots pine forest soil I & II; II. Short-term dynamics of carbon and nitrogen pools in soil and the contents of plant nutrients in the forest floor. Swed Conif For Proj Tech Rep 34:25–66
Berg B, Staaf H (1987) Release of nutrients from decomposing white birch leaves and Scots pine needle litter. Pedobiologia 30:55–63
Berg B, Tamm CO (1991) Decomposition and nutrient dynamics of litter in long-term optimum nutrition experiments. I. Organic matter decomposition in Norway spruce (*Picea abies*) needle litter. Scand J For Res 6:305–321
Berg B, Theander O (1984) The dynamics of some nitrogen fractions in decomposing Scots pine needles. Pedobiologia 27:161–167
Berg B, von Hofsten B, Pettersson G (1972) Electron microscopic observations on the degradation of cellulose fibres by *Cellvibrio fulvus* and *Sporocytophaga myxococcoides*. J Appl Bact 35:215–219
Berg B, Hannus K, Popoff T, Theander O (1980) Chemical components of scots pine needles and needle litter and inhibition of fungal species by extractives. In: Persson T (ed) Structure and function of northern coniferous forests—an ecosystem study. Ecol Bull (Stockh) 32:391–400
Berg B, Hannus K, Popoff T, Theander O (1982a) Changes in organic-chemical components during decomposition. Long-term decomposition in a Scots pine forest I. Can J Bot 60:1310–1319
Berg B, Wessen B, Ekbohm G (1982b) Nitrogen level and lignin decomposition in Scots pine needle litter. Oikos 38:291–296

Berg B, Ekbohm G, McClaugherty CA (1984) Lignin and holocellulose relations during long-term decomposition of some forest litters. Long-term decomposition in a scots pine forest IV. Can J Bot 62:2540–2550

Berg B, Jansson PE, Meentemeyer V (1984) Litter decomposition and climate—regional and local models. In: Ågren G (ed) State and change of forest ecosystems—indicators in current research. Swed Univ Agric Sci, Dept Ecol Environ Res Rep 13:389–404

Berg B, Staaf H, Wessén B (1987) Decomposition and nutrient release in needle litter from nitrogen-fertilized Scots pine (*Pinus sylvestris*) stands. Scand J For Res 2:399–415

Berg B, Booltink HGW, Breymeyer A, Ewertsson A, Gallardo A, Holm B, Johansson MB, Koivuoja S, Meentemeyer V, Nyman P, Olofsson J, Pettersson AS, Staaf H, Staaf I, Uba L (1991a) Data on needle litter decomposition and soil climate as well as site characteristics for some coniferous forest sites, 2nd edn, sect 2, Data on needle litter decomposition. Swed Univ Agric Sci, Dept Ecol Environ Res Rep 42:450

Berg B, Ekbohm G, Söderström B, Staaf H (1991a) Reduction of decomposition rates of Scots pine needle litter due to heavy metal pollution. Water Air Soil Pollut 69:165–177

Berg B, Berg M, Bottner P, Box E, Breymeyer A, Calvo de Anta R, Couteaux M, Gallardo A, Escudero A, Kratz W, Madeira M, Mälkönen E, Muñoz F, Meentemeyer V, Piussi P, Remacle J, Virzo De Santo A (1993a) Litter mass loss in pine forests of Europe and eastern United States as compared to actual evapotranspiration on a European scale. Biogeochemistry 20:127–153

Berg B, Berg M, Bottner P, Box E, Breymeyer A, Calvo de Anta R, Couteaux M, Gallardo A, Escudero A, Kratz W, Madeira M, Meentemeyer V, Muñoz F, Piussi P, Remacle J, Virzo De Santo A (1993b) Litter mass loss in pine forests of Europe: relationships with climate and litter quality. In: Breymeyer A (ed) Proceedings of SCOPE seminar conference paper 18. Geography of carbon budget processes in terrestrial ecosystems. Szymbark, 17–23 Aug 1991, pp 81–110

Berg B, Berg M, Cortina J, Escudero A, Gallardo A, Johansson M, Madeira M (1993c) Soil organic matter in some European coniferous forests. In: Breymeyer A (ed) Proceedings of SCOPE seminar conference paper 18. Geography of carbon budget processes in terrestrial ecosystems. Szymbark, 17–23 Aug 1991, pp 111–122

Berg B, Berg M, Flower-Ellis JGK, Gallardo A, Johansson M, Lundmark J-E,Madeira M (1993d) Amounts of litterfall in some European coniferous forests. In: Breymeyer A (ed) Proceedings of SCOPE seminar conference paper 18. Geography of carbon budget processes in terrestrial ecosystems. Szymbark, 17–23 Aug 1991, pp 123–146

Berg B, McClaugherty C, Johansson M (1993e) Litter mass-loss rates in late stages of decomposition at some climatically and nutritionally different pine sites. Long-term decomposition in a Scots pine forest VIII. Can J Bot 71:680–692

Berg B, Calvo de Anta R, Escudero A, Johansson M-B, Laskowski R, Madeira M, McClaugherty C, Meentemeyer V, Reurslag A, Virzo De Santo A (1995a) The chemical composition of newly shed needle litter of different pine species and Scots pine in a climatic transect. Long-term decomposition in a Scots pine forest X. Can J Bot 73:1423–1435

Berg B, McClaugherty C, Virzo De Santo A, Johansson M-B, Ekbohm G (1995b) Decomposition of forest litter and soil organic matter—a mechanism for soil organic matter buildup? Scand J For Res 10:108–119

Berg B, Johansson M-B, Lundmark J-E (1996a) Uppbyggnad av organiskt material i skogsmark—har gödsling och trädslagsval en inverkan? In: Berg B (ed) Markdagen 1996. Dept For Ecol For Soil, Swed Univ Agric Sci Rep 72:33–44 (in Swedish)

Berg B, Ekbohm G, Johansson M-B, McClaugherty C, Rutigliano F, Virzo De Santo A (1996b) Some foliar litter types have a maximum limit for decomposition—a synthesis of data from forest systems. Can J Bot 74:659–672

Berg B, McClaugherty C, Johansson M-B (1997) Chemical changes in decomposing plant litter can be systemized with respect to the litter's initial chemical composition. Dept For Ecol For Soil, Swed Univ Agric Sci Rep 74:85

Berg B, Meentemeyer V, Johansson M-B, Kratz W (1998) Decomposition of tree root litter in a climatic transect of forests in northern Europe—a synthesis. Scand J For Res 13:402–412
Berg B, Albrektson A, Berg M, Cortina J, Johansson M-B, Gallardo A, Madeira M, Pausas J, Kratz W, Vallejo R, McClaugherty C (1999a) Amounts of litterfall in pine forests in the northern hemisphere, especially Scots pine. Ann For Sci 56:625–639
Berg B, Laskowski R, Virzo De Santo A (1999b) Estimated N concentration in humus as based on initial N concentration in foliar litter—a synthesis. Can J Bot 77:1712–1722
Berg B, Meentemeyer V, Johansson M-B (2000) Litter decomposition in a climatic transect of Norway spruce forests—climate and lignin control of mass-loss rates. Can J For Res 30:1136–1147
Berg B, McClaugherty C, Virzo De Santo A, Johnson D (2001) Humus buildup in boreal forests—effects of litter fall and its N concentration. Can J For Res 31:988–998
Berg B, Virzo De Santo A, Rutigliano F, Ekbohm G (2003) Limit values for plant litter decomposing in two contrasting soils—influence of litter elemental composition. Acta Oecologia 24:295–302
Berg B, Steffen K, McClaugherty C (2006) Litter decomposition rates as dependent on litter Mn concentration. Biogeochemistry 82:29–39
Berg B, Gundersen P, Akselsson C, Johansson MB, Nilsson Å, Vesterdal L (2007) Carbon sequestration rates in nordic forest soils—some results from three approaches. Silva Fennica 41(3):541–558
Berg B, Johansson M-B, Nilsson Å, Gundersen P, Norell L (2009) Sequestration of carbon in soil organic matter layers in Swedish forests—direct measurements. Can J For Res 39:962–975
Berg B, De Marco A, Davey M, Emmett B, Hobbie S, Liu C, McClaugherty C, Norell L, Johansson M-B, Rutigliano F, Vesterdal L, Virzo De Santo A (2010) Limit values for foliar litter decomposition—pine forests. Biogeochemistry 100:57–73
Berg B, Liu C, Laskowski R, Davey M (2013) Relationships between nitrogen, AUR, and climate among tree foliar litters. Can J For Res 43:103–107
Berg B, Erhagen B, Johansson MB, Vesterdal L, Faituri M, Sanborn P, Nilsson M (201Xb) Manganese dynamics in decomposing foliar litter. Can J For Res XX: XXX–XXX (Accepted for publication)
Bergkvist B (1986) Metal fluxes in spruce and beech forest ecosystems of south Sweden. Ph.d thesis, Univeristy of Lund, Sweden
Bergstrand M, Brandt M, Arheimer B, Grahn G, Gyllander A, Pers C, Svensson P, Ejhed H, Johnsson H, Olsson K, Mårtensson K, Löfgren S, Westling O (2002) TRK—nutrient load in Sweden—an operational system for catchment modelling of nutrient transport, retention and source apportionment. In: Killingtveit Å (ed) Proceedings of nordic hydrologic programme (NHP). Report 47(1). Nordic Association of Hydrology, Röros, pp 211–220
Bethge PO, Rådeström R, Theander O (1971) Kvantitativ kolhydratbestämning—en detaljstudie. Comm Swed For Prod Res Lab 63B. SE-114 86 Stockholm, p 48 (in Swedish)
Blackwood CB, Buyer JS (2007) Evaluating the physical capture method of terminal restriction fragment length polymorphism for comparison of soil microbial communities. Soil Biol Biochem 39:590–599
Blair JM (1988a) Nitrogen, sulphur and phosphorus dynamics in decomposing deciduous leaf litter in the southern appalachians. Soil Biol Biochem 20:693–701
Blair JM (1988b) Nutrient release from decomposing foliar litter of three tree species with special reference to calcium, magnesium and potassium dynamics. Plant Soil 110:49–55
Blair JM, Parmelee RW, Beare MH (1990) Decay rates, nitrogen fluxes, and decomposer communities of single- and mixed-species foliar litter. Ecology 71:1976–1985
Blanchette RA (1984) Manganese accumulation in wood decayed by white rot fungi. Phytopathology 74:725–730
Blanchette RA (1991) Delignification by wood-decay fungi. Annu Rev Phytopathol 29:381–398
Blanchette RA (1995) Degradation of the lignocellulose complex in wood. Can J Bot 73(Suppl):S999–S1010

Blanchette RA, Shaw CG (1978) Associations among bacteria, yeasts, and basidiomycetes during wood decay. Phytopathology 68:631–637

Blanchette RA, Krueger EW, Haight JE, Akhtar M, Akin DE (1997) Cell wall alterations in loblolly pine wood decayed by the white-rot fungus *Ceriporiopsis subvermispora*. J Biotech 53:203–213

Bloomfield J, Vogt KA, Vogt DJ (1993) Decay rate and substrate quality of fine roots and foliage of two tropical tree species in the Luquillo experimental forest, Puerto Rico. Plant Soil 150:233–245

Bockheim JG, Leide LE (1986) Litter and forest floor dynamics in Wisconsin. Plant Soil 96:393–406

Bocock KL, Gilbert O, Capstick CK, Twinn DC, Waid JS, Woodman MJ (1960) Changes in leaf litter when placed on the surface of soils with contrasting humus types. I. Losses in dry weight of oak and ash leaf litter. J Soil Sci 11:1–9

Boddy L, Watkinson SC (1995) Wood decomposition, higher fungi, and their role in nutrient redistribution. Can J Bot 73(Suppl 1):S1377–S1383

Boddy L, Owens EM, Chapela IH (1989) Small scale variation in decay rate within logs one year after felling: effect of fungal community structure and moisture content. FEMS Microbiol Ecol 62:173–184

Boerner REJ, Rebbeck J (1995) Decomposition and nitrogen release from leaves of three hardwood species grown under elevated O_3 and/or CO_2. In: Collins HP, Robertson GP, Klug MJ (eds) The significance and regulation of soil biodiversity. Kluwer, Amsterdam, pp 169–177

Bogatyrev L, Berg B, Staaf H (1983) Leaching of plant nutrients and total phenolic substances from some foliage litters—a laboratory study. Swed Conif For Proj Tech Rep 33, p 59

Bolin B, Doos BR, Jager J, Warrick R (eds) (1986) The greenhouse effect, climatic change and ecosystems. SCOPE 29. Wiley, Chichester, p 541

Bollag JM, Minard RD, Liu SY (1983) Cross-linkage between anilines and phenolic constituents. Environ Sci Technol 17:72–80

Bono JJ, Gas G, Boudet M, Fayret J, Delatour C (1984) Etude comparee de la degradation de lignocelluloses par differentes souches de *Fomes annosus*. Can J Microbiol 29:1683–1688

Bormann BT, DeBell DS (1981) Nitrogen content and other soil properties to age of red alder stands. Soil Sci Soc Am J 45:428–432

Bosatta E, Ågren G (1985) Theoretical analysis of decomposition of heterogeneous substrates. Soil Biol Biochem 17:601–610

Bosatta E, Ågren G (1991) Dynamics of carbon and nitrogen in the organic matter of the soil: a general theory. Am Nat 138:227–245

Botkin DB (1990) Discordant harmonies: a new ecology for the twenty-first century. Oxford University, New York, p 241

Boxman AW, Blanck K, Brandrud TE, Emmett BA, Gundersen P, Hogervorst RF, Kjønaas OJ, Persson H, Timmermann V (1998) Vegetation and soil biota response to experimentally-changed nitrogen inputs in coniferous forest ecosystems of the NITREX project. For Ecol Manage 101:65–79

Brandt M, Ejhed H (2003) TRK transport—retention—källfördelning. Belastning på havet. Swedish environmental protection agency, Report 5247, p 44 (In Swedish)

Bray MW, Andrews TM (1924) Chemical changes of groundwood during decay. Indus Eng Chem 16(2):137–139

Bremer E, van Houtum W, van Kessel C (1991) Carbon dioxide evolution from wheat and lentil residues affected by grinding, added nitrogen, and absence of soil. Biol Fertil Soils 11:221–227

Breymeyer A, Laskowski R (1999) Ecosystem process studies along a climatic transect at 52–53° N, 12–32° E: pine litter decomposition. Geog Polon 72:45–64

Bringmark E, Bringmark L (1991) Large-scale pattern of mor layer degradation in Sweden measured as standardized respiration. In: Humic substances in the aquatic and terrestrial environments. Proceedings of an international symposium, Linköping, Sweden, 21–23 Aug 1989. Lecture notes in earth sciences, no 33. Springer, Berlin, pp 255–259

Broadbent FE, Stevenson FJ (1966) Organic matter interactions. In: McVickar HN et al. (eds) Agricultural anhydrous ammonia. Technology and use. Proceedings of symposium St Louis, Mo, 29–30 Sep 1965. Agric Ammonia Inst, Memphis, Tenn; Am Soc Agron and Soil Sci Soc Am, Madison, pp 169–187

Bunell F, Tait DEN, Flanagan PW, Van Cleve K (1977) Microbial respiration and substrate weight loss. I. A general model of the influence of abiotic variables. Soil Biol Biochem 9:33–40

Burke MK, Raynal DJ (1994) Fine root growth phenology, production, and turnover in a northern hardwood forest ecosystem. Plant Soil 162:135–146

Cameron MD, Aust SD (2001) Cellobiose dehydrogenase—an extracellular fungal flavocytochrome. Enzyme Microbiol Tech 28:129–138

Camiré C, Côté B, Brulotte S (1991) Decomposition of roots of black alder and hybrid poplar in short rotation plantings: nitrogen and lignin control. Plant Soil 138:123–132

Carpenter SR (1981) Decay of heterogeneous detritus: a general model. J Theor Biol 89:539–547

Carreiro MM, Howe K, Parkhurst DF, Pouyat RV (1999) Variation in quality and decomposability of red oak leaf litter along an urban rural gradient. Biol Fertil Soils 30:258–268

Chadwick DR, Ineson P, Woods C, Piearce TG (1998) Decomposition of *Pinus sylvestris* litter in litter bags: Influence of underlying native litter. Soil Biol Biochem 30:47–55

Chambers JQ, Higuchi N, Schimel JP, Ferreira LV, Melak JM (2000) Decomposition and carbon cycling of dead trees in tropical forests of the central Amazon. Oecologia 122:380–388

Cole DW, Compton JE, Edmonds RL, Homann PS, Van Miegroet H (1995) Comparison of carbon accumulation in douglas fir and red alder forests. In: McFee WW, Kelly JM (eds) Carbon forms and functions in Forest Soils. Soil Sci Soc Am, Madison, pp 527–546

Core HA, Cote WA, Day AC (1979) Wood structure and identification. Syracuse University Press, Syracuse, p 182

Cotrufo MF, Ineson P (1995) Effects of enhanced atmospheric CO_2 and nutrient supply on the quality and subsequent decomposition of fine roots of *Betula pendula* Roth. and *Picea sitchensis* (Bong.) Carr. Plant Soil 170:P267–P277

Cotrufo MF, Ineson P (1996) Elevated CO_2 reduces field decomposition rates of *Betula pendula* (Roth.) leaf litter. Oecologia 106:525–530

Cotrufo F, Berg B, Kratz W (1998) Increased atmospheric CO_2 concentrations and litter quality. Environ Rev 6:1–12

Coughtrey PJ, Jones CH, Martin MH, Shales SW (1979) Litter accumulation in woodlands contaminated by Pb, Zn Cd and Cu. Oecologia 39:51–60

Couteaux M–M, McTiernan K, Berg B, Szuberla D, Dardennes P (1998) Chemical composition and carbon mineralisation potential of Scots pine needles at different stages of decomposition. Soil Biol Biochem 30:583–595

Crawford RL (1981) Lignin biodegradation and transformation. Wiley, New York, p 137

Currie WS, Harmon ME, Burke IC, Hart C, Parton JW, Silver W (2010) Cross-biome transplants of plant litter show decomposition models extend to a broader climatic range but lose predictability at the decadal time scale. Global Change Biology 16(6):1744–1761

Dahlgren RA, Vogt KA, Ugolini FC (1991) The influence of soil chemistry on fine root aluminum concentrations and root dynamics in a sub alpine Spodosol, Washington State, USA. Plant Soil 133:117–129

Dalias P, Anderson JM, Bottner P, Coûteaux MM (2001) Long-term effects of temperature on carbon mineralisation processes. Soil Biol Biochem 33:1049–1057

Davey M, Berg B, Emmett B, Rowland P (2007) Controls of foliar litter decomposition and implications for C sequestration in oak woodlands. Can J Bot 85:16–24

David MB, Vance GF, Rissing JM, Stevenson FJ (1989) Organic carbon fractions in extracts of O and B horizons from a New England Spodosol: effects of acid treatment. J Environ Qual 18:212–217

De Haan S (1977) Humus, its formation, its relation with the mineral part of the soil and its significance for soil productivity. In: Organic matter studies, vol 1. pp 21–30

De Marco A, Esposito F, Berg B, Giordano M, Virzo De Santo A (2013) Soil C and N accumulation in forest floor and mineral soil under two coeval forest stands implanted on pyroclastic material at Mount Vesuvius. Geoderma. 209–210: 128–135

De Marco A, Spaccini R, Vittozzi P, Esposito F, Berg B, Virzo De Santo A (2012) Decomposition of black locust and black pine leaf litter in two coeval forest stands on Mount Vesuvius and dynamics of organic components assessed through proximate analysis and NMR spectroscopy. Soil Biol Biochem 51:1–15

de Saussure HB (1796) Voyages dans les Alpes 5:208-xxx. (in French)

Dean JFD (1997) Lignin analysis, chap 17. In: Dashek WV (ed) Methods in plant biochemistry and molecular biology. CRC Press, New York, pp 199–215

Dekker RFH (1985) Biodegradation of hemicelluloses. In: Higuchi T (ed) Biosynthesis and biodegradation of wood components. Academic Press, Tokyo, pp 505–533

Delaney M, Brown S, Lugo AE, Torres-Lezama A, Quintero NB (1998) The quantity and turnover of dead wood in permanent forest plots in six life zones of Venezuela. Biotropica 30(1):2–11

Delcourt HR, Harris WF (1980) Carbon Budget of the South-Eastern US Biota: analysis of historical change in trend from source to sink. Science 210:321–323

DeLuca TH, Boisvenue C (2012) Boreal forest soil carbon: distribution, function and modelling. Forestry 85(2):161–184

DeLuca H, Zackrisson O, Nilsson M-C, Sellstedt A (2002) Quantifying nitrogen-fixation in feather moss carpets of boreal forests. Nature 419:917–920

Dornbusch ME, Isenhart TM, Raich J (2002) Quantifying fine-root decomposition: an alternative to buried litterbags. Ecology 83:2985–2990

D'Souza TM, Merritt CS, Reddy CA (1999) Lignin-modifying enzymes of the white-rot basidiomycete *Ganoderma lucidum*. Appl Environ Microbiol 65:5307–5313

Dugger WM (1983) Boron in plant metabolism. In: Läuckli A, Bielski RL (eds) Inorganic plant nutrition, vol 15B. Springer, Berlin, pp 626–650

Dwyer LM, Merriam G (1981) Influence of topographic heterogeneity on deciduous litter decomposition. Oikos 37:228–237

Dwyer LM, Merriam G (1983) Decomposition of natural litter mixtures in a deciduous forest. Can J Bot 62:2340–2344

Dyer ML (1986) A model of organic decomposition rates based on climate and litter properties. M. A. thesis, University of Georgia, Athens, p 78

Dyer ML, Meentemeyer V, Berg B (1990) Apparent controls of mass loss rate of leaf litter on a regional scale. Scand J For Res 5:311–323

Dziadowiec H (1987) The decomposition of plant litter fall in an oak-linden-hornbeam forest and oak-pine mixed forest of the Bialowieza national park. Acta Soc Bot Polon 56:169–185

Edmonds RL (1979) Decomposition and nutrient release in Douglas-fir needle litter in relation to stand development. Can J For Res 9:132–140

Effland MJ (1977) Modified procedure to determine acid insoluble lignin in wood and pulp. Tech Assoc Pulp Pap Ind J 60(10):143–144

Egnell G, Nohrstedt H-Ö, Weslien J, Westling O, Örlander G (1998) Miljökonsekvens-beskrivning av skogsbränsleuttag, asktillförsel och övrig näringskompensation. National board of forestry, Report 1:1998, Jönköping, Sweden (In Swedish)

Emmett BA, Brittain SA, Hughes S, Kennedy V (1995) Nitrogen additions ($NaNO_3$ and NH_4NO_3) at Aber forest, Wales: II. Response of trees and soil nitrogen transformations. For Ecol Manage 71:61–73

Erickson HE, Edmonds RL, Peterson CE (1985) Decomposition of logging residues in douglas-fir, western hemlock, pacific silver fir, and ponderosa pine ecosystems. Can J For Res 15:914–921

Ericsson E (2003) Carbon sequestration and fossil fuel substitution during different rotation scenarios. Scand J For Res 18:269–278

Eriksson K-E, Blanchette RA, Ander P (1990) Microbial and enzymatic degradation of wood and wood components. Springer, Berlin, p 407

Fahey TJ, Hughes JW (1994) Fine root dynamics in a northern hardwood forest ecosystem, Hubbard Brook Experimental Forest, NH. J Ecol 82:533–548

Fahey TJ, Hughes JW, Pu M, Arthur M (1988) Root decomposition and nutrient flux following whole-tree harvest of northern hardwood forest. For Sci 34:744–768

Faituri MY (2002) Soil organic matter in Mediterranean and scandinavian forest ecosystems and dynamics of nutrients and monomeric phenolic compounds. Silvestra 236:136

Fengel D, Wegener G (1983) Wood: chemistry, ultrastructure, reactions. De Gruyter, Berlin, p 613

Fenn M (1991) Increased site fertility and litter decomposition rate in high-pollution sites in the San Bernadino mountains. For Sci 37:1163–1181

Fenn ME, Dunn PH (1989) Litter decomposition across an air-pollution gradient in the San Bernardino mountains. Soil Sci Soc Am J 53:1560–1567

Flaig W, Schobinger U, Deuel H (1959) Umwandlung von Lignin in huminsäuren bei der verrottung von weizenstrah. Chem Ber 92:1973–1982 (in German)

Flessa H, Ludwig B, Heil B, Merbach W (2000) The origin of soil organic C, dissolved organic C and respiration in a long-term maize experiment in Halle, Germany, determined by ^{13}C natural abundance. J Plant Nutr Soil Sci 163:157–163

Flower-Ellis J (1985) Litterfall in an age series of Scots pine stands: summary of results for the period 1973–1983. Dept Ecol Environ Res Swed Univ Agric Sci Rept 19:75–94

Fog K (1988) The effect of added nitrogen on the rate of decomposition of organic matter. Biol Rev 63:433–462

Fogel R, Cromack K (1977) Effect of habitat and substrate quality on Douglas fir litter decomposition in western Oregon. Can J Bot 55:1632–1640

Forrest WG, Ovington JD (1970) Organic matter changes in an age series of *Pinus radiata* plantations. J Appl Ecol 7:110–120

Franck VM, Hungate BA, Chapin FS, Field CB (1997) Decomposition of litter produced under elevated CO_2: dependence on plant species and nutrient supply. Biogeochemistry 36:223–237

Freedman B, Hutchinson TC (1980) Effects of smelter pollution on forest leaf litter decomposition near a nickel-copper smelter at Sudbury, Ontario. Can J Bot 58:1722–1736

Freer SN, Detroy RW (1982) Biological delignification of ^{14}C-labeled lignocelluloses by basidiomycetes: degradation and solubilization of the lignin and cellulose components. Mycologia 74:943–951

Fritze H, Kiikkilä O, Pasanen J, Pietikäinen J (1992) Reaction of forest soil microflora to environmental stress along a moderate pollution gradient next to an oil refinery. Plant Soil 140:175–182

Gadgil RL, Gadgil PD (1978) Influence of clearfelling on decomposition of *Pinus radiata* litter. N Z J Sci 8:213–224

Gholz HL, Wedin DA, Smitherman SM, Harmon ME, Parton WJ (2000) Long-term dynamics of pine and hardwood litter in contrasting environments: toward a global model of decomposition. Glob Change Bio 6:751–765

Giardina CP, Ryan MG (2000) Evidence the decomposition rates of organic carbon in mineral soil do not vary with temperature. Nature 404:858–861

Gilbertson RL (1980) Wood-rotting fungi of North America. Mycologia 72:1–49

Gilliam FS, Yurish BM, Adams MB (2001) Temporal and spatial variation of nitrogen transformations in nitrogen-saturated soils of a central appalachian hardwood forest. Can J For Res 31:1768–1785

Goodburn JM, Lorimer CG (1998) Cavity trees and coarse woody debris in old-growth and managed northern hardwood forests in Wisconsin and Michigan. Can J For Res 28:427–438
Gore JA, Patterson WA (1986) Mass of downed wood in northern hardwood forests in New Hampshire: potential effects of forest management. Can J For Res 16:335–339
Gosz JR (1981) Nitrogen cycling in coniferous ecosystems. In: Clark FE, Rosswall T (eds) Terrestrial nitrogen cycles. Processes, ecosystem strategies, and management impacts. Ecol Bull (Stockh) 33:405–426
Gove PB (ed) (1996) Webster's new encyclopedic dictionary, New revised edition. Könemann, Köln, p 1637
Graham RL, Cromack K (1982) Mass, nutrient content, and decay rate of dead boles in rain forests of Olympic national park. Can J For Res 17:304–310
Green F, Highley TL (1997) Mechanisms of brown-rot decay: paradigm or paradox. Int Biodet Biodeg 39:113–124
Griffith GS, Boddy L (1990) Fungal decomposition of attached angiosperm twigs. I. Decay community development in ash, beech, and oak. New Phytol 116:407–415
Griffiths R, Caldwell BA, Cromack K, Morita RY (1990) Douglas-fir forest soils colonized by ectomycorrhizal mats. 1. Seasonal variation in nitrogen chemistry and nitrogen transformation rates. Can J For Res 20:211–218
Griffiths RP, Harmon ME, Caldwell BA, Carpenter SE (1993) Acetylene reduction in conifer logs during early stages of decomposition. Plant Soil 148:53–61
Guggenberger G (1994) Acidification effects of dissolved organic matter mobility in spruce forest ecosystems. Environ Int 20:31–41
Güsewell S, Gessner MO (2008) N:P ratios influence litter decomposition and colonization by fungi and bacteria in microcosms. Funct Ecol 23:211–219
Güsewell S, Verhoeven JTA (2006) Litter N:P ratios indicate whether N or P limits the decomposability of graminoid leaf litter. Plant Soil 287:131–143
Hagen-Thorn A, Varnagiryte I, Nihlgård B, Armolaitis K (2006) Autumn nutrient resorption and losses in four deciduous forest tree species. Forest Ecol Manage 228:33–39
Hägglund B (1985) A new swedish national forest survey. Swedish university of agricultural sciences, Report 37, Uppsala, Sweden (In Swedish with english summary)
Hånell B (1990) Torvtäckta marker, dikning och sumpskogar i Sverige. *Skogsfakta* 22. Swedish university of agricultural sciences, Uppsala, Sweden (In Swedish)
Hanson PJ, Edwards NT, Garten CT, Andrews JA (2000) Separating root and soil microbial contributions to soil respiration: a review of methods and observations. Biogeochemistry 48:115–146
Harley JL, Smith SE (1983) Mycorrhizal symbiosis. Academic Press, London, p 483
Harmon ME, Sexton J (1996) Guidelines for measurement of woody detritus in forest ecosystems. US long term ecological research network, Albuquerque, p 42
Harmon ME, Franklin JF, Swanson FJ, Sollins P, Gregory SV, Lattin JD, Anderson NH, Cline SP, Aumen NG, Sedel JR, Lienkaemper GW, Cromack K, Cummins KW (1986) Ecology of coarse woody debris in temperate ecosystems. Adv Ecol Res 15:133–302
Harmon ME, Sexton J, Caldwell BA, Carpenter SE (1994) Fungal sporocarp mediated losses of Ca, Fe, K, Mg, Mn, N, P, and Zn from conifer logs in the early stages of decomposition. Can J For Res 24:1883–1893
Harmon ME, Whigham DF, Sexton J, Olmsted I (1995) Decomposition and mass of woody detritus in the dry tropical forests of the northeastern Yucatan peninsula, Mexico. Biotropica 27:305–316
Harmon ME, Krankina ON, Sexton J (2000) Decomposition vectors: a new approach to estimating woody detritus decomposition dynamics. Can J For Res 30:76–84
Hatakka A (2001) Biodegradation of lignin. In: Hofman M, Stein A (eds) Biopolymers, Lignin, humic substances and coal, vol 1. Wiley, Weinheim, pp 129–180

Hatfield RD, Jung HG, Ralph J, Buxton DR, Weimer PJ (1994) A comparison of the insoluble residues produced by the Klason lignin and acid detergent lignin procedures. J Sci Food Agric 65:51

Hedges JI, Ertel JR (1982) Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. Anal Chem 370(54):174–178

Hendrick RL, Pregitzer KS (1992) The demography of fine roots in a northern hardwood forest. Ecology 73:1094–1104

Hendricks JJ, Nadelhoffer KJ, Aber JD (1993) Assessing the role of fine roots in carbon and nutrient cycling. Trend Ecol Evol 8:174–178

Highley TL (1987) Changes in chemical components of hardwood and softwood by brown-rot fungi. Mater Organ 21:39–45

Highley TL (1988) Cellulolytic activity of brown-rot and white-rot fungi on solid media. Holzforschung 42:211–216

Highley TL, Murmanis LL, Palmer JG (1985) Micromorphology of degradation in western hemlock and sweet gum by the brown-rot fungus *Poria placenta*. Holzforschung 39:73–78

Higuchi T (1993) Biodegradation mechanism of lignin by white-rot basidiomycetes. J Biotech 30:1–8

Hintikka V, Näykki O (1967) Notes on the effects of the fungus *Hydnellum ferrugineum* on forest soil and vegetation. Commun Inst For Fenn 62:1–22

Hirano T, Tanaka H, Enoki A (1997) Relationship between production of hydroxyl radicals and degradation of wood by the brown-rot fungus, *Tyromyces palustris*. Holzforschung 51:389–395

Hobbie S, Eddy WC, Buyarski CR, Adair C, Ogdahl ML, Weisenhorn P (2012) Response of decomposing litter and its microbial community to multiple forms of nitrogen enrichment. Ecol Monogr 82:389–405

Hofrichter M (2002) Review: lignin conversion by manganese peroxidase (MnP). Enzyme Microbiol Technol 30:454–466

Högberg P, Nordgren A, Buchmann N, Taylor A, Ekblad A, Högberg M, Nyberg G, Ottosson-Löfvenius M, Read D (2001) Large-scale forest girdling shows that current photosynthesis drives soil respiration. Nature 411:789–792

Holmsgaard E, Bang C (1977) Et traeartsforsØg med nåletraeer, bØg og e.g. De fØrste 10 år. Forstl ForsØgsvaes Dan 35:159–196 (In Danish)

Houghton RA (2001) Counting terrestrial sources and sinks of carbon. Clim Change 48:525–534

Howard PJA, Howard DM (1974) Microbial decomposition of tree and shrub leaf litter. Oikos 25:311–352

Howard DM, Howard PJA (1980) Effect of species, source of litter, type of soil, and climate on litter decomposition. Microbial decomposition of tree and shrub leaf litter 3. Oikos 34:115–124

Hristovski S, Berg B, Melovski Lj (201X) Decomposition patterns in some litter components of a common beech forest. Pedobiologia XX; XXX–XXX (submitted)

Huang Y, Street-Perrott FA, Metcalfe SE, Brenner M, Moreland M, Freeman KH (2001) Climate change as the dominant control on glacial-interglacial variations in C3 and C4 plant abundances. Science 293:1647–1651

Huhta V, Persson T, Setälä H (1998) Functional implications of soil fauna diversity in boreal forests. Appl Soil Ecol 10:277–288

Hutchinson TC, Havas M (1980) Effects of acid precipitation on terrestrial ecosystems. In: Proceedings of NATO conference on effects of acid precipitation on vegetation and soils, Toronto, Ontario, 1978. Plenum Press, New York, p 654

Hyvönen R, Ågren GI, Dalias P (2005) Analysing temperature response of decomposition of organic matter. Global Change Biol 11:770–778

Intergovernmental Panel on Climate Change (2001) Climate change 2001: the scientific basis. Contribution of working group I to the third assessment report. Cambridge University Press, Cambridge, p 881

Jansson PE, Berg B (1985) Temporal variation of litter decomposition in relation to simulated soil climate. Long-term decomposition in a scots pine forest V. Can J Bot 63:1008–1016
Jefferies RL, Maron JL (1997) The embarrassment of riches: atmospheric deposition of nitrogen and community and ecosystem processes. Trends Ecol Evol 12:74–78
Jenkinson DS (1977) Studies on the decomposition of plant material in soil V. The effects of plant cover and soil type on the loss of carbon from ^{14}C labeled ryegrass decomposing under field conditions. J Soil Sci 28:424–434
Jenny H (1980) The soil resource. Origin and behavior. Springer, Berlin
Jenny H, Gessel SP, Bingham FT (1949) Comparative study of decomposition rates of organic matter in temperate and tropical regions. Soil Sci 68:419–432
Jin L, Schultz TP, Nicholas DD (1990) Structural characterization of brown-rotted lignin. Holzforschung 44:133–138
Joffre R, Ågren GI, Gillon D, Bosatta E (2001) Organic matter quality in ecological studies: theory meets experiment. Oikos 93:451–458
Johansson M-B (1987) Radikal markberedning—ett olämpligt sätt att utnyttja kväveförrådet i avverknings-resterna. Sveriges Skogsvårdsförbunds Tidskrift 2:35–41 (in Swedish)
Johansson M-B, Berg B, Meentemeyer V (1995) Litter mass-loss rates in late stages of decomposition in a climatic transect of pine forests. Long-term decomposition in a Scots pine forest IX. Can J Bot 73:1509–1521
Johnson D, Lindberg SE (1992) Atmospheric deposition and forest nutrient cycling—a synthesis of the integrated forest study. Ecol Stud 91
Johnson D, Todd DE (1998) Effects of harvesting intensity on forest productivity and soil carbon storage in a mixed oak forest. In: Lal R, Kimble JR, Follett J, Stewart BA (eds) Management of carbon sequestration in soil. CRC Press, New York, pp 351–364
Johnson D, Todd DE Jr, Trettib CF, Sedinger JS (2007) Soil carbon and nitrogen changes in forests of Walker branch watershed, 1972–2004. Soil Sci Soc Am J 71(5):1639–1646
Jones PCT, Mollison JE (1948) A technique for the quantitative estimation of soil microorganisms. J Gen Microbiol 2:54–69
Jurgensen MF, Larsen MJ, Spano SD, Harvey AE, Gale MR (1984) Nitrogen fixation associated with increased wood decay in douglas-fir residue. For Sci 30:1038–1044
Kang H, Berg B, Liu C, Westman CJ (2009) Variation in mass-loss rate of foliar litter in relation to climate litter quality in Eurasian forests: differences among functional groups of litter. Silva Fennica 43(4):549–575
Kang H, Zhuang H, Wu L, Shen G, Liu Q, Berg B, Man R, Liu C (2011) Variation of leaf nitrogen and phosphorus stoichiometry in *Picea abies* across Europe: an analysis based on local observations. For Ecol Manage 261:195–202
Kaspari M, Yanoviak SP, Dudley R, Yuan M, Clay NA (2009) Sodium shortage as a constraint on the carbon cycle in an inland tropical rainforest. PNAS 106(46):19405–19409
Kayang H (2001) Fungi and bacterial enzyme activities in *Alnus nepalensis* D. Don. Eur J Soil Sci 37:175–180
Kelsey RG, Harmon ME (1989) Distribution and variation of extractable total phenols and tannins in the logs of four conifers after 1 year on the ground. Can J For Res 19:1030–1036
Kerr TJ, Goring DAI (1975) The ultrastructural arrangement of the wood cell wall. Cell Chem Technol 9:563–573
Keyser P, Kirk TK, Zeikus IG (1978) Ligninolytic enzyme of *Phanerochaete chrysosporium*: synthesized in the absence of lignin in response to nitrogen starvation. J Bacteriol 135:790–797
Killingbeck KT (1996) Nutrients in senesced leaves: keys to the search for potential resorption and resorption proficiency. Ecology 77:1716–1727
Kirk TK (1980) Physiology of lignin metabolism by white rot fungi. In: Kirk TK, Higuchi T, Chang H (eds) Lignin biodegradation: microbiology, chemistry, and potential applications, vol 2. CRC Press, Boca Raton, pp 51–63

Kirk TK (1984) Degradation of lignin. In: Gibson DT (ed) Microbial degradation of organic compounds. Marcel Dekker, New York, pp 399–437
Kiser LC, Kelly JM, Mays PA (2009) Changes in forest soil carbon and nitrogen after a thirty-year interval. Soil Sci Soc Am J 73(2):647–653
Klotzbücher T, Filley TR, Kaiser K, Kalbitz K (2011) A study on lignin degradation in leaf and needle litter using ^{13}C-labelled tetramethylammonium hydroxide (TMAH) thermo-chemolysis: Comparison with CuO oxidation and Van Soest methods. Org Geochem 42:1271–1278
Klotzbücher T, Kkaiser K, Guggenberger G, Gatzek C, Kalbitz K (2011) A new conceptuaö model for the fate of lignin in decomposing plant litter. Ecology 95:1052–1062
Knapp EB, Elliott LF, Campbell GS (1983) Microbial respiration and growth during the decay of wheat straw. Soil Biol Biochem 15:319–323
Knicker N (2004) Stabilization of N-compounds in soil and organic-matter-rich sediments—what is the difference? Mar Chem 92:167–195
Kögel I (1986) Estimation and decomposition pattern of the lignin component in forest humus layers. Soil Biol Biochem 18(6):402, 589–594
Kögel I, Bochter R (1985) Characterization of lignin in forest humus layer by high-performance liquid chromatography of cupric oxide oxidation products. Soil Biol Biochem 17(5):637–640
Kögel-Knabner I, Ziegler F, Riederer M, Zech W (1989) Distribution and decomposition pattern of cutin and suberin in forest soils. Z Pflanzenernähr Bodenkd 152:409–413
Kolattukudy PE (1980) Biopolyester membranes of plants: cutin and suberin. Science 208:990–1000
Kolattukudy PE (1981) Structure, biosynthesis, and biodegradation of cutin and suberin. Annu Rev Plant Physiol 32:359–367
Kolattukudy PE (1984) Biochemistry and function of cutin and suberin. Can J Bot 62:2918–2933
Kranabetter JM, Chapman BK (1999) Effects of forest soil compaction and organic matter removal on leaf litter decomposition in central British Columbia. Can J Soil Sci 79:543–550
Krankina ON, Harmon ME, Griazkin AV (1999) Nutrient stores and dynamics of woody debris in a boreal forest: modeling potential implications at the stand level. Can J For Res 29:20–32
Kuperman RG (1999) Litter decomposition and nutrient dynamics in oak-hickory forests along a historic gradient of nitrogen and sulfur deposition. Soil Biol Biochem 31:237–244
Kurz WA, Kimmins JP (1987) Analysis of some sources of error in methods used to determine fine root production in forest ecosystems: a simulation approach. Can J For Res 17:909–912
Kurz-Besson C, Coûteaux MM, Thiéry JM, Berg B, Remacle J (2005) Litterbag method versus direct observation for describing scots pine needle decomposition. Soil Biol Biochem 37:2315–2318
Langner J, Persson C, Robertson L, Ullerstig A (1996) Air pollution assessment study using the MATCH modelling system. Application to sulphur and nitrogen compounds over Sweden 1994. Swedish meteorological and hydrological institute, Report no. 69. CA-Tryck AB, Norrköping, Sweden
Larsen MJ, Jurgensen MF, Harvey AE (1978) N_2 fixation associated with wood decayed by some common fungi in western Montana. Can J For Res 8:341–345
Larsen MJ, Jurgensen MF, Harvey AE (1982) N_2 fixation in brown-rotted soil wood in an intermountain cedar-hemlock ecosystem For Sci 28:292–296
Laskowski R, Berg B (1993) Dynamics of mineral nutrients and heavy metals in decomposing forest litter. Scand J For Res 8:446–456
Laskowski R, Berg B, Johansson M, McClaugherty C (1995) Release pattern for potassium from decomposing forest leaf litter. Long-term decomposition in a scots pine forest XI. Can J Bot 73:2019–2027
Leatham GF, Kirk TK (1983) Regulation of lignolytic activity by nutrient nitrogen in white-rot basidiomycetes. FEMS Microbiol Lett 16:65–67
Lee PC, Crites S, Neitfeld M, Van Nguyen H, Stelfox JB (1997) Characteristics and origins of deadwood material in aspen-dominated boreal forests. Ecol Appl 7:691–701

Lewis DH (1980) Boron, lignification and the origin of vascular plants—a unified hypothesis. New Phytol 84:209–229
Lindbeck MR, Young JL (1965) Polarography of intermediates in the fixation of nitrogen by p-quinone-aqueous ammonia systems. Anal Chim Acta 32:73–80
Lindeberg G (1944) Über die Physiologie ligninabbauender Bodenhymenomyzeten. Symbol Botan Upsal VIII/2, p 183
Linkins AE, Sinsabaugh RL, McClaugherty CA, Melillo JM (1990) Cellulase activity on decomposing leaf litter in microcosms. Plant Soil 123:17–25
Liski J, Ilvesniemi A, Mäkelä A, Starr M (1998) Model analysis of the effects of soil age, fires and harvesting on the carbon storage of boreal forest soils. Europ J Soil Sci 49:407–416
Liski J, Ilvesniemi H, Mäkelä A, Westman CO (1999) CO_2 emissions from soil in response to climatic warming are overestimated—the decomposition of old soil organic matter is tolerant to temperature. Ambio 28:171–174
Liski J, Perruchoud D, Karjalainen T (2002) Increasing carbon stock in the forest soils of western Europe. For Ecol Manage 169:159–175
Liu S-Y, Freyer AJ, Minard RD, Bollag J-M (1985) Enzyme-catalyzed complex-formation of amino esters and phenolic humus constituents. Soil Sci Soc Am J 49:337–342
Liu C, Westman CJ, Berg B, Kutsch W, Wang GZ, Man R, Ilvesniemi H (2004) Variation in litterfall-climate relationships between coniferous and broadleaf forests in Eurasia. Glob Ecol Biogeogr 13:105–114
Liu C, Berg B, Kutsch W, Westman CJ, Ilvesniemi H, Shen X, Shen G, Chen X (2006) Leaf litter nitrogen concentration as related to climatic factors in Eurasian forests. Glob Ecol Biogeogr 15:438–444
Lockaby BG, Miller JH, Clawson RG (1995) Influences of community composition on biogeochemistry of loblolly pine (*Pinus taeda*) systems. Am Midl Nat 134:176–184
Löfgren S, Westling O (2002) Modell för att beräkna kväveförluster från växande skog och hyggen i Sydsverige. Swedish university of agricultural sciences, Department of environmental assessment, Report 2002:1. Uppsala, Sweden (in Swedish)
Lõhmus K, Ivask M (1995) Decomposition and nitrogen dynamics of fine roots of Norway spruce (*Picea abies* (L.) Karst.) at different sites. Plant Soil 168(169):89–94
Lousier JD, Parkinson D (1976) Litter decomposition in a cool temperate deciduous forest. Can J Bot 54:419–436
Lueken H, Hutcheon WL, Paul EA (1962) The influence of nitrogen on the decomposition of crop residues in the soil. Can J Soil Sci 42:276–288
Lundmark J-E, Johansson MB (1986) Markmiljön i gran- och björkbestånd. Sver Skogsvårdsförbunds Tidskr 2:31–37 (in Swedish)
MacMillan PC (1988) Decomposition of coarse woody debris in an old-growth Indiana forest. Can J For Res 18:1353–1362
Magill AH, Aber JD (1998) Long-term effects of experimental nitrogen additions on foliar litter decay and humus formation in forest ecosystems. Plant Soil 203:301–311
Mahlander C, Hellsten S, Akselsson C, Ekstrand S (2004) National land cover mapping for air pollution studies, IVL Report B-1499, p 19
Mälkönen E (1974) Annual primary production and nutrient cycling in some Scots pine stands. Commun Inst For Fenn 84(5):85
Marra JL, Edmonds RL (1994) Coarse wood debris and forest floor respiration in an old-growth coniferous forest on the olympic peninsula, Washington, USA. Can J For Res 24:1811–1817
Marra JL, Edmonds RL (1996) Coarse wood debris and soil respiration in a clearcut on the olympic peninsula, Washington, USA. Can J For Res 26:1337–1345
Maser C, Anderson R, Cromack K, Williams JT, Martin RE (1979) Dead and down woody material. In: Thomas JW (ed) Wildlife habitats in managed forests, the blue mountains of Oregon and Washington, chap 6. USDA For Serv Agric Handb 553, pp 79–85
McCarthy BC, Bailey RR (1997) Distribution and abundance of coarse woody debris in managed forest landscape of the central Appalachians. Can J For Res 24:1317–1329

McClaugherty CA (1983) Soluble polyphenols and carbohydrates in throughfall and leaf litter decomposition. Acta Oecol 4:375–385
McClaugherty C, Berg B (1987) Cellulose, lignin and nitrogen levels as rate regulating factors in late stages of forest litter decomposition. Pedobiologia 30:101–112
McClaugherty CA, Aber JD, Melillo JM (1982) The role of fine roots in the organic matter and nitrogen budgets of two forested ecosystems. Ecology 63:1481–1490
McClaugherty CA, Aber JD, Melillo JM (1984) Decomposition dynamics of fine roots in forested ecosystems. Oikos 42:378–386
McClaugherty CA, Pastor J, Aber JD, Melillo JM (1985) Forest litter decomposition in relation to soil nitrogen dynamics and litter quality. Ecology 66:266–275
McClellan MH, Bormann BT, Cromack K (1990) Cellulose decomposition in southeast Alaskan forests: effects of pit and mound microrelief and burial depth. Can J For Res 20:1242–1246
McHale PJ, Mitchell MJ, Bowles FP (1998) Soil warming in a northern hardwood forest: trace gas fluxes and leaf litter decomposition. Can J For Res 28:1365–1372
Means JE, MacMillan PC, Cromack K (1992) Biomass and nutrient content of Douglas-fir logs and other detrital pools in an old-growth forest, Oregon, USA. Can J For Res 22:1536–1546
Meentemeyer V (1978) Macroclimate and lignin control of litter decomposition rates. Ecology 59:465–472
Meentemeyer V (1984) The geography of organic decomposition rates. Ann Assoc Am Geogr 74:551–560
Meentemeyer V, Gardner J, Box E (1985) World patterns and amounts of detrital soil carbon. Earth Surface Processes 10: 557–567
Meentemeyer V, Berg B (1986) Regional variation in mass-loss of *Pinus sylvestris* needle litter in Swedish pine forests as influenced by climate and litter quality. Scand J For Res 1:167–180
Meentemeyer V, Box E, Thompson R (1982) World patterns of terrestrial plant litter production. BioScience 32:125–128
Meesenburg H, Meiwes KJ, Bartens H (1999) Veränderung der Elementvorräte im Boden von Buchen- und Fichtenökosystemen in Solling. Berichte Freiburger Forstliche Forschung 7:109–114 (in German)
Meiwes KJ, Meesenburg H, Bartens H, Rademacher P, Khanna PK (2002) Accumulation of humus in the litter layer of forest stands at solling. Possible causes and significance for the nutrient cycling. Forst and Holz 13–14:428–433. (in German, English summary)
Melillo JM, Aber JD, Muratore JF (1982) Nitrogen and lignin control of hardwood leaf litter dynamics in forest ecosystems. Ecology 63:621–626
Melillo JM, Aber JD, Linkins AE, Ricca A, Fry B, Nadelhoffer KJ (1989) Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter. In: Clarholm M, Bergström L (eds) Ecology of arable lands. Kluwer, Dordrecht, pp 53–62
Miller H (1979) The nutrient budgets of even-aged forests. In: Ford ED, Malcolm DC, Atterson J (eds) The ecology of even-aged forest plantations, Proceeding of meeting division I. Internat union For Res Org, Edinburgh, Sept 1978, pp 221–238
Miller HG, Miller JD (1976) Analysis of needle fall as a means of assessing nitrogen status in pine. Forestry 49:57–61
Mindermann G (1968) Addition, decomposition, and accumulation of organic matter in forests. J Ecol 56:355–362
Møller J, Miller M, Kjøller A (1999) Fungal-bacterial interaction on beech leaves: influence on decomposition and dissolved organic carbon quality. Soil Biol Biochem 31:367–374
Monleon VJ, Cromack K (1996) Long-term effects of prescribed burning on litter decomposition and nutrient release in ponderosa pine stands in central Oregon. For Ecol Manage 81:143–152
Moorehead DL, Sinsabaugh RL, Linkins AE, Reynolds JF (1996) Decomposition processes: modeling approaches and applications. Sci Total Environ 183:137–149
Muller RN, Liu Y (1991) Coarse woody debris in an old-growth forest on the Cumberland Plateau, southeastern Kentucky. Can J For Res 21:1567–1572

Musha Y, Goring DAI (1975) Distribution of syringyl and guaiacyl moieties in hardwoods as indicated by ultraviolet microscopy. Wood Sci Technol 9:45–58
Nadelhoffer KJ, Aber JD, Melillo JM (1985) Fine roots, net primary production, and soil nitrogen availability: a new hypothesis. Ecology 73:1377–1390
Næsset E (1999) Decomposition rate constants of *Picea abies* logs in southeastern Norway. Can J For Res 29:372–381
Newsham KK, Boddy L, Frankland JC, Ineson P (1992a) Effects of dry deposited sulphur dioxide on fungal decomposition of angiosperm tree leaf litter III. Decomposition rates and fungal respiration. New Phytol 122:127–140
Newsham KK, Frankland JC, Boddy L, Ineson P (1992b) Effects of dry deposited sulphur dioxide on fungal decomposition of angiosperm tree leaf litter I. Changes in communities of fungal saprotrophs. New Phytol 122:97–11040
Newsham KK, Ineson P, Boddy L, Frankland JC (1992c) Effects of dry deposited sulphur dioxide on fungal decomposition of angiosperm tree leaf litter II. Chemical content of leaf litters. New Phytol 122:111–125
Nikolov N, Helmisaari H (1992) Silvics of the circumpolar boreal forest tree species. In: Shugart HH, Leemans R, Bonan GB (eds) A systems analysis of the global boreal forest. Cambridge University Press, Cambridge, pp 13–84
Nilsson T, Daniel G, Kirk TK, Obst JR (1989) Chemistry and microscopy of wood decay by some higher ascomycetes. Holzforschung 43:11–18
Nohrstedt H-Ö, Jacobson S, Sikström U (2000) Effects of repeated urea doses on soil chemistry and nutrient pools in a Norway spruce stand. Forest Ecol Manage 130:47–56
Nömmik H, Möller G (1981) Nitrogen recovery in soil and needle biomass after fertilization of a scots pine stand, and growth responses obtained. Stud Forest Suec 159:37
Nömmik H, Vahtras K (1982) Retention and fixation of ammonium and ammonia in soils. In: Stevenson FJ (ed) Nitrogen in agricultural soils. Agronomy monographs, no 22. Agron Soc Am, Madison, pp 123–171
Norden B, Berg B (1990) A non-destructive method (solid state 13C-NMR) determining organic-chemical components in decomposing litter. Soil Biol Biochem 22:271–275
Oleksyn J, Reich PB, Zytkowiak R, Karolewski P, Tjoelker MG (2003) Nutrient conservation increases with latitude of origin in European *Pinus sylvestris* populations. Oecologica 136:220–235
Olson JS (1963) Energy storage and the balance of producers and decomposers in ecological systems. Ecology 44:322–331
Olsson M (2000) Kol i marken. In: LUSTRA-programmet 1999. Department of Forest Soils. Swedish university of agricultural sciences, Uppsala. (in Swedish)
Olsson B, Bengtsson J, Lundkvist H, Staaf H, Rosen K (1996) Carbon and nitrogen in coniferous forest soils after clear-felling and harvests of different intensity. For Ecol Manage 82:19–32
O'Neill RV, Harris WF, Ausmus BS, Reichle DE (1975) A theoretical basis for ecosystem analysis with particular reference to element cycling. In: Howell FG, Gentry JB, Smith MH (eds) Proceedings of the symposium on mineral cycling in southeastern ecosystems. US Depart Comm, Springfield, pp 28–40
Onega TL, Eickmeier WG (1991) Woody detritus inputs and decomposition kinetics in a southern temperate deciduous forest. Bull Torr Bot Club 118:52–57
Ono Y (1998) A study on the initial decomposition process of needle litter in a *Chamaecyparis obtusa* forest. Master thesis, Kyoto university, Kyoto (in Japanese)
Ono K, Hirai K, Morita S, Ohse K, Hiradate S (2009) Organic carbon accumulation processes on a forest floor during an early humification stage in a temperate deciduous forest in Japan: Evaluations of chemical compositional changes by ^{13}C NMR and their decomposition rates from litterbag experiment. Geoderma 151:351–356
Ono K, Hiradate S, Morita S, Ohse K, Hirai K (2011) Humification processes of needle litters on forest floors if Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*) plantations in Japan. Plant Soil 338:171–181

Osono T, Takeda H (2001) Organic chemical and nutrient dynamics in decomposing beech leaf litter during 3-year decomposition process in a cool temperate deciduous forest in Japan. Ecol Res 16:649–670

Otto A, Simpson MJ (2006) Evaluation of the CuO oxidation parameters for determining the source and stage of lignin degradation in soil. Biogeochemistry 80:121–142

Ovington JD (1959) The circulation of minerals in plantations of *Pinus sylvestris* L. Ann Bot NS 23:229–239

Panikov NS (1999) Understanding and prediction of soil microbial community dynamics under global change. Appl Soil Ecol 11:161–176

Panshin AJ, de Zeeuw C (1980) Textbook of wood technology, 4th edn. McGraw-Hill, New York, p 722

Paramesvaran N, Liese W (1982) Ultrastructural localization of wall components in wood cells. Holz Roh Werkst 40:145–155

Pastor J, Aber JD, McClaugherty CA, Melillo JM (1982) Geology, soils, and vegetation of Blackhawk island, Wisconsin. Am Midl Nat 108:265–277

Pastor J, Aber JD, McClaugherty CA, Melillo JM (1984) Aboveground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk island, Wisconsin. Ecology 65:256–268

Paul E (1984) Dynamics of organic matter in soils. Plant Soil 76:75–285

Perakis S, Matekis JJ, Hibbs DE. (2012) Interactions of tissue and fertilizer nitrogen on decomposition dynamics of lignin-rich litter. Ecosphere 3(6) (in press)

Perala DA, Alban DH (1982) Rates of forest floor decomposition and nutrient turnover in aspen, pine, and spruce stands on two soils. US Dept Agric, For Serv, N Cent For Exp Stn, Res Pap NC-227, p 5

Perez J, Jeffries TW (1992) Roles of manganese and organic acid chelators in regulating lignin degradation and biosynthesis of peroxidases by *Phanerochaete chrysosporium*. Appl Environ Microbiol 58:2402–2409

Perruchoud D. (1996) Modelling the dynamics of nonliving organic carbon in a changing climate: a case study for temperate forests. Ph. D. thesis, Diss. ETH No. 11900. Swiss federal institute of technology, Zürich

Persson H (1980) Spatial distribution of fine-root growth, mortality and decomposition in a young Scots pine stand in Central Sweden. Oikos 34:77–87

Persson T, Bååth E, Clarholm M, Lundkvist H, Söderström B, Sohlenius B (1980) Trophic structure, biomass dynamics and carbon metabolism of soil organisms in a scots pine forest. Ecol Bull (Stockholm) 32:419–462

Persson T, Karlsson PS, Seyferth U, Sjöberg RM, Rudebeck A (2000) Carbon mineralization in European forest soils. In: Schulze E-D (ed) Carbon and nitrogen cycling in European forest ecosystems. Ecological studies, vol 142. Springer, Berlin, pp 257–275

Persson T, Rudebeck A, Jussy JH, Colin-Belgrand M, Priemé A, Dambrine E, Karlsson PS, Sjöberg RM (2000) Soil nitrogen turnover—mineralisation, nitrifica-tion and denitrification in European forest soils. In: Schulze E-D (ed) Carbon and nitrogen cycling in European forest ecosystems. Ecological studies vol 142. pp 297–231

Poinsot-Balaguer N, Tabone E (1995) Impact of chronic gamma irradiation on the litter decay of a mixed Mediterranean forest in Cadarache—France—microarthropod's response. Pedobiologia 39:344–350

Prentice IC et al (2001) The carbon cycle and atmospheric carbon dioxide. climate change 2001: The scientific basis. In: Houghton J.T, Yihui D. (eds) Contribution of working group 1 to the third assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

Prescott CE (1995) Does nitrogen availability control rates of litter decomposition in forests? Plant Soil 168(169):83–88

Prescott CE, Blevins LL, Staley CL (2000) Effects of clear-cutting on decomposition rates of litter and forest floor in forests of British Columbia. Can J For Res 30:1–7

Preston CM, Sollins P, Sayer BG (1990) Changes in organic components for fallen logs in old-growth Douglas-fir forests monitored by ^{13}C nuclear magnetic resonance spectroscopy. Can J For Res 20:1382–1391

Preston C, Trofymov JA, Sayer B, Niu J (1997) ^{13}C nuclear magnetic resonance spectroscopy with cross-polarizartion and magic angle spinning investigation of the proximate analysis fractions used to assess litter quality in decomposition studies. Can J Bot 75:1601–1613

Preston C, Nault JR, Trofymow JA, Smyth C, CIDET Working Group (2009) Chemical changes during 6 years of decomposition of 11 litters in some Canadian forest sites. Part 1. Elemental composition, tannins, phenolics, and proximate fractions. Ecosystems 12:1053–1077

Preston C, Nault JR, Trofymow JA (2009) Chemical changes during 6 years of decomposition of 11 litters in some Canadian forest sites. Part 2. 13C abundance, solid-state 13C NMR spectroscopy and the meaning of 'lignin'. Ecosystems 12:1078–1102

Prietzel J, Wagoner G, Harrison R (2004) Long-term effects of repeated urea fertilization in Douglas-fir stands on forest floor nitrogen pools and nitrogen mineralization. Forest Ecol Manage 193:413–426

Prietzel J, Stetter U, Klemmt HJ, Rehfüss KE (2006) Recent carbon and nitrogen accumulation in soils of two Scots pine ecosystems in Southern Germany. Plant and Soil 289:153–170

Pyle C, Brown MM (1998) A rapid system of decay classification for hardwood logs of the eastern deciduous forest. J Torr Bot Soc 125:237–245

Pyle C, Brown MM (1999) Heterogeneity of wood decay classes within hardwood logs. For Ecol Manage 114:253–259

Raich JW, Nadelhoffer KJ (1989) Belowground carbon allocation in forest ecosystems; global trends. Ecology 70:1346–1354

Rapp M, Leonardi S (1988) Evolution de la litiere au sol au cours d'une annee dans un taillis de chene vert (*Quercus ilex*). Pedobiologia 32:177–185 (in French)

Rashid GH, Schaefer R (1988) Seasonal variation in the nitrogen mineralization and mineral nitrogen accumulation in two temperate forest soils. Pedobiologia 31:381–390

Rehfüss KE (1990) Waldböden, Entwicklung, Eigenschaften und Nutzung, 2nd edn. Pareys Studientexte 29, Parey, Hamburg, pp 294 (in German)

Reich PB, Oleksyn J (2004) Global patterns of plant leaf N and P in relation to temperature and latitude. PNAS 101:11001–11006

Reid ID, Seifert KA (1982) Effect of an atmosphere of oxygen on growth, respiration, and lignin degradation by white-rot fungi. Can J Bot 60:252–260

Reurslag AM, Berg B (1993) Rapport över litteraturstudie rörande mängd och kemisk sammansättning av fallförna samt mängd av organiskt material i skogsmark. Vattenfalls rapportserie No UB 1993/2, pp 110 (in Swedish, English summary)

Robertson PA, Bowser YH (1999) Coarse woody debris in mature *Pinus ponderosa* stands in Colorado. J Torr Bot Soc 126(3):255–267

Roo-Zielinska E, Solon J (1997) Effect of geographical location on species composition, vegetation structure, diversity and phytoindicative characteristics in pine forests. Environ Poll 98:347–360

Roo-Zielinska E, Solon J (1998) A geobotanical characteristic and analysis of the range of forest communities at study sites along climatic in pine and mixed pine forests along a climatic (52o N, 12-32oE) and a "Silesian" transect. In: Breymeyer A, Roo-Zielinska E (eds) Pine forests in central European gradient of continentality and pollution—geoecological studies, vol 13. Docum Geogr, pp 79–98

Rose RE, Lisse MW (1916) The chemistry of wood decay paper I—introductory. J Ind Eng Chem 9:284–287

Rustad LE, Fernandez IJ (1998) Soil warming: consequences for foliar litter decay in a spruce-fir forest in Maine, USA. Soil Sci Soc Am J 62:1072–1080

Rutigliano FA, Virzo De Santo A, Berg B, Alfani A, Fioretto A (1996) Lignin decomposition in decaying leaves of *Fagus sylvatica* L. and needles of *Abies alba* Mill. Soil Biol Biochem 28:101–106

Ryan MG, Melillo JM, Ricca A (1990) A comparison of methods for determining proximate carbon fractions of forest litter. Can J For Res 20:166–171
Saka S, Thomas RJ (1982a) Evaluation of the quantitative assay of lignin distribution by SEM-EDXA technique. Wood Sci Technol 16:1–18
Saka S, Thomas RJ (1982b) A study of lignification in loblolly pine tracheids by the SEM-EDXA technique. Wood Sci Technol 16:167–179
Salonius PO (1983) Effects of organic-mineral soil mixtures and increasing temperature on the respiration of coniferous raw humus material. Can J For Res 13:102–107
Sanger LJ, Cox P, Splatt P, Whelan M, Anderson JM (1998) Variability in the quality and potential decomposability of *Pinus sylvestris* litter from sites with different soil characteristics: acid detergent fibre (ADF) and carbohydrate signatures. Soil Biol Biochem 30:455–461
Santantonio D, Hermann RK (1985) Standing crop, production, and turnover of fine roots on dry, moderate, and wet sites of mature Douglas-fir in western Oregon. Ann Sci For 42:113–142
Schiffman PM, Johnson WC (1989) Phytomass and detrital carbon storage during forest regrowth in the southeastern United States Piedmont. Can J For Res 19:67–78
Schlesinger WH (1977) Carbon balance in terrestrial detritus. Annu Rev Ecol Syst 8:51–81
Schlesinger WH, Andrews JA (2000) Soil respiration and the global carbon cycle. Biogeochemistry 48:7–20
Schlesinger WH, Hasey MM (1981) Decomposition of chaparral shrub foliage; losses of organic and inorganic nutrients from deciduous and evergreen leaves. Ecology 62:762–774
Schmidt EL, Ruschmeyer OR (1958) Cellulose decomposition in soil burial beds. I. Soil properties in relation to cellulose degradation. Appl Microbiol 6:108–114
Schowalter TD (1992) Heterogeneity of decomposition and nutrient dynamics of oak (*Quercus*) logs during the first 2 years of decomposition. Can J For Res 22:161–166
Schowalter TD, Zhang YL, Sabin TE (1998) Decomposition and nutrient dynamics of oak (*Quercus* spp.) logs after five years of decomposition. Ecography 21:3–10
Schulze E-D, de Vries W, Hauhs M, Rosen K, Rasmussen L, Tamm CO, Nilsson J (1989) Critical loads for nitrogen deposition on forest ecosystems. Water Air Soil Pollut 48:451–456
Scott NA, Cole CV, Elliott ET, Huffman SA (1996) Soil textural control on decomposition and soil organic matter dynamics. Soil Sci Soc Am J 60:1102–1109
Silver WL, Miya RK (2001) Global patterns in root decomposition: comparisons of climate and litter quality effects. Oecologia 129:407–419
Singh JS, Gupta SR (1977) Plant decomposition and soil respiration in terrestrial ecosystems. Bot Rev 43:449–528
Singh AP, Nilsson T, Daniel GF (1987) Ultrastructure of the attack of the wood of two high lignin tropical hardwood species, *Alstonia scholaris* and *Homalium foetidum*, by tunneling bacteria. J Inst Wood Sci 11:237–249
Sogn TA, Stuanes AO, Abrahamsen G (1999) The capacity of forest soil to absorb antrropogenic N. Ambio 28(4):346–349
Spaccini R, Piccolo A (2012) The carbon dynamics in the experimental plots.Chemical and physical–chemical aspects. In: Alessandro, Piccolo (Ed.), Carbon sequestration in agricultural soils e a multidisciplinary approach to innovative methods. Springer, sHeidelberg
Staaf H (1982) Plant nutrient changes in beech leaves during senescence as influenced by site characteristics. Acta Oecol/Oecol Plant 3:161–170
Staaf H, Berg B (1977) A structural and chemical description of litter and humus in the mature Scots pine stand at Ivantjärnsheden. Swed Conif For Proj Int Rep 65, p 31
Staaf H, Berg B (1981) Plant litter input. In: Clark FE, Rosswall T (eds) Terrestrial nitrogen cycles. Processes, ecosystem strategies and management impacts. Ecol Bull (Stockh) 33:147–162
Staaf H, Berg B (1982) Accumulation and release of plant nutrients in decomposing Scots pine needle litter. Long-term decomposition in a scots pine forest II. Can J Bot 60:1561–1568

Staaf H, Berg B (1989) Förnanedbrytning som variabel för miljökvalitetskontroll i terrester miljö. I. Substraturval och inledande studier. Statens Naturvårdsverk Rapport Nr 3591. p 62 (in Swedish)

Steffen KT, Hofrichter M, Hatakka A (2000) Mineralisation of ^{14}C-labelled synthetic lignin and ligninolytic enzyme activities of litter-decomposing basidiomycetous fungi. Appl Microbiol Biotechnol 54:819–825

Steffen KT, Hatakka A, Hofrichter M (2002) Degradation of humic acids by the litter decomposing basidiomycete *Collybia dryophila*. Appl Environm Microbiol 68:3442–3448

Stevenson FJ (1982) Humus chemistry. Genesis, composition, reactions. Wiley, New York, p 443

Stewart GH, Burrows LE (1994) Coarse woody debris in old-growth temperate beech (*Nothofagus*) forests of New Zealand. Can J For Res 24:1989–1996

Stone JN, MacKinnon A, Parminter JV, Lertzman (1998) Coarse woody debris decomposition documented over 65 years on southern Vancouver Island. Can J For Res 28:788–793

Strojan CL (1978) Forest leaf litter decomposition in the vicinity of a zinc smelter. Oecologia 32:203–212

Strömgren M (2001) Soil-surface CO_2 flux and growth in a boreal Norway spruce stand. Effects of soil warming and nutrition. Doctoral dissertation, Acta Universitatis Agriculturae Sueciae, Silvestria 220, p 44

Sturtevant BR, Bissonette JA, Long JN, Roberts DW (1997) Coarse woody debris as a function of age, stand structure, and disturbance in boreal Newfoundland. Ecol Appl 7:702–712

Sun T, Mao Z, Dong L, Hou L, Song Y, Wang X (2012) Further evidence for slow decomposition of very fine roots using two methods: litterbags and intact cores. Plant and Soil. doi: 10.1007/s11104-012-1457-3

Swedish Natl Survey of Forest Soils and Vegetation (1983–1987) Department of Forest Soils, Swed Univ Agric Sci, Uppsala

Swift MJ (1977) The ecology of wood decomposition. Sci Prog Oxf 64:175–199

Swift MJ, Heal OW, Anderson JM (1979) Decomposition in terrestrial ecosystems. Blackwell, Oxford

Tamm CO (1991) Nitrogen in terrestrial ecosystems. Questions of productivity, vegetational changes, and ecosystem stability. Ecological studies, vol 81. Springer, Berlin, p 115

Tamm CO (1999) Optimum nutrition and nitrogen saturation in Scots pine stands. Stud Forest Suec 206:1–126

Tamm CO, Nilsson Å, Wiklander G (1974) The optimum nutrition experiment Lisselbo: a brief description of an experiment in a young stand of Scots pine (*Pinus sylvestris* L.). Rapporter och uppsatser no 18, Institutionen för växtekologi och marklära. Skogshögskolan, Stockholm, p 25

Taylor BR, Parkinson D, Parsons WFJ (1989) Nitrogen and lignin content as predictors of litter decay rates: a microcosm test. Ecology 70:91–104

Tenney FG, Waksman SA (1929) Composition of natural organic materials and their decomposition in the soil. IV. The nature and rapidity of decomposition of the various organic complexes in different plant materials, under aerobic conditions. Soil Sci 28:55–84

Theander O, Westerlund EA (1986) Studies on dietary fiber. 3 Improved procedures for analysis of dietary fiber. J Agric Food Chem 34:330

Thevenot M, Dignac M-F, Rumpel C (2010) Fate of lignins in soils: a review. Soil Biol Biochem 42:1200–1211

Thorn KA, Mikita MA (1992) Ammonia fixation by humic substances: a nitrogen-15 and carbon-13 NMR study. Sci Total Environ 113:67–87

Thornthwaite CW, Mather JR (1957) Instructions and tables, for computing potential evapotranspiration and the water balance. Publ Climatol 10:185–311

Tien M, Kirk TK (1984) Lignin-degrading enzyme from *Phanerochaete chrysosporium*: purification, characterization, and catalytic properties of a unique H2O2- requiring oxygenase. Proc Natl Acad Sci USA 81:2280–2284

Tietema A (2004) WANDA, a regional dynamic nitrogen model (With Aggregated Nitrogen DynAmics) for nitrate leaching from forests. Hydrol Earth Syst Sci 8:803–812

Torsvik VL, Goksøyr J, Daae FL (1990) High diversity of DNA in soil bacteria. Appl Environ Microbiol 56:782–787

Townsend AR, Vitousek M, Trumbore S (1995) Soil organic matter dynamics along gradients in temperature and land use on the island of Hawaii. Ecology 76:721–733

Townsend AR, Vitousek P, Desmarais DJ, Tharpe A (1997) Soil carbon pool structure and temperature sensitivity inferred using CO_2 and $^{13}CO_2$ incubation fluxes from five Hawaiian soils. Biogeochemistry 38:1–17

Tsuneda A, Thorn RG (1995) Interactions of wood decay fungi with other microorganisms, with emphasis on the degradation of cell walls. Can J Bot 73:S1325–S1333

Turner J, Long JN (1975) Accumulation of organic matter in a series of Douglas-fir stands. Can J For Res 5:681–690

Tyrell LE, Crow TR (1994) Dynamics of deadwood in old-growth hemlock-hardwood forests of northern Wisconsin and Northern Michigan. Can J For Res 24:1672–1683

Ulrich B (1981) Teoretische Betrachtung des Ionenkreislaufs in Waldökosystemen. Z Pflanzenern Bodenkd 144:289–305 (in German)

UNECE/FAO (2000) Forest resources of Europe, CIS, North America, Australia, Japan, and New Zealand, United nations economic commission for Europe and food and agricultural organization. Geneva timber and forest studies papers, no 17. United Nations, Geneva, p 467

Unestam T (1991) Water repellency, mat formation, and leaf-stimulated growth of some ectomycorrhizal fungi. Mycorrhiza 1:13–20

Upadhyay VP, Singh JS (1985) Nitrogen dynamics of decomposing hardwood leaf litter in a central Himalayan forest. Soil Biol Biochem 17:827–830

Van Cleve K (1974) Organic matter quality in relation to decomposition. In: Holding AJ, Heal OW, MacLean SF, Flanagan PW (eds) Soil organisms and decomposition in Tundra. Tundra Biome Steering Committee, Stockholm, pp 311–324

Van Cleve K, Oechel WC, Hom JL (1990) Response of black spruce (*Picea mariana*) ecosystems to soil temperature modification in interior Alaska, USA. Can J For Res 20:1530–1535

Van Soest PJ (1963) Use of detergent in the analysis of fibrous feed. II. A rapid method for the determination of fibre and lignin. J Assoc Official Anal Chem 46(5):829–835

Verburg PSJ, Van Loon WKP, Lükewille (1999) The CLIMEX soil-heating experiment: soil response after 2 years of treatment. Biol Fertil Soils 28:271–276

Vesterdal L, Raulund-Rasmussen K (1998) Forest floor chemistry under seven tree species along a fertility gradient. Can J For Res 28:1636–1647

Vesterdal L, Ritter E, Gundersen P (2002) Change in organic carbon following afforestation of former arable land. For Ecol Manag 169:137–147

Viljoen JA, Fred ED, Peterson WH (1926) The fermentation of cellulose by thermophilic bacteria. J Agric Sci 16:1–17

Vogt KA, Vogt DJ, Gower ST, Grier CC (1990) Carbon and nitrogen interactions for forest ecosystems. In: Persson H (ed) Above- and below-ground nitrogen interactions in forest trees in acidified soils. Air pollution report 32. Commission of the european communities, Directorate-general for science, Research and development, environment research programme. Brussels, Belgium, pp 203–235

Vogt KA, Vogt DJ, Bloomfield J (1991) Input of organic matter to the soil by tree roots. In: Persson H, McMichael BL (eds) Plant roots and their environments. Elsevier, Amsterdam, pp 171–190

Vogt KA, Vogt DJ, Palmiotto PA, Boon P, O'Hara J, Asbjornsen H (1996) Review of root dynamics in forest ecosystems grouped by climate, climatic forest type and species. Plant Soil 187:159–219

von Liebig J (1847) Chemistry in its applications to agriculture and physiology. Taylor and Walton, London, p 418

Waksman SA (1936) Humus. Williams and Wilkins, Baltimore

Waksman SA, Reuszer HW (1932) On the origin of the uronic acids in the humus of soil. peat, and composts. Soil Sci 33:135–151

Waksman SA, Tenney FG, Stevens KR (1928) The role of microorganisms in the transformation of organic matter in forest soils. Ecology 9:126–144

Wang Y, Amundson R, Trumbore S (1996) Radiocarbon dating of soil organic matter. Quat Res 45:282–288

Wardle DA, Zachrisson O, Hörnberg G, Gallet C (1997) The influence of island area on ecosystem properties. Science 277:1296–1299

Watson RT, Meira Filho LG, Sanhueza E, Janetos A (1992) Greenhouse gases: sources and sinks. In: Houghton JT, Callander BA, Varney SK (eds) Climate change 1992: the supplementary report to the IPCC scientific assessment. Cambridge University Press, Cambridge, pp 25–46

Wieder RK, Lang GE (1982) A critique of the analytical methods used in examining decomposition data obtained from litter bags. Ecology 63:1636–1642

Wiegel J, Dykstra M (1984) *Clostridium thermocellum*: adhesion and sporulation while adhered to cellulose and hemicellulose. Appl Microbiol Biot 20:59–65

Wolter KE, Highley TL, Evans FJ (1980) A unique polysaccharide- and glycoside-degrading enzyme complex from the wood decay fungus *Poria placenta*. Biochem Biophys Res Commun 97:1499–1504

Woodwell GM, Marples TG (1968) The influence of chronic gamma irradiation on production and decay of litter and humus in an oak-pine forest. Ecology 49:456–465

Woodwell GM, Mackenzie FT, Houghton RA, Apps M, Gorham E, Davidson E (1998) Biotic feedbacks in the warming of the earth. Clim Change 40:495–518

Wookey PA, Ineson P (1991) Chemical changes in decomposing forest litter in response to atmospheric sulphur dioxide. J Soil Sci 42:615–628

Wookey PA, Ineson P, Mansfield TA (1991) Effects of atmospheric sulphur dioxide on microbial activity in decomposing forest litter. Agric Ecosyst Environ 33:263–28

Worrall JJ, Wang CJK (1991) Importance and mobilization of nutrients in soft rot of wood. Can J Microbiol 37:864–868

Worrall JJ, Anagnost SE, Wang CJK (1991) Conditions for soft-rot of wood. Can J Microbiol 37:869–874

Worrall JJ, Anagnost SE, Zabel RA (1997) Comparison of wood decay among diverse lignicolous groups. Mycologia 89:199–219

Wright RF, Tietema A (1995) Ecosystem response to 9 years of nitrogen addition at Sogndal, Norway. For Ecol Manage 71:133–142

Wright RF, Roelofs JGM, Bredemeier M, Blanck K, Boxman AW, Emmett BA, Gundersen P, Hultberg H, Kjønaas OJ, Moldan F, Tietema A, van Breeman N, van Dijk HFG (1995) NITREX: responses of coniferous forest ecosystems to experimentally changed deposition of litter. For Ecol Manage 71:163–169

Yin X (1999) The decay of forest woody debris: numerical modeling and implications based on some 300 data cases from North America. Oecologia 121:81–98

Yin XW, Perry JA, Dixon RK (1989) Influence of canopy removal on oak forest floor decomposition. Can J For Res 19:204–214

Zachrisson O (1977) Influence of forest fires on the northern Swedish boreal forest. Oikos 29:22–32

Zak DR, Blackwood CB, Waldrop MP (2006) A molecular dawn for biogeochemistry. Trends Ecol Evol 21:288–295

Zanetti S, Hartwig UA (1997) Symbiotic N2 fixation increases under elevated atmospheric pCO_2 in the field. Acta Oecol 18:285–290

Zhang Q, Liang Y (1995) Effects of gap size on nutrient release from plant litter decomposition in a natural forest ecosystem. Can J For Res 25:1626–163

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