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LITTER DECOMPOSITION: A GUIDE TO CARBON AND NUTRIENT TURNOVER

BJÖRN BERG AND RYSZARD LASKOWSKI

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Preface

The idea of this book, which we are able to offer you now, thanks to Elsevier, was born several years ago when we were working together on review articles summarizing knowledge on litter decomposition, nutrient dynamics, and humus buildup in forests of the Northern Hemisphere. After years of studying organic matter decomposition, we considered ourselves to have good insight into the progress in this branch of ecology/biogeochemistry, and it was not difficult to notice that, although intensively studied by a number of research teams all over the world, the subject was not very well represented on the bookshelves. Virtually no single comprehensive book devoted to this subject had been published for a long time, and, in fact, very few have ever been published (see the References at the end of this volume). To both of us—teaching ecology as well as more specialized courses in soil ecology and ecotoxicology—this situation was not merely unsatisfactory, considering the importance of decomposition processes for almost every aspect of life on earth, but also very inconvenient for our students who did not have any source summarizing the state of current research in the discipline.

When you lack a proper handbook, you must write one yourself and we decided to do just that. Although many years have passed from the birth of the idea until we could submit the manuscript, not much has changed in the general market. One notable exception is the book coauthored by one of us and published by Springer-Verlag in 2003. However, while that book is directed toward specialists, the present one has been written mostly with students and teachers in mind. We hope that this book will be useful at all levels of study, from general ecology courses, where decomposition processes often are covered briefly, through more advanced courses in ecosystems ecology, soil ecology, and biogeochemistry, where at least some deeper aspects of organic matter decay should be covered, ending with courses for graduate students who decide to take the first step in their research careers in this topic. While teachers and students in more general subjects will find the most basic information on decomposition processes in this book, we hope that scientists and graduate students working on decomposition processes will be satisfied with the more detailed information and the overview of the latest publications on the topic as well as the methodological chapter where

practical information on methods useful in decomposition studies can be found. We hope that university teachers like us will find the book useful in preparing their courses. In particular, those who do not specialize in decomposition studies should find a wealth of knowledge gathered in one, relatively compact volume. A useful addition for classes and self-teaching is Appendix II, with real research data and an Internet link that can be used for learning different statistical techniques mentioned in the book or even for organizing minor research projects without the necessity of spending long years on field studies, which, in most cases, is simply impossible during regular courses.

Of course, we do not believe that our book will satisfy the needs of everyone. Throughout the book, we have had to find a balance between completeness of the knowledge presented and compactness of particular chapters. We realize that our personal opinion on what is the best tradeoff was not necessarily optimal in all cases. Therefore, we will be happy to hear your opinions and suggestions. If the book appears useful, there is the possibility of publishing an updated version in a few years. Our e-mail addresses are given below this Preface: you may be certain that every message will be carefully read and thought through.

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This book would never have been written without generations of students who participated actively in our courses in general ecology, soil ecology, and ecotoxicology at the Jagiellonian University in Kraków, Poland. Further, graduate students and colleagues at the University of Bayreuth, Germany, and Oregon State University were helpful at different stages of writing the book.

Ryszard Laskowski: A number of our colleagues should be acknowledged because, without their encouragement and help, we would never have undertaken the challenge of writing this handbook. Professor Władysław Grodziński, the late head of the Department of Ecosystem Studies at the Jagiellonian University, was the first who turned my research interests toward litter decomposition studies and led the first research projects on this subject at the Jagiellonian University. We had the great pleasure to work together in a number of projects with Professor Krystyna Grodzińska, Head of the Department of Botany, Polish Academy of Sciences. Her knowledge matches her personal charm and friendliness, and it is hard for me to imagine my scientific career without her help and cooperation. Among those without whom this book would probably never have come into being is January Weiner, professor and Head of the Department of Ecosystem Studies at the Jagiellonian University. No other person has ever offered me so much encouragement and taught me so much about science in general. Finally, I express my greatest gratitude to my colleagues from the Department of Ecotoxicology, Jagiellonian University: Paulina Kramarz, Maciej Maryański, and Maria Niklińska, who helped me in my research for many years. Particularly Maria and Maciej spent countless hours on our common research on litter decomposition in European forests. The joy of common fieldwork, long days and nights spent on chemical analyses, the excitement of new findings is unforgettable.

Björn Berg: I want to thank Professor C. O. Tamm for all his support of my work, both within the SWECON project and after, allowing a period of no fewer than 18 years to be devoted to work on litter decomposition. During the same period, I had really skilled, not to say fantastic, assistance from my three laboratory assistants, Annette Ewertsson, Birgitta Holm, and Ann-Sofi Pettersson. The patient preparation and cleaning work of

hundreds of thousands of litter-bags at Jädraås Experimental Park resulted in the creation of a large database that allowed, among other work, this book to be written.

The support of Senior Scientist Per Gundersen during the European Union CNTER project (Contract number QLK5–2001–00596) and during my stay as a guest scientist at the Center for Forest Landscape and Planning, KVL, Hörsholm, Denmark, was essential for this book to be written. I also thank Professor Egbert Matzner of the institute BITÖK, University of Bayreuth, Germany, for his support of this book.

Copenhagen, August 2005
Björn Berg

Kraków, August 2005
Ryszard Laskowski

Contents

Decomposers: Soil Microorganisms and Animals

Changes in Substrate Composition and Rate-Regulating Factors during Decomposition

Nitrogen Dynamics in Decomposing Litter

Origin and Structure of Secondary Organic Matter and Sequestration of C and N

Climatic and Geographic Patterns in Decomposition

Anthropogenic Impacts on Litter Decomposition and Soil Organic Matter

Methods in Studies of Organic Matter Decay

Introduction

I. GENERAL REMARKS

Very few people without some ecological background turn their attention to dead organic matter and its decay. The reason is simple: the processes on which this book focuses occur, to some extent in an ''invisible'' way, without such spectacular events as blooming flowers, singing birds, or colorful butterflies. What more easily attracts our attention is the opposite side of the organic matter turnover: the production. The importance of organic matter production seems obvious to everybody, not only to specialists—this is the source of our crops and fodder for animals which are, in turn, utilized as food for humans; this is the timber used for housing, furniture, and paper production. The list can easily be made much longer. Life is production, and production means the synthesis of organic compounds from inorganic chemical elements. Nevertheless, those of us closer to agriculture or forestry are perfectly familiar also with the opposite side of the story—organic matter decomposition. For centuries, well before the development of modern science, farmers knew that in order to sustain agricultural production for years to come, their fields must be supplemented with nutrients. Agricultural fields are fertilized with manure, which undergoes the natural process of decomposition, eventually leading to the release of mineral nutrients indispensable for plants to grow. Some agriculture practices show that farmers have known that fertilization with organic manure is not the goal by itself—yearly burning of stubble on meadows, still a common practice in many parts of the world, reveals recognition of the necessity of mineralization of organic matter. The burning of organic residues dramatically shortens the time needed for release of nutrients and supplements soil with mineral nutrients, which can be easily utilized by plants.

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Considering the cycle of life, there is no exaggeration in the statement that decomposition of dead organic matter is a crucial process for sustaining life on Earth. Without decay (and fires), with constant production of organic matter by plants and a yearly primary production reaching ca. 4 kg m^{-2} in the most productive ecosystems, the whole land surface of the Earth would be soon covered with a meters-thick layer of undecomposed organic matter. Nutrients would be fixed in a form unavailable to plants, making further production impossible. Thus, even if common connotation of decay is dead matter, its rotting and decomposition, in fact, decay is so tightly connected to biomass production that neither can exist without the other. They are just the two sides of the same phenomenon called life. The most simplified description of these two processes making Earth alive can be summarized in two well-known equations:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \quad \text{(photosynthesis; organic matter production)}$$
$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \text{(organic matter mineralization)}$$

These two equations summarize the initial synthesis and the final mineralization. The enormous set of processes is much more complicated, of course, with an overwhelming variety of organic compounds produced by plants from a range of inorganic compounds and mineral nutrients, transformed and complicated even further by consumers. The chemical composition of litter—the substrate for decomposition processes—is described in detail in Chapter 2.

Decomposition undergoes a number of steps, leading from complicated organic compounds through simpler compounds to mineral nutrients, and, under certain circumstances, not all chemical elements return to their original inorganic form (Chapter 4). Actually, under the common term "decomposition," most scientists understand a whole set of biochemical/microbial processes, even those opposite to the strict meaning of the term, such as polymerization of long chains of secondary organic matter collectively called "humus." However, such processes, going in a direction opposite to actual degradation, rely on substrates released by earlier partial decay of primary organic matter. In that sense, they belong to the long list of complicated processes of dead organic matter transformations and cannot be considered separately from strict decomposition (cf. Chapter 6). These processes would be impossible without the billions of microorganisms per gram soil, either directly engaged in microbial enzymatic degradation of dead organic matter or indirectly affecting these processes. The taxonomy of soil organisms, belonging to such divergent groups as bacteria, fungi, protozoans, potworms, earthworms, insects, and even vertebrates, exceeds the scope of this book. However, our feeling is that the book would be incomplete without at least a short introduction to soil ecology and a presentation of the principal

decomposers. This gap is filled to some extent by Chapter 3, devoted entirely to soil organisms and their role in organic matter decay.

Although photosynthesis—the source of virtually all organic matter on Earth—is an extremely complicated process from a biochemical point of view, it has already been understood and explained in detail decades ago. Surprisingly, the opposite side of organic matter turnover—organic matter decomposition—is still poorly understood; moreover, it seems that we are a long way from a full explanation not only of minor details, but of even the most important processes, such as formation and structure of humus. One reason for this discrepancy in the level of understanding of the two most important processes on Earth lies in the fact that while photosynthesis is restricted to a very limited set of possible photochemical and biochemical reactions, organic matter decomposition can follow a plethora of pathways, each consisting of a virtually indefinite number of possible combinations of different physicochemical and biochemical reactions. While organic matter production, leading from carbon dioxide and water to a variety of complicated organic compounds, can take place in a single plant cell, the decomposition of these substances back to minerals can be performed at different stages and, to a different degree, step by step, primarily by fungi and bacteria, but also through vertebrate and invertebrate animals and by purely physicochemical reactions.

Although it seems unlikely that we will reach a full understanding of even a limited set of the decay processes, substantial progress in decomposition studies has been made during the last two to three decades. In spite of numerous scientific articles on the subject published every year, there are surprisingly few handbooks summarizing the findings in decomposition science, most of them quite old and, at least to some extent, outdated. The only newer books available on the market are those by Reddy and Reddy (1996), Cadish and Giller (1997), and Berg and McClaugherty (2003). With this in mind, we decided to summarize contemporary knowledge on organic matter decomposition in a form of book that could, in part, serve as a state-of-the-art summary on decomposition for scientists, and also as a textbook/handbook for graduate students interested in research on this aspect of ecosystem function.

A. Decomposition, Nutrient Turnover, and Global Climate Change

As has been stressed, organic matter decomposition is indispensable for sustaining life on Earth, as it is the only process enabling massive recycling of chemical elements on the scale of ecosystems and the whole biosphere. Turnover of these huge quantities of matter requires enormous amounts of energy and almost all of it is delivered as photosynthetically active solar

radiation. After the fixation of carbon in the process of photosynthesis, the sole carriers of this energy are the organic compounds, which usually pass through a number of trophic levels before they are completely decomposed. Although there are millions of different organic compounds synthesized and used by organisms for various purposes, the energy transfer is generally fixed to carbon transformations since it is carbon oxidation that eventually releases energy from organic compounds. This implies that carbon turnover rate is ultimately linked directly to the rate of energy transfer in ecosystems. In fact, ecologists use carbon to trace and calculate energy transfers through trophic chains in ecosystems. The complete decomposition of organic matter means, thus, the release of all energy fixed in organic compounds, which is tied to oxidation of carbon to carbon dioxide. As we will see in the following chapters, such complete decomposition may take place only in some ecosystems and, if it happens at all, it can take thousands of years or more. One of the commonly known results of incomplete organic matter mineralization is one on which our civilization heavily relies, namely, all fossil fuels: coal, crude oil, and methane.

The turnover rate of a chemical element in the biosphere, that is, the time needed to complete the cycle from inorganic form through fixation to organic matter and its decomposition back to mineral form, determines its retention time in a particular pool. While the turnover rate depends on rates of organic matter synthesis and decomposition only, the retention time in a particular pool is a net outcome of the turnover rate and the pool size. For example, all terrestrial ecosystems fix approximately 1.05×10^{17} g carbon per year, which stands for approximately 12% of the total atmospheric pool of CO_2. Assuming no change in atmospheric CO_2 concentration (which is now not entirely true due to human activity), the average retention time of a carbon atom in the atmosphere is $1/0.12 = 8.3$ years (Rickelfs, 1979). Although oxygen release rate is fixed strictly to photosynthesis (two oxygen atoms are released per each carbon atom fixed), its retention time in the atmosphere is very different from that of carbon, due simply to the difference in pool sizes. The atmospheric oxygen pool is estimated to be approximately 1.1×10^{21} g. Knowing the amount of carbon fixed yearly by terrestrial plants, the amount of oxygen released to the atmosphere can be calculated as $2 \times 16/12 \times 10^{17}$ g. This produces approximately 1/4000 of the atmospheric oxygen pool, thus the average retention time of an oxygen atom in the atmosphere equals approximately 4000 years. The retention time of both carbon dioxide and oxygen gives us an appropriate perspective on the importance of nutrient cycling—and this means decomposition of dead organic matter. Both numbers are indeed low in ecological and geological perspectives, but the 8-year-long retention time for carbon in the atmosphere is particularly striking: if carbon fixed in organic compounds was not released quickly to the atmosphere, its whole pool would be consumed in

just 8 years. Even if such a dramatic event is improbable (especially as we neglect here the carbon exchange between the atmosphere and the huge carbon deposits in oceans), everybody is familiar nowadays with the problem that even minor changes in concentration in the atmospheric CO_2 can cause. Carbon dioxide is one of the main "greenhouse" gases in the atmosphere, which are responsible for maintaining the global temperature at a certain level. The public has become familiar with the danger of global warming due to the increase in CO_2 level in the atmosphere caused by massive fuel combustion and deforestation. Still, it has to be remembered that only due to the warming effect of carbon dioxide and other greenhouse gases the life on Earth is possible in the form we know it. To put it another way, present climatic conditions on Earth are controlled to a large extent by the balance between primary productivity and organic matter decomposition rate. Any deviation from the present balance between carbon fixation and its release back into the atmosphere must inevitably lead to climatic changes.

Considering organic matter decomposition from the point of view of balancing the atmospheric CO_2 pool, its other function crucial for life on Earth is apparent: without decomposition, the atmospheric CO_2 concentration would continually decrease. This would be followed by a decrease of the atmospheric greenhouse effect and decreasing Earth surface temperature toward the level resulting from purely physical balance between the input of solar radiation and escape of energy from Earth back to space. The latter is proportional to the Earth surface, and calculations estimate the resulting average Earth surface temperature without any greenhouse effect to be approximately $-18°C$. The current average global temperature is $+15°C$, and it is not hard to imagine consequences of a temperature decrease of $30°C$ that would be caused by removing main part of the greenhouse gases (CO_2, CH_4, N_2O, water vapor) from the atmosphere, with carbon dioxide being the most important of them. Of course, this scenario is not very probable even if decomposition were completely halted, first, because primary productivity would gradually proceed at a lower rate and a point would be reached at which no more CO_2 would be fixed in organic matter, and secondly, because other atmospheric gases, such as CH_4 and water vapor, add their effects to climate warming. Nevertheless, it has to be realized that even minor changes in the balance between rates of production and carbon mineralization can cause significant climate shifts simply due to the difference in atmospheric pool sizes between O_2 and CO_2. For example, moving the balance toward increased carbon dioxide evolution due to, for example, burning fossil fuels would use atmospheric oxygen proportionally to CO_2 production, but would cause a significant change in the carbon dioxide pool only. A change in the balance between oxygen production and carbon fixation that would cause only a negligible 0.001% change in

O_2 atmospheric concentration would be accompanied by a parallel change in CO_2 concentration by as much as 0.7%. As carbon dioxide is the main greenhouse gas, such a change in concentration would inevitably cause climatic effects at a global scale. Thus, detailed knowledge of organic matter decomposition and the effects of anthropogenic activities on these processes are of prime importance for understanding such problems as predicted global climate change. Because organic matter decomposition is only one side of the atmospheric carbon balance equation, we should ask the question, will the increase in CO_2 concentration promote plant productivity (that is, carbon fixation) to a larger extent than organic matter will decompose or just the opposite? Without answering this single question, any prediction on climate change is worthless because the final outcome will depend on atmospheric CO_2 as dependent on rates of organic matter production and its mineralization to CO_2.

Decomposition also means a return of nutrients other than carbon to mineral form, which can be reused by plants for production of fresh organic matter. As cycling of several chemical elements is not connected tightly to the energy flow, their rotation rates and residence times may vary vastly and differ substantially from those of carbon or oxygen. For example, some nutrients that are present in soil at concentrations that are growth-limiting to plants, (e.g., nitrogen or phosphorus) and which, at the same time, are used in structural compounds, for example, cell walls or nucleic acids, can be retained in live or dead organisms for much longer time than can carbon or oxygen. This results in a relatively long residence time in soil organic matter or in litter. On the contrary, some very mobile elements, which are present in organisms and dead organic matter mainly in ionic forms, such as potassium, can be lost from an organism at a much higher rate than the energy flow—their rotation rates can be very high and residence time in a biomass short. Again, the balance between their uptake rate by plants, mineralization rates, and their pool sizes determine their availability to primary producers and, in consequence, to the whole primary productivity. Release rates and patterns of nitrogen during organic matter decay will be covered in detail in Chapter 5.

While changes in carbon and oxygen turnover rates and the production/decomposition balance may have global consequences, the cycling of many other nutrients is local, for example, within a particular ecosystem. It is generally assumed that natural, unpolluted, mature ecosystems are characterized by relatively closed cycles of most nutrients, having only minor exchange with external environments (Fig. 1). Even if there is always some input of chemical elements with precipitation and dust fall, and a certain amount escapes the ecosystem with stream water or wind, the massive element turnover occurs chiefly between plants and the surface soil layer where dead organic matter accumulates and decomposes to simpler compounds to

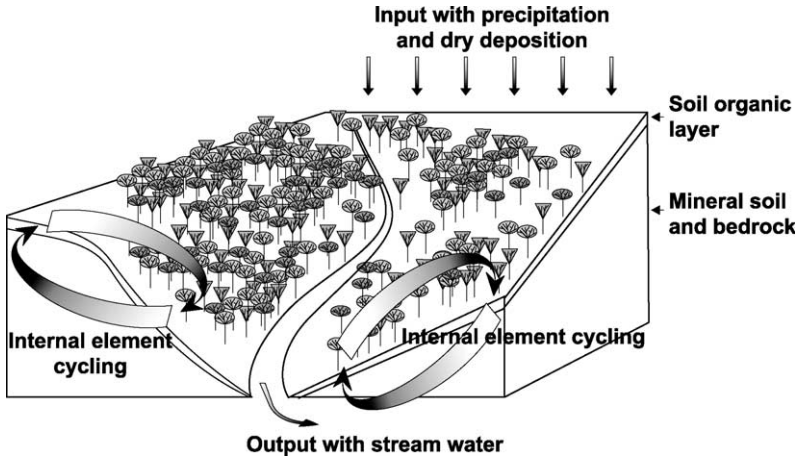


Figure 1 Natural ecosystems have relatively closed internal cycles of most nutrients, with only minor exchange with the environment outside the ecosystem, such as input with precipitation and output with water; in some ecosystems, aerial weathering may be also important.

finally become mineralized. A general schedule of element fluxes in a forest ecosystem is presented in Fig. 2.

The amount of nutrients stored in the soil organic matter differs between ecosystems and major climatic zones. In the tropical rainforest ecosystems, with the highest organic matter production rate on Earth (next to tropical bogs and marshes, which occupy only a relatively small area), virtually all matter produced is decomposed and mineralized the same year it was shed as litter. As a result, the net oxygen production and carbon sequestration in such forests are close to nil—not much more O_2 is produced in photosynthesis than is used in respiration and, consequently, not much more CO_2 is fixed than is produced during organic matter oxidation (Richey *et al.*, 2002) and the accumulation rate of dead organic matter is very low. In contrast, long-term sequestration of carbon and other nutrients is most effective in those biomes where production and decomposition diverge most from each other. Such biomes have been found mostly at medium and high latitudes, with their typical ecosystems—the temperate and boreal forests. Although their productivity is approximately 25 to 50% that of tropical rainforests, only a minor part of the organic matter produced every year decomposes during the next 12 months and the amount of dead organic matter accumulates in soil and on its surface relatively quickly. This ''imbalance'' between CO_2 fixed and CO_2 released can be very different for various ecosystem types of the same climatic zone (e.g., beech forests versus oak–hornbeam versus pine versus spruce forests), yet soil organic matter accumulates in all of

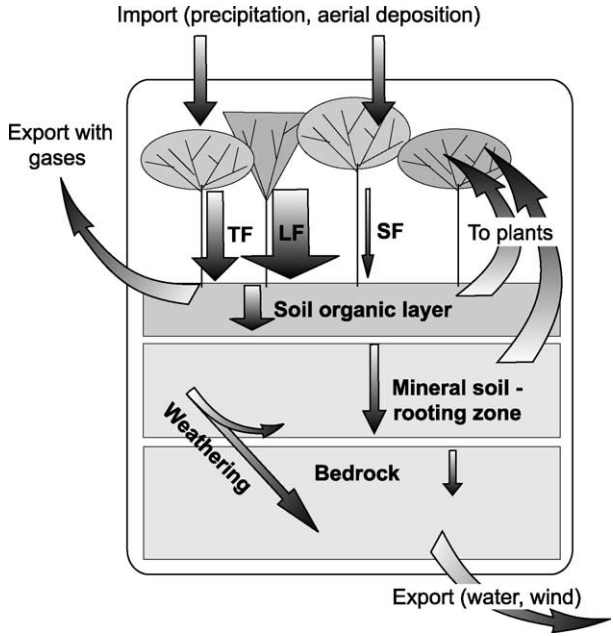


Figure 2 General representation of nutrient fluxes in an ecosystem: TF, throughfall; LF, litterfall; SF, stemflow.

them. In the following chapters, we will discuss these differences in more detail, presenting both their causes and consequences.

The major long-term consequence of this imbalance between carbon fixation and release is large deposits of soil organic matter across a range of ecosystems. Despite a number of studies published during the last decade, the behavior of these deposits in response to changing climatic conditions is one of the major unknowns in global climate change models. It is often assumed that the rise of temperature, which is supposed to be most significant at high latitudes, will increase the decomposition rate of dead organic matter. However, some studies indicate that temperature does not affect decomposition of undisturbed stable organic matter, which constitutes a major part of soil organic matter at high latitudes. That would mean that increase of temperature by a few degrees should not increase decomposition rates significantly. There are also studies indicating that secondary organic matter formed under higher temperature is more stable (Chapters 4 and 8) than that formed under lower temperatures. Such a negative feedback mechanism may counteract the greenhouse effect, at least to some extent. We may thus see two contradictory scenarios. With the ''positive feedback'' mechanism, more CO_2 is produced by increased decomposition, raising CO_2

atmospheric concentration and the global temperature further, which again increases decomposition rate and CO_2 release. In the "negative feedback" scenario, an elevated CO_2 level increases primary productivity and promotes production of more recalcitrant organic matter, leading to decreased mineralization rates. With increased production and slower decomposition, soil would serve as an important sink for carbon and could counterbalance effects of global warming (Fig. 3). The problem of global climate change is discussed more in depth in Chapter 8.

B. Biomass Distribution between Soil and Above-Ground Ecosystem Compartments

People with little knowledge of soil biology tend to notice only aboveground life, manifested by an amazing richness of plants and animals. However, most heterotrophic life is tied to the soil. Considering the biomass of the most common groups of terrestrial heterotrophs (animals and microorganisms), it appears that those animals which most people consider the most abundant and, possibly, most important for ecosystem function, are, in fact, negligible in comparison to the ground-living and soil-dwelling ones (Table 1). One of the most spectacular examples among those given in Table 1 are earthworms, which, in certain agricultural soils, can reach a biomass of up to two tons per hectare. There is no group of aboveground animals that compares to earthworms. The comparison is even more striking for microorganisms, such as bacteria and fungi—the two groups responsible for most of the organic matter decomposition in soil. Moreover, the distribution of live biomass between soil and the aboveground ecosystem compartments illustrates the importance of decomposers to a limited extent only, because the actual energy flow through any trophic level is proportional not to the biomass itself (the "standing crop", [Sc]) but to its total production per time unit (e.g., a year). This, in turn, is the product of the standing crop and the rotation time θ, the value indicating how many times a year the biomass of a certain group of organisms (e.g., a population) is produced. The rotation time is the reciprocal of the average life span $\bar{t}$ of an individual in a population: $\theta = \frac{1}{\bar{t}}$ where $\bar{t}$ is given in years. Then, the yearly production is $P = Sc \times \theta$. This simple equation has far-reaching consequences for explaining the relative importance of decomposers in an ecosystem. As these are mostly microorganisms and invertebrates with very high rotation times (especially the former), their effect on energy transfer is a few orders of magnitude higher than would result directly from their biomass. Because, as has been mentioned, the energy transfer is linked directly to carbon oxidation ("respiration"); also, CO_2 production by soil organisms is much higher than would be expected from their biomass alone, making these particular groups of

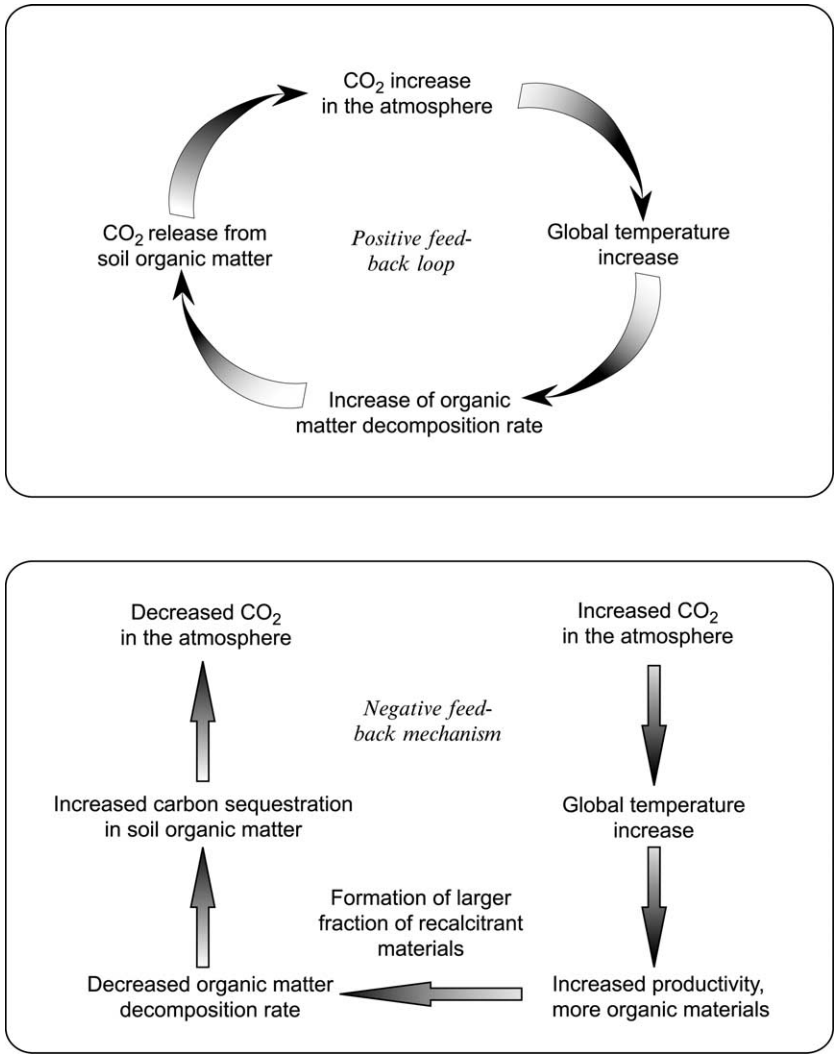


Figure 3 Two extreme and contradictory but still possible scenarios for the effect of increased atmospheric CO_2 concentration on soil organic matter: a positive feedback loop leads to even further increase in CO_2 concentration and global temperature; a negative feedback mechanism counterbalances the effect of global warming through increased carbon sequestration in soil organic matter.

heterotrophs especially important for ecosystem functioning. In fact, in boreal forests, the microbial component alone may carry out more than 95% of the decomposition of litter and soil organic matter (see Chapter 3).

Table 1 The biomass of various groups of animals in european forest ecosystems (after Ovington, 1962, and Jensen, 1974)

Group	Site	Biomass (kg ha^{-1})
I. Vertebrates and invertebrates without soil fauna		
Canopy invertebrates (without Acarina and Collembola)	U. K.	0.01–5.0 (dry weight)
Birds	Czechoslovakia	0.50–1.2
Apodemus sylvaticus	U. K.	0.25–2.0
Clethrionomys glareolus	U. K.	0.25–2.0
Sorex araneus	U. K.	0.12–1.0
Talpa europea	U. K.	1.00–4.9
Oryctolagus cuniculus	U. K.	3.20–12.8
Dama dama	U. K.	2.1
II. Soil and litter invertebrates		
Microarthropoda	Denmark	110
Nematoda	Denmark	40–50
Enchytraeidae	Denmark	30–250
Acarina and Collembola	Denmark	98–708
Lumbricidae	Europe	20–2000

So far, very few detailed studies have been done on biomass and nutrient distribution among different compartments of forest ecosystems because of the extreme laboriousness of such research. One notable exception is an extensive study done in selected mixed forests in Belgium in the 1960s, which was summarized by Duvigneaud and Denaeyer-De Smet (1970). The research team measured and calculated virtually every detail of the biogeochemical cycles in the forests, giving an unmatched body of data on biomass and dead organic matter distribution in the ecosystems, uptake of nutrients from soil, their retention in plants, and their return to forest floor with litter fall. The results of such studies clearly stress the importance of soil organic matter deposits and mineralization. For example, in the forest presented by Duvigneaud and Denaeyer-De Smet (1970), the total aboveground plant biomass was estimated at 121 t ha^{-1}, which together with belowground biomass of 35 t ha^{-1} (plant roots) gave 156 t of live plant organic matter biomass per hectare. These researchers were among the first who noticed that the soil organic matter (SOM) pool was larger than that of aboveground biomass and not much lower than the total plant biomass in that forest: it was estimated to 125 t ha^{-1} plus approximately 4.8 t ha^{-1} accumulated on the soil surface as plant litter—the most easily degradable pool of dead organic matter. Thus, in temperate hardwoods similar to those studied by the Belgian group, we may expect that approximately as much organic

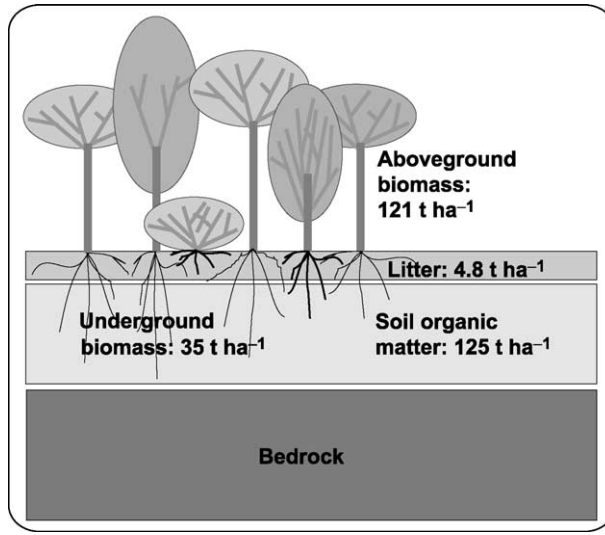


Figure 4 Main organic matter pools in a typical temperate forest ecosystem: live biomass (aboveground and underground) and dead organic matter (forest litter and soil organic matter). Data from Duvigneaud and Denaeyer-De Smet, 1970.

matter is accumulated as litter and soil organic matter as in living biomass (Fig. 4). Later, this finding was confirmed for coniferous boreal forests.

C. The Importance of Balance

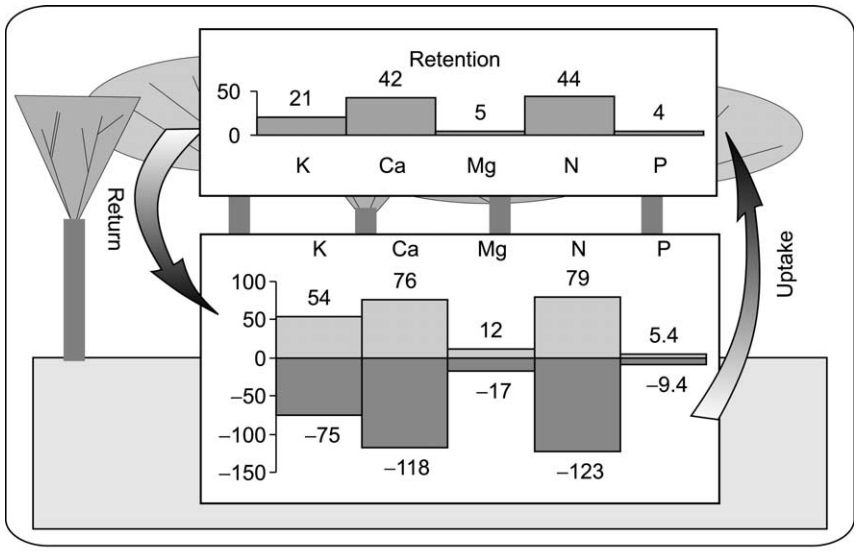
According to ecological theory, every mature ecosystem develops under specific constraints of climatic and edaphic conditions. Climatic conditions lead to formation of distinctive communities of plants, animals, and microorganisms called ''biomes,'' which cover large geographic regions. Typical examples of biomes are those considered in detail in this book—the boreal and temperate forests. However, large areas covered by such forests, although relatively well defined by specific climate, are not uniform from the point of view of bedrock, landscape, and soils. These latter factors differentiate ecosystems belonging to a single biome and a number of different ecosystem types may exist in the same climatic zone. For example, among European temperate forests, one may find beech forests in foothills, oak–hornbeam forests on richer brown soils, pine forests on pure sandy soils, and riparian forests on the banks of rivers. Similar types of forests can be found on other continents. Even if boreal forests are generally more uniform in

terms of number of species, a significant spatial variability can also be found with pine forests on sandy, nutrient-poor soils and spruce and birch on wetter and more nutrient-rich soils.

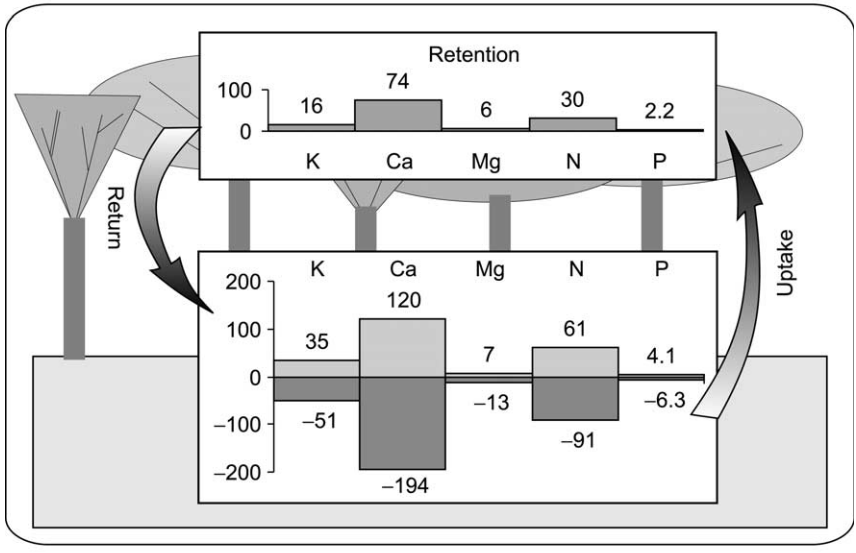
There has been a substantial climatic variability in the temperate and boreal zones since the end of the last glaciation, approximately 7 to 11 millennia ago, depending on the latitude. Nevertheless, the plant communities that have been established in these areas have had at least a few hundred years to reach a certain level of equilibrium with environmental conditions. By "equilibrium," we understand here the state when a species assemblage occupying a specific area is well adapted to local climatic and edaphic conditions. The species per se as well as the succession of species is a primary factor for the development of the humus layers and the soil, not only in terms of nutrient richness but also as regards the rate of development of the humus layer. The character of a well-developed soil thus does not depend solely on the bedrock and the climate; it is a result of interaction of these two factors with plant and microbial communities. For example, such an important soil-forming process as podsolization is dominated by leaching of metal cations carried by organic acids from the upper soil layers down the soil profile. These acids are formed by the microbial decomposition of dead plant organic matter and physicochemical factors.

Plant communities that have reached their mature succession stage will remain constant as long as the climate does not change and as long as no catastrophic events, such as wildfire, resets the system or moves it back to an earlier successional stage. The communities are composed of plant species that have evolved specific adaptations not only to climate but also to edaphic conditions. The latter designation refers to a given soil type, its moisture and, above all, nutrient supply. Mixed pine forests (for example oak–pine, Pino–Quercetum) are characteristic for sandy, acidic soils, while on richer soils, oak–hornbeam forests develop and, in their turn, form brown earth. These tree species produce foliar litter with very different properties, and in the soils of both systems specific microbial communities have developed and adapted to decompose the particular litter types of that system. Different ecosystems also harbor different invertebrate communities, whose abundance and composition are crucial for matter cycling in some ecosystems, whereas in other ones, for example, in boreal coniferous forests, their importance is negligible. Thus, all plants growing at specific climatic and edaphic conditions have special requirements not only with respect to such obvious factors as temperature, moisture, and the length of the growing season, but also with respect to specific nutrient availability. This nutrient supply is secured through release from organic matter and through weathering. When mineralization from dead organic matter becomes, for some reason, too slow for a particular ecosystem, it results in a decrease in the amount of available nutrients and, as a consequence, decreased plant production.

"Balance" is an often used term in ecology studies and the term is also used with respect to humus layers and nutrients stored in humus. There are numerous articles using synonymous terms, such as "steady state," which,



Mixed oak-ash forest (Belgium)



Mixed oak forest (Belgium)

Figure 5 (*continued*)

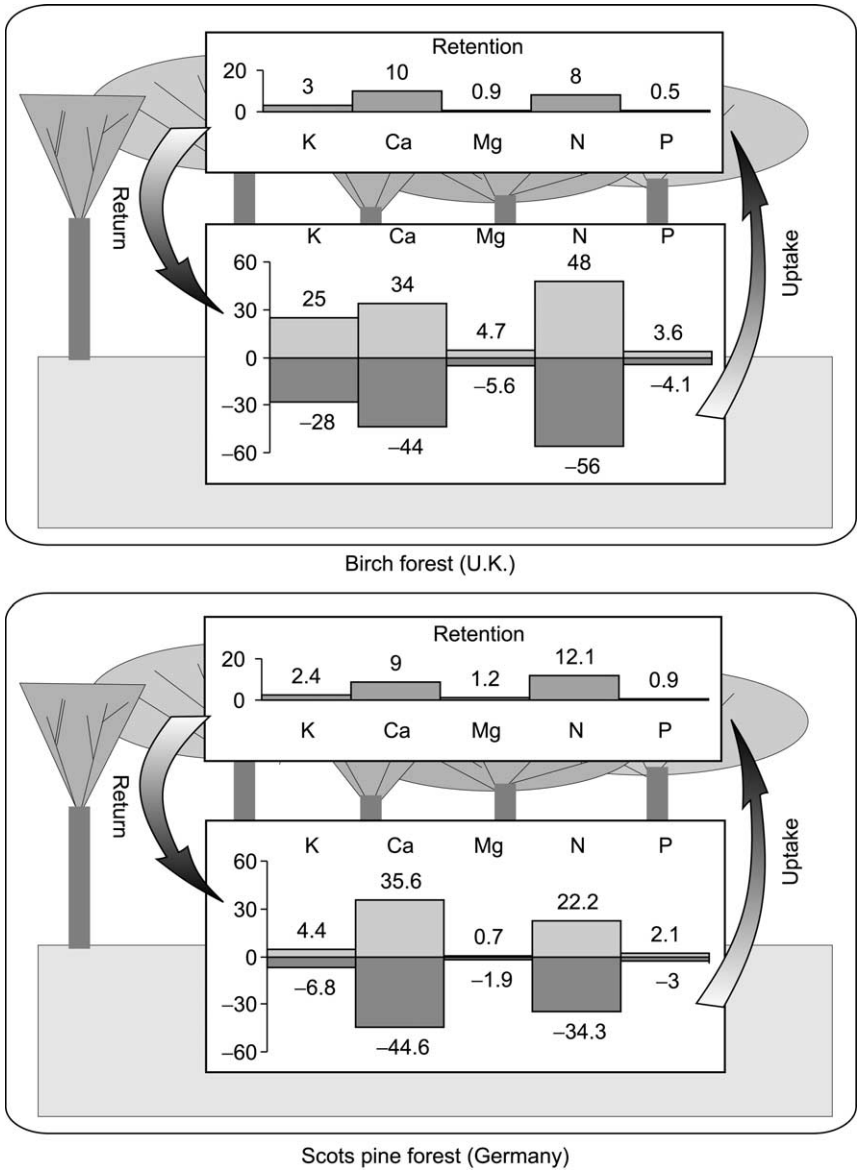


Figure 5 Annual nutrient cycling in temperate forest ecosystems. Data from Duvigneaud and Denaeyer-De Smet (1970) and the literature cited therein. Numbers in kg ha^{-1} yr^{-1}.

for the amount of stored humus, is assumed to reflect a balance between the production of litter and the decomposition. In other words, the amount of

humus is supposed to grow until an equilibrium is reached. The existence of such a steady state has been widely accepted and although it is considered to be more than a hypothesis, it has never been proven. We cannot exclude that there are ecosystems in which some kind of balance exists for the amount of humus on the forest floor. However, in the case studies presented in this book, we show that the humus amount can increase so far and over such long time periods that the concept of a steady state may be questioned. It rather seems that humus layers grow, if not infinitely, at least over millennia. That may mean that natural catastrophic events such as wildfires and, in more recent years, forest management practices are the main factors reducing the amount of humus stored on a forest floor. Instead of a real balance, we may thus see a slow buildup followed by a quicker decrease through such a catastrophic event. We could thus rather expect that the humus amount roughly follows a sinusoid-like function, with amplitude and frequency depending on the ecosystem.

The nutrient distribution in some ecosystems includes an increasing storage of nitrogen and weathered nutrients in organic matter, and the amounts of nutrients thus stored may increase considerably with time. Examples of this as a natural phenomenon are found over several climatic areas, (e.g., in Europe) from the subarctic climate through temperate regions to the Mediterranean zone. In several systems, for example, dry pine forests on sand, wildfires may prevent such an increase. In northern Scandinavia such wildfires have burnt off at least part of the soil organic matter layers every 50 to 60 years, thus preventing an ever increasing storage of nutrients in organic matter. However, the sudden outflow and loss of nutrients after a fire may be significant enough to set the successional stage back to an earlier state, for example, from spruce back to pine in a boreal forest, where the normal succession is pine to spruce to mixed forest. The forests growing under such conditions, with naturally low nutrient release, are characterized by very low productivity, and low nutrient supply, often together with low water availability, is the most important constraint.

While the phenomena described above are natural, and the forests growing in such conditions can be assumed to have adapted to them, the situation is different in forests where a high rate of organic matter accumulation results from anthropogenic disturbance. For example, in heavily polluted forests, it is not climate but pollution itself and a decreasing pool of available nutrients that limits their productivity below limits natural for particular climatic conditions. Such phenomena should certainly be of a concern since they shift an ecosystem from its natural state, toward, most probably, a less productive and less stable one. These topics are covered in detail in Chapter 8.

The opposite situation—periodically exceptionally high mineralization rates—may also paradoxically result in decreased nutrient supply in the

long run because plants adapted to poorer soil conditions are not able to use all available soluble mobile nutrients in a short time, and their excess can be irreparably leached from the ecosystem. The extreme example of such quick leaching of nutrients from an ecosystem can be events such as wildfires, already mentioned, and human-made fires, such as those still used in many countries to "fertilize" meadows in the spring.

The important message that emerges from these considerations is that the existence of any natural ecosystem depends, to a large extent, on the balance between the release rate of nutrients from decomposing organic matter and the rate of their uptake by plants. Specifically, this also means that ecosystems differ not only from the structural point of view, such as species composition, but also functionally. As well as an untrained person can distinguish a pine forest from an alder wood with the naked eye, an ecologist can recognize them by looking at their productivity, nutrient pools, and fluxes.

This, together with the biomass distribution in a forest presented on preceding pages, clearly underlines the importance of nutrient release from the nutrient pool in decomposing organic matter for ensuring uninterrupted mineral cycling in an ecosystem. The significance of nutrient release is even more evident when considering not only the pools but also the fluxes of nutrients in a forest. Figure 5 shows cycles of selected nutrients in a few European forests. Note the relatively small nutrient retention in plant biomass in comparison to nutrient uptake from soil and return with litter fall.

The fragile balance between availability of nutrients for building new organic matter and their return to the soil mineral pool can be relatively easily lost as a consequence of anthropogenic disturbances, as has been mentioned. The prime example of this is found in intensively exploited forests, which need to be fertilized because large quantities of nutrients are withdrawn with harvest of biomass. Similar problems of decrease in pools of available mineral nutrients may also result from industrial pollution, which frequently suppresses organic matter decay rate. More details on these problems are found in Chapter 8.

Litter Fall

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I. INTRODUCTION

In forested ecosystems, litter fall is the largest source of organic material that will form humus substances and organic layers. Also, nutrients bound in the litter are deposited into the soil and become associated with the humic substances in the mineral soil and bound in the organic layers where such are found, for example, in most boreal and temperate forests. The chemical composition of plant litter has a large influence on the soil microbial communities and is one of the main factors affecting litter decay rates and the dynamics of soil organic matter. Thus, not only litter-fall quantity but also its quality affects the storage rate of humus and the quantities of released and stored nutrients.

With knowledge about the initial chemical composition of litter and the chemical changes taking place during decomposition, it has been possible to predict not only humus buildup rates (see Chapter 6) but also, for example, the concentration of N in humus formed from a given litter species and thus the buildup rate of N in humus (Chapter 5). With a close connection between the chemical composition of newly shed litter and the relative amount of recalcitrant residual litter (Chapter 6), we may see a direct connection between litter chemical composition and the rate of humus (soil organic matter, [SOM]) buildup. Thus, detailed knowledge about initial litter chemical composition may be a useful tool to estimate humus buildup and nutrient storage. It will, of course, also be possible to estimate the release of some nutrients in the forest floor. There appears, however, to be a severe lack of systematically collected data on the chemical composition of newly shed litter so we are forced to use just a few examples. There is even a lack of generally accepted methodology for sampling litter. This simply means that data given in the literature on this topic has to be studied with some care and results should be evaluated considering the methods used.

The aim of this chapter, which focuses on the foliar litter fall from trees, is to give an insight into the present state of our knowledge on quantitative litter fall and its chemical composition, and also to identify regional factors which may influence both the litter fall quantities and litter chemical composition. To determine the factors regulating the magnitude and the pattern of litter fall may be a complex task and several species-specific properties may influence the outcome. We present here a few main factors.

The chapter has three main sections. The first section presents a general overview to quantitative litter fall; the second gives an overview to litter chemical composition with Scots pine as a case study, followed by other species. The third section presents methods of how to measure litter fall and suggestions on how to sample foliar litter for determination of the

chemical composition. Again, we have used Scots pine as the main example since there is more data available for this species than for any other.

II. LITTER FALL AMOUNTS—MAIN PATTERNS AND REGULATING FACTORS

A. Patterns on the Forest Stand Level

In the boreal and temperate zones, we may distinguish different patterns of foliar litter fall among species. There is not only a difference between the deciduous and the coniferous trees as groups but also among species within each group. No fewer than three main patterns may be distinguished and we have selected some genera and species as examples (Fig. 1). Of the conifers, the pines shed foliar litter in a regular manner, meaning that the oldest shoots still holding needles, normally 2 to 5 years old, shed them in the autumn (see also Section II.B.). Dryness may influence the pattern and cause a fall at other times of the year but normally, for a species like Scots pine, approximately 70% of the needle fall takes place in a short part of the autumn (Fig. 1), with the remaining 30% distributed evenly over the year. The spruce presents an entirely different pattern. Having needles that may remain up to 10 years on the shoots, the trees continuously shed needles of different age classes, that is, needles located on shoots of different years. Thus, in contrast to pines, not all needles on a shoot are shed at the same time but single needles die and stay attached dead for several months before they finally fall. Although dry periods may cause a heavier fall, spruce has no clear litter-fall period but needles are shed about evenly over the year, with a somewhat higher fall in wintertime (Fig 1).

Among the deciduous trees, there is normally a heavy litter fall during a short period in the autumn when the trees shed all their foliage. The timing of litter-fall peak varies, depending on the species (Fig. 1) and geographic location. Further, some species of oak, for example, have a prolonged litter fall over the autumn, winter, and spring. This means that although leaves die in the autumn, they stay attached dead on the twigs and fall occasionally during the winter but a large part stays until spring, to be finally shed when the new buds develop. This may occasionally be seen also with common beech.

Within a group of stands on soils of similar richness and under climatically similar conditions, annual leaf and needle fall may be related to stand properties, such as stand age, basal area, or canopy cover. When investigating data over larger regions (see Section IV.C.), the factors that are important, either at a stand level or at a local level, may become less significant.

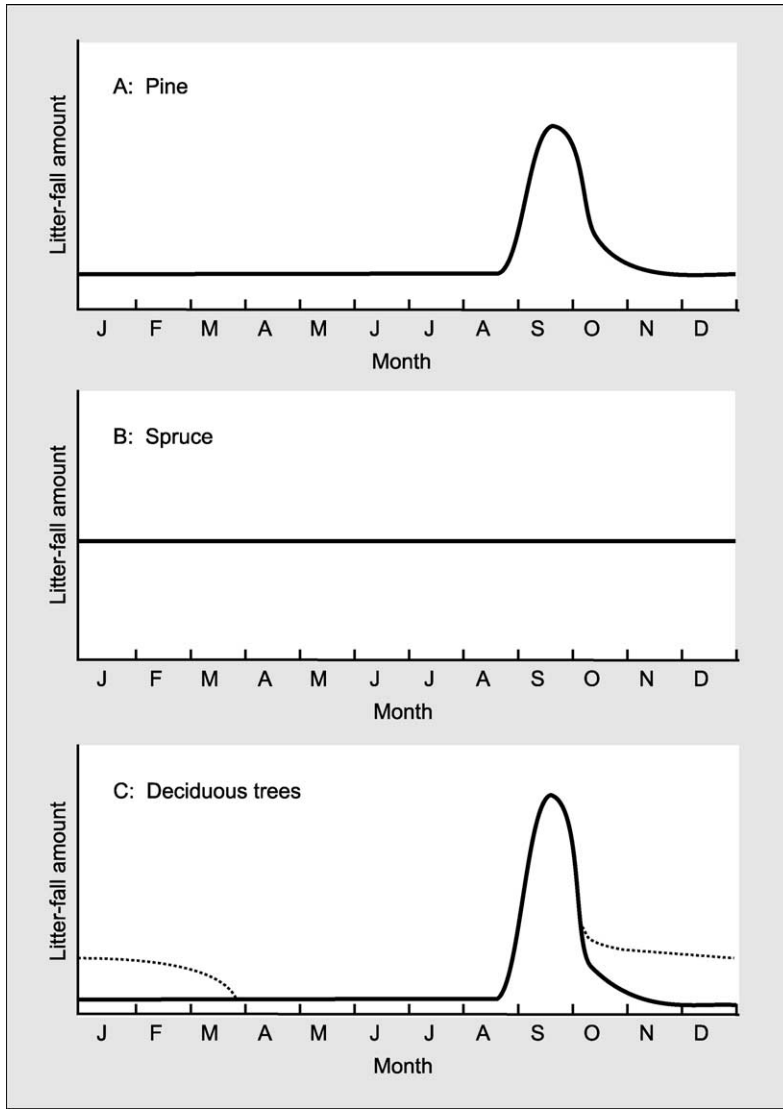

Figure 1 A generalization of typical needle and leaf litter-fall patterns for some coniferous and deciduous tree species. (A) Pines, such as Scots pine, generally have relatively low litter fall over the year and in early to late autumn a sharp peak in fall occurs with about 70% of all needle fall of the year. The peak has a duration of about a month and may occur in August at the northern border for Scots pine, in Europe at approximately 70°N, and as late as November in continental Europe. Under a climate with dry summers, such as the Mediterranean, the litter fall peak may occur in July. (B) Spruce has no pronounced litter-fall period and higher falls occur in connection with events such as drought. (C) Deciduous trees normally shed

The factors regulating the amount of litter fall vary with the litter component, and foliar litter fall and woody litter are shed due to very different factors and events. Normally, foliar litter fall is the largest component and this discussion will focus on that subject. Two tree species, namely, Scots pine and Norway spruce, have provided us with data allowing for a detailed description of two case studies, both on a local scale and over the boreal and the temperate regions.

B. Litter Fall Patterns in Scots Pine—A Case Study

As a case study, we use an 8-year survey on a Scots pine cronosequence in central Sweden (ca. 61°N), in which litter fall was observed in three stands, aged 18, 55, and 120 years, at the onset of the investigation. The stands were even-aged monocultures and the measured litter-fall fractions were needles, cones, bark, and twigs. Over the 8 years, there was an increase in total litter fall (all litter components combined) in all three stands.

In the youngest stand, an increasing trend in litter fall may be attributed to an increase in total tree biomass. Similarly, the 55-year-old stand also increased in biomass, which was reflected in increased litter fall. In contrast, mature stands, such as those of 120 to 130 years, are normally considered stable from the point of view of their litter production, that is, they have a rather constant litter-fall rate. Our case study was very detailed and the observed increase in litter fall in this mature stand cannot be undermined. However, the increase rate was substantially lower than those in the two younger stands. This raises a question about correctness of the "no litter-fall increase" assumption for mature Scots pine stands or, alternatively, suggests that litter fall is cyclic, with each cycle covering rather long periods.

Across the cronosequence, an overall trend in litter-fall composition was noted: from the highest proportion of the needle component in the youngest stand to successively lower proportions of needles in the older stands and increasing proportions of cones, twigs, and branches. Cones develop and are dropped as trees reach their physiological maturity, which, in our case study, happened when they were approximately 18 years old. Bark and twigs start falling later, in this cronosequence, at the age of about 22 to 23 years. At the age of 18 to 25, the needle litter made up approximately 83% of the litter fall; at 55 to 61 years, it had decreased to about 68%, and at 120 to 126 years, to

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their foliar litter in a short period in the autumn. As for pine, that litter-fall period depends on latitude and climate. For some oak and beech species, the old leaves are not all shed in the autumn but drop during winter until finally all leaves fall in spring with the development of the new buds (indicated with a dotted line).

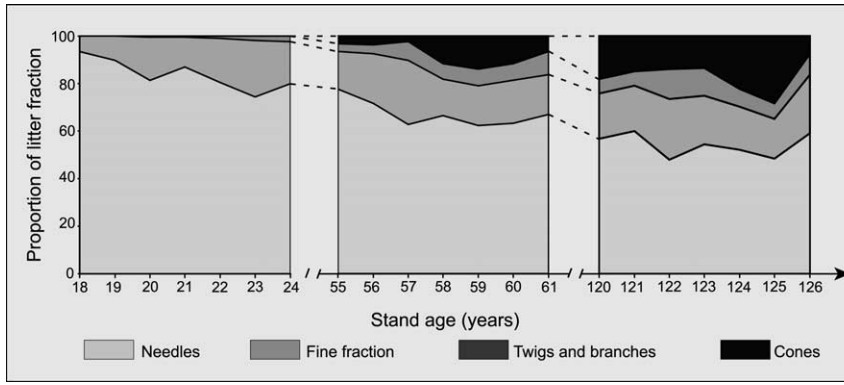


Figure 2 Generalized development of the relative proportions of main components in litter fall (needles, fine litter, twig, and branch litter as well as cones) as observed in a boreal chronosequence of Scots pine. Data from Berg *et al.* (1993a).

58%. This picture, with an increasing proportion of woody parts, is typical for pine stands (Fig. 2) and a high proportion of woody parts and cone litter is characteristic of middle-aged to old stands, in which branch mortality is high.

Needle litter is formed throughout the year, especially during drier periods, and at this latitude (61°N), almost all needles shed come from the 4-year-old shoots. Each stand in this monocultural Scots pine case study site had even-aged trees and the needles of the 4-year-old shoots withdraw their nutrients (Section VI.B.) starting in late July or early August, a process that continues until the needles are shed. In the case of a very dry summer, there may be a summer litter-fall period; otherwise, the main needle fall takes place in September during a relatively short period which produces 70% of the annual needle litter fall. The remaining needle litter is shed, in part, during winter. In younger stands, needle litter fall increases steeply with stand age until the canopy cover is closed (Fig. 3), or until a stage in which the canopies do not develop further and there is no net increase in the green biomass. However, in northern forests like those in the present case study, there is no real canopy closure but rather a maximum canopy size.

For younger stands, it is often possible to create a linear relationship for foliar litter fall versus stand age in the development phase before canopy closure. For older stands which do not develop any further, a decline in needle or leaf fall with age may be observed; still, in our case study, an increase took place over 8 years in the 120- to 130-year-old stand (see previous comments).

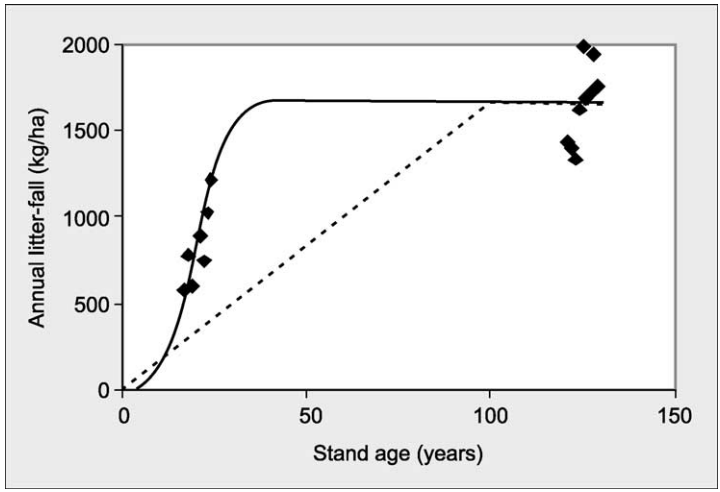


Figure 3 Two simplified models for predicting litter fall of different stand ages. Broken line, the model assuming that litter fall increases linearly with age up to canopy closure, in this case study at 100 years and remains constant thereafter. Solid line, a logistic, nonlinear model fitted to litter fall data for Scots pine stands 18 to 25 and 120 to 130 years old. From Berg *et al.* (1995). Adapted with permission from the Scandinavian Journal of Forest Research.

For mature Scots pine stands, the variation in annual needle litter fall between years is considered rather low. For longer measurement series, the ratio between maximum and minimum annual needle litter fall has been found to be in the range between 1.1 and 2.1. Such comparisons are made within a stand only.

As can be seen from Fig. 2, litter consists of a number of different fractions that not only look different but also behave in different ways, during both the litter fall and the decomposition. The term "fine litter" is often used as a collective name for a group of small-sized, not well-defined components. "Branch and twig litter" usually does not have any really regular periodic litter fall. Their fall is connected, rather, to specific events such as heavy winds, especially storms, and to heavy rain or snowfall. In turn, the pattern of "cone litter" fall strongly reflects a periodicity in cone production, with peaks at intervals of about 5 years for Scots pine (Flower-Ellis, 1985; Hagner, 1965). Cone production shows a very clear increase with increasing age of the stand, from virtually nil to over 25% of the total litter fall, following a year with high cone production (see the 120- to 130-year-old stand of the case study, Fig. 2). A term such as "cone litter" may seem inappropriate; still, when the cones have fallen to the ground, the main part of the organic matter starts decomposing and should be regarded as litter.

III. A MODEL FOR ACCUMULATED LITTER FALL, STAND LEVEL

A. General Comments

To construct a model of litter fall for a given stand, relatively little information is needed, although more data makes the model more reliable. In our discussion, we focus on litter fall from the trees but information about that of the understory could be included in the same discussion. Over a stand age, the information required for the model includes time for canopy closure, stand age, and quantitative litter fall, ideally in a cronosequence including a mature stand. That the canopy cover closes means that the canopies do not expand any further and that, in a long-term perspective, total and foliar litter fall may be assumed not to increase any more but reach rather constant values, although still with annual variation. For forests in nutrient-poor areas and in many boreal stands, no complete canopy cover is reached but rather a maximum coverage (cf. Fig. 3). In this case, that would correspond to a maximum canopy cover and thus to a maximum litter fall.

We will describe two simple models of litter fall, which we call *linear* and *logistic*. For the linear model, it is assumed that litter fall increases linearly from a stand age of one year up until canopy closure, after which the litter fall may be considered constant. The model would thus be described as two straight linear relationships crossing each other at the time of canopy closure. This model is based on common observations and is sometimes used, for example, in forestry. In the logistic model, litter fall increases initially at an exponential rate until about a maximum canopy cover, when the increase rate slows down approaching an asymptotic level, and litter fall becomes about constant. Both models will be described in detail, using our case study as an example (Fig. 3).

B. A Case Study for a Scots Pine Stand

Litter fall was monitored for 7 to 10 years in each of two adjacent Scots pine stands, initially 18 and 120 years of age, on soil of similar nutrient status. The stands thus represented age periods of 18 to 25 years, and 120 to 130 years, giving a certain age distribution. Detailed measurements and analyses of the total annual litter fall as well as the deposition of single litter components, such as needles, cones, branches, and fine litter, were made providing basic data (Flower-Ellis, 1985; Berg *et al.,* 1993) and some temporal trends were evident within the stands.

The series of observations revealed that total litter fall in the young stand clearly increased with stand age (Fig. 3; cf. Berg *et al*., 1995). A mature stand

should ideally have a maximum canopy cover, not increase its biomass, and thus also reach a constant litter fall. Still, also in mature stands, there is an annual variation in litter fall which may obscure an ideal picture—or a theory. So, we may assume a long-term steady level with an annual variation. The average litter fall during the 10-year study was 1621.5 kg ha^{-1} in the initially 120-year-old stand and that value was used as an average for a maximum litter fall.

1. A Logistic Model

The logistic model can be stated as:

$$\frac{dLF}{dt} = g \cdot LF \cdot (Max - LF)$$

and may be developed to

$$LF = \frac{Max \cdot LF_0}{LF_0 + (Max - LF_0) \cdot e^{-g \cdot Max \cdot t}}$$

where
LF_0 = annual litter fall at $t = 0$; LF = annual litter fall
Max = maximum ("steady-state") annual litter fall
g = constant, intrinsic for rate of increase in litter fall with stand age.

Using serial approximations to achieve the best fit to the data from both stands, the following parameters were derived: Max = 1620, g = 0.37. Using this model, the value estimated for accumulated litter fall over 120 years was 164,500 kg ha^{-1}. The logistic model predicted a maximum litter fall at a stand age of approximately 30 years. We have used this litter-fall data in Chapter 6, Section VI.B., for a discussion on humus buildup rates.

2. A Linear Model

Following the assumptions previously described, the linear model for this case study assumes a linear increase in litter fall from an estimated initial value of 16.2 kg ha^{-1} in year 1 to 1620 kg ha^{-1} in year 100, with litter fall remaining constant for 20 years thereafter. This model gave an estimate of approximately 116,300 kg ha^{-1} over the 120 years. However, the assumed model, with linear increase in litter fall until canopy closure, does not fit the observed data well (Fig. 3). In fact, the linear regression of needle litter fall on stand age gives a good relationship for the 18-year-old stand for only

the 7 years for which data are available but that relationship is much steeper than the assumed model.

The larger estimate produced by the logistic model is due to the fact that this model predicted a much higher litter input in the early years of stand development. The logistic model predicted that the stand reaches its maximum litter production after only 30 years, whereas the linear model assumes that maximum is not attained until year 100 (Fig. 3).

IV. MAIN LITTER-FALL PATTERNS ON A REGIONAL LEVEL: SCOTS PINE AND NORWAY SPRUCE

A. Distribution of Species

In Europe, Scots pine grows from Barents Sea in the north to the Pyrenees in the south, although it forms forests only to about the Alps and the Carpathians. Norway spruce forms forests from about the Arctic Circle to the south side of the Alps. Over such long distances, the magnitude and pattern of litter fall vary with the geographical position and climate. We have chosen to present these two species for case studies since they represent two different types of litter fall. Further, at present, these are the only species for which data on such a broad geographic scale are available.

B. Factors Influencing Amounts of Litter Fall

The factors influencing litter fall may be divided into factors such as climate, which have an influence on a continental to regional scale, and more local factors such as soil nutrient status. Soil nutrients is a factor which can vary substantially on a local scale or stand level. Finally, on forest-stand properties such as basal area and canopy cover, both reflecting the status of stand development. Stand age is often seen as a factor reflect stand development for rather even-aged stands but may be less useful as an index for litter fall in managed forests where, for example, thinnings take place.

Regarding effects of soil nutrient status versus climate, we may take as an example three paired stands of Scots pine, all within a radius of 100 m but growing on different soils with a stand age that can be considered constant (range from 45 to 48 years). The average annual total litter fall was 1360, 1680, and 2084 kg ha^{-1} for a stand on dry and nutrient-poor sandy soil, on a mesic and more nutrient-rich one, and on a very nutrient-rich and moist soil, respectively. Thus, within a rather small area, the litter fall within one species can have a large variability due to site factors, a variability that would correspond to considerable differences in climate if the soil nutrient

conditions were constant. Thus, if the lower value of 1360 kg ha^{-1} reflects litter fall at an AET value of 385 mm, the value of 2084 kg ha^{-1} would correspond to an AET value of 490 mm.

Thus, when comparing litter fall on a regional basis in stands under different climates, factors such as soil nutrient status and stand properties must not be neglected. These properties can vary considerably among single stands at similar climatic conditions, enough to cause significant deviations from a general climate-driven trend. As such, they must be considered in litter-fall studies on a regional scale.

C. Needle Litter Fall—Pattern and Quantities: Scots Pine and Other Pine Species

For different species, differences in litter fall may reflect physiological differences, such as species-specific relative distribution of resources to woody and photosynthetic parts. Over a continent, the magnitude of annual foliar litter fall may be related mainly to climate and thus to the productivity of the trees. It may be related to climate (temperature and precipitation) as a main factor and stand density (e.g., basal area) as a second one. The stand density may be a result of different factors, such as soil nutrient level, soil moisture, and solar radiation.

For Scots pine, we describe a transect ranging from Barents Sea to Central Europe, with truly boreal forest in the main part of Fennoscandia and temperate forest in southern Scandinavia and the northern part of the European continent. We also extend the transect to forests of other pine species, reaching as far south as to the subtropical Mediterranean climate (see Fig. 4). In this long transect, the magnitude and pattern of litter fall vary with climate and thus with the geographical position of each stand.

1. The Seasonal Pattern in Pine Litter Fall Varied Over the Transect

Over the range of Scots pine sites, the onset of litter fall in the autumn was related to climate and thus to latitude. In northernmost Finland, close to 70°N and the northern border for this species, the needle litter is shed in early August. About 3° to the south, that is, at the Arctic Circle (about 66°57′N), the litter fall starts in late August, whereas at 60°49′N (Central Sweden), it starts in late September. Further south, for example, at the latitude of Berlin (52°28′N), the main litter fall takes place in late October and early November and in south Poland and south Germany (about 48–49°N) in November. Scots pine stands located in a Mediterranean climate have a different pattern altogether, with the heavy litter fall taking

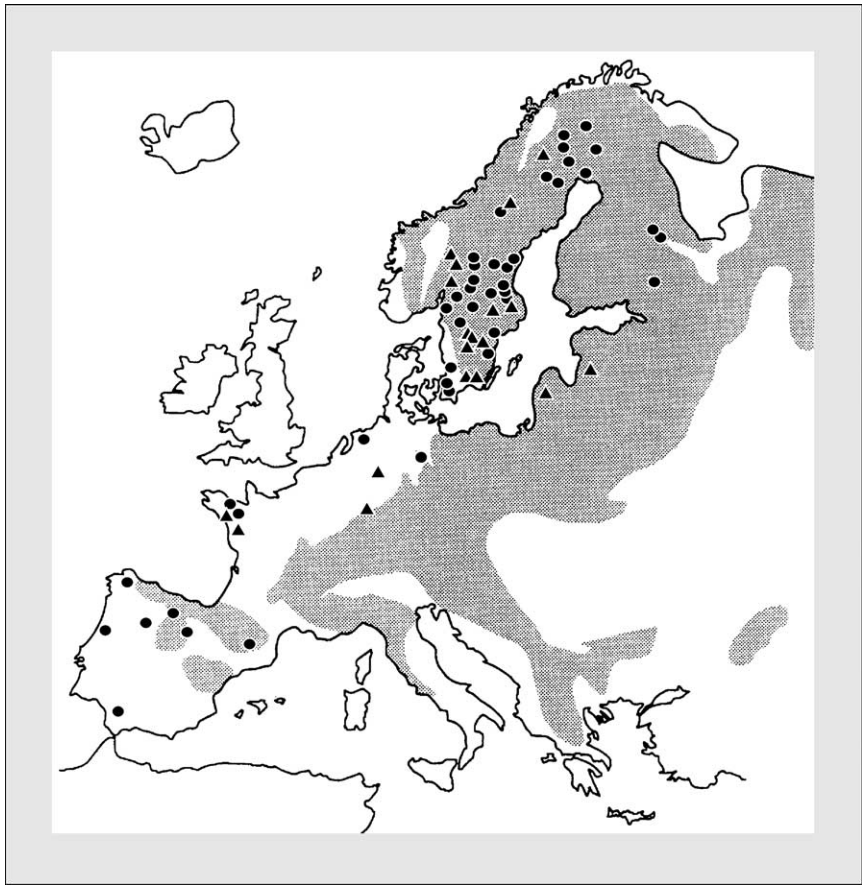


Figure 4 Map of Europe giving approximate locations of the sites used in two transects, one with Scots pine and one with Norway spruce. Pine (●), spruce and fir (▲). The shaded area indicates the extent of main range of Scots pine forests.

place in June owing to the Mediterranean drought period. Other pine species growing in this latter region, such as Aleppo pine, stone pine, and maritime pine, follow about the same pattern.

In boreal systems, Scots pine shows a mean annual needle litter fall ranging from 530 kg ha^{-1} close to the Arctic Circle to 3700 kg ha^{-1} at 57°N, which is approximately 1500 km further south, in southern Scandinavia (Fennoscandia).

The temperate continental pine forests all have a relatively high litter fall as compared to the Scots pine sites in boreal Scandinavia. Thus, a stand of

Austrian pine on the northern coast of Holland had a high annual needle litter fall of 4400 kg ha^{-1}. Further south in the temperate zone, needle litter fall for pine was as high as 6604 kg ha^{-1} on the French Atlantic coast. A stand in central Portugal, with a mixed culture of maritime pine and Monterey pine, also had a very high needle litter fall, with a bit more than 5005 kg ha^{-1} at the age of 24 years. In contrast, a stone pine stand in a clearly Mediterranean climate in southern Spain (Doñana National Park) had a much lower annual needle litter fall with 1200 kg ha^{-1}. We will present the main factors influencing the litter fall, show available data, and discuss them as far as the data set allows.

An often used climate index for biological activity and productivity is annual actual evapotranspiration (AET) (see Textbox 1). This index includes both temperature and precipitation. In our case study, investigating

Textbox 1 Climate indices

The climate indices presented in this box are often used for analysis of biological processes on large geographic scales. In the book they are used on an annual basis and below they are presented in that way together with the abbreviations used in the text. As the litter fall often is studied over different periods, even within the same site (as are also the decomposition processes), we use long-term annual averages.

AET	*Annual actual evapotranspiration* (mm). A climate index considering mainly precipitation and the energy input at a given site. Soil properties may be included or standardized (e.g. when a set of sites are considered). AET is often used as an index for biological processes. It should be remembered that a calculated AET value does not always reflect exactly the ground climate but rather serves as an index of ground conditions. Forests with different canopy characteristics could thus have different ground climates.
PET	*Potential evapotranspiration (mm)*. The amount of the precipitation which potentially can evaporate. PET – DEF = AET
AVGT	*Annual average temperature* (°C).
JULT	*Average temperature in July* (°C). July is thus considered the warmest month of the year in the northern hemisphere.
PRECIP	*Annual precipitation* (mm).
DEF	*Water deficit* (mm).

Table 1 Litter fall for Scots pine and Norway spruce regressed against some commonly used and available parameters[a]

Parameter	r	R^2_{adj}	n	p<
Scots pine:				
Actual evapotranspiration	0.682	0.449	35	0.001
Average annual temperature	0.668	0.429	35	0.001
Latitude	−0.587	0.328	41	0.001
Basal area	0.569	0.307	41	0.001
Stand age	−0.425	0.16	41	0.01
Site altitude	−0.406	0.144	41	0.01
Norway spruce:				
Actual evapotranspiration	0.84	0.679	13	0.001
Latitude	−0.552	0.242	13	ns
Basal area	0.579	0.275	13	0.05
Stand age	−0.598	0.3	13	0.05

[a]The sites used cover Fennoscandia at a range from the Arctic Circle to the latitude of Copenhagen (66°57′N to 55°40′N). Such parameters as latitude and actual evapotranspiration were well correlated. Data from Berg *et al.* (1999) and from Berg and Meentemeyer (2001). The R^2_{adj} transfers the R^2 values to comparable values for different number of degrees of freedom.

Scots pine litter fall in the boreal zone, the best reported relationship for pine needle litter fall to climatic factors was that to AET with an R^2_{adj}* value of 0.449 in a transect with 35 stands (Table 1). The Fennoscandian boreal systems are energy limited, meaning that temperature is a limiting factor and also that variables based on temperature provide good relationships (Berg and Meentemeyer, 2001). Thus, in our case study, annual average temperature alone gave a relationship that was almost as good as AET (Table 2).

Also, over larger regions, the best relationships for pine and spruce needle litter fall to climate are those to AET; for combined boreal, temperate, and subtropical (Mediterranean) pine and spruce systems, a very good relationship was seen with a $R^2_{adj} = 0.61$ using data for 64 stands ($p < 0.001$). When we compared litter fall from pine species only, AET gave an R^2_{adj} of 0.578, and average annual temperature gave an R^2_{adj} value of 0.424 (Table 2). Also, the relationships to temperature and to potential evapotranspiration (PET) were almost as good and significant at the level of $p < 0.001$, with values for R^2_{adj} of 0.424 and 0.410, respectively (cf. Textbox 1 and Table 2).

*R^2_{adj} – the determination coefficient (R^2) adjusted for degrees of freedom is more useful and correct for comparing regressions with different number of independent variables.

Table 2 Compilation of needle litter-fall data from a climatic transect covering Europe from the Arctic Circle (66°57′N) to the Mediterranean (37°N)[a]

Parameter	r	R^2_{adj}	n	p<
Actual evapotranspiration[b]	0.766	0.578	48	0.001
Average annual temperature	0.66	0.424	48	0.001
Potential evapotranspiration	0.65	0.41	48	0.001
Latitude[b]	−0.539	0.277	58	0.05
Basal area	0.338	0.098	58	ns
Stand age	−0.52	0.257	58	0.05

[a]Different pine species are combined, namely Austrian pine, Corsican pine, lodgepole pine, maritime pine, Monterey pine, Scots pine and stone pine.
[b]Please note that the relationship between litter fall and latitude given below encompasses all available data for boreal, temperate and Mediterranean forests. Figure 5 shows the same data but divided and that latitude as a parameter gives better relationship where it is related to a climate index.

2. *Latitude*

Although latitude is not a causal factor for litter fall, it is commonly used in the scientific literature since it is often related at least to annual average temperature. Litter fall is thus related to latitude in a general way but with limitations and, since it is not a causal variable itself, it must be used with caution. Using boreal Fennoscandian data for 41 stands gave for our case study a negative relationship between latitude and needle litter fall ($R^2_{adj} = 0.328$; $p < 0.001$) (Table 1). For a longer Scots pine transect, latitude would be acceptable as a regressor as long as it was related to climate indices. Thus, in western Europe, for example, over the boreal and temperate zones, latitude gives an acceptable relationship. However, when including Mediterranean data, this relationship did not hold. We may see this from Fig. 5, in which litter-fall data from the same transect is related to AET and to latitude. When the co-variation between AET and latitude ceases under the Mediterranean climate, the relationship between litter fall and latitude also ceases.

3. *Stand Age*

Age does not give any clear relationship for litter fall in transects, with results actually varying across studies, and Rodin and Basilewich (1967) suggested that no general relationship existed. Some scientists report good relationships, however (Albrektson, 1988). For our case study transect (Barents Sea to Central Europe), we obtained a significant negative

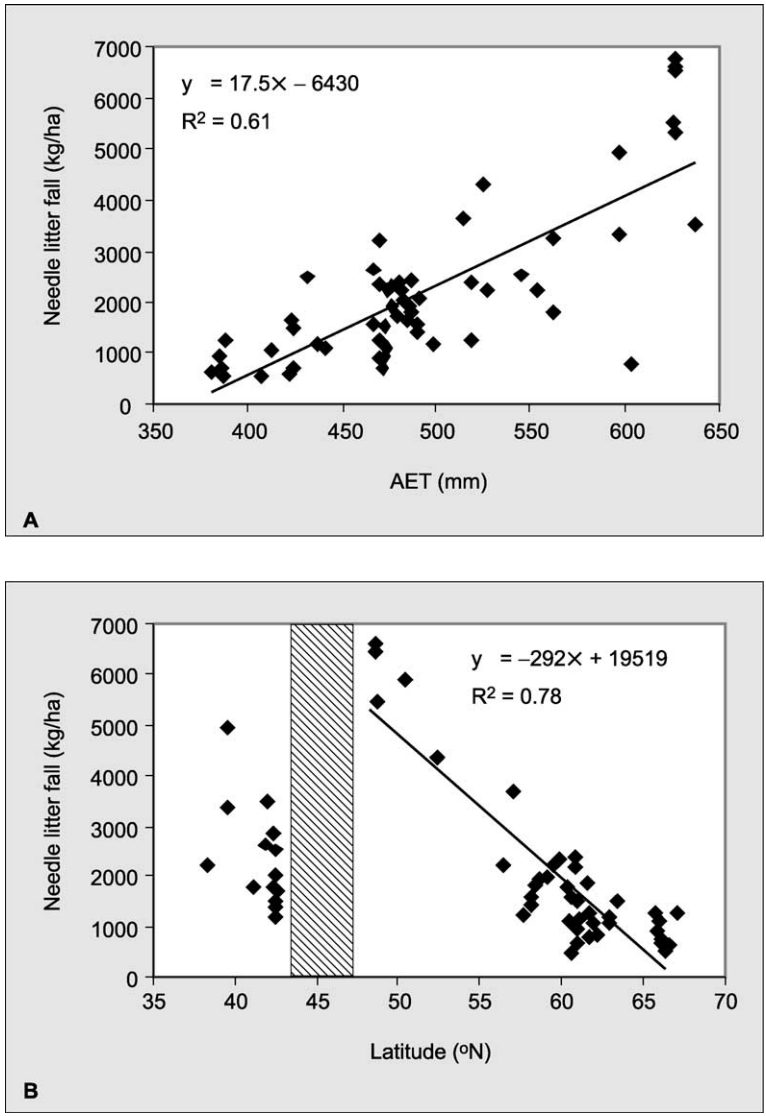


Figure 5 Needle litter fall for some different pine species over Europe related to two different parameters. The two figures give the same data set for litter fall. (A) As compared to actual evapotranspiration (AET). From Berg and Meentemeyer (2000). (B) As compared to latitude. The bar separates the Mediterranean stands from those of temperate and boreal climates. From Berg *et al.* (1999). For the sites on the right-hand side of the bar, latitude and AET are correlated.

relationship with an R^2_{adj} value of 0.160. Such a negative relationship using data from a climate transect may simply reflect an indirect effect of latitude/climate, with trees generally being older at higher latitudes, age not reflecting a difference in biomass. Thus, in reality, we just compare the lower litter fall at higher latitudes (with older trees) with the higher litter fall at lower latitudes (younger trees). We would conclude that although age may be important for developing younger stands (cf. Section II.B.), it is probably not correct to use it when comparing mature stands. In fact, Liu *et al.* (2003), when comparing litter fall in Europe and Asia to climate, excluded younger stands to avoid this kind of problem with their data.

D. Basal Area and Canopy Cover

Basal area and canopy cover are expressions of the stand biomass and are related to litter fall within at least species and possibly genus. Although both may be described as typical stand properties, basal area has been found to give significant relationships with litter fall over a region the magnitude of Scandinavia (Table 1). Still, a relationship on such a regional level is poor due to the large climate variation in the same region, which may dominate over basal area as an index. For 41 stands over Fennoscandia, R^2_{adj} was 0.307 and $p < 0.001$ (Table 1) as compared to the annual average temperature with an R^2_{adj} of 0.429. When using this variable in a regression model, it probably should be used together with a regional factor. Combining basal area or canopy cover with climatic factors in a model may go a long way in explaining the variation. Thus, in a multiple linear regression combining AET and basal area, R^2_{adj} increased from 0.449 for AET alone to 0.557 ($n = 45$) with $p < 001$.

The lowest amounts of annual litter fall are found at nutrient-poor sites, where the basal area would be low. At more nutrient-rich sites, for example, those with till deposits or clays, litter-fall mass is generally higher than in stands on granite sand. Among sites of similar fertility, needle litter fall is lower for sites situated under drier and colder climate, and thus lower AET, than for sites under a higher AET. This may be illustrated with an example. Amounts of needle litter fall are compared at two sites, one at latitude 66°32'N (AET = 382) and another at latitude 58°07'N (AET = 491). These sites had nearly identical basal areas (17.5 and 18.3 $m^2\ ha^{-1}$, respectively), but the annual needle-litter fall at the northern site (608 kg ha^{-1}) was only about one-third of the amount obtained at the southern one (1571 kg ha^{-1}). See also the example in Section IV.B.

E. Needle Litter Quantities: Norway Spruce

1. Climate Indices

There are few data available for Norway spruce litter fall and, as an example, we have used a transect within all 16 sites across northern Europe. In this case, climate as indexed by AET gave highly significant relationships for all available data, ranging from the Arctic Circle to about the latitude of Paris, Munich, and Budapest, with an R^2_{adj} of 0.778 ($n = 16$) (Table 3). Annual average temperature as a single factor gave an R^2_{adj} of 0.685, which shows that temperature has a strong influence on litter fall for spruce also.

2. Latitude

Latitude did not give a significant relationship for Norway spruce over the range of Fennoscandia alone. However, for a longer transect covering the area from the Arctic Circle to the Alps, an R^2 value of 0.518 was highly significant ($p < 0.001$). This is a substantially weaker relationship than that with AET, a result that should be expected, considering that latitude gives only a rough image of climatic conditions.

F. Comparison of and Combination of Species

Litter-fall measurements including several species may be combined successfully in the same regression model, which indicates that, at least in mature stands with fully developed trees, the foliar litter fall is of similar magnitude across species. Still, there are differences between species and between groups of species (softwoods versus hardwoods; pine versus spruce versus fir, etc.). A number of comparisons of litter fall between species have been made using paired stands with identical environmental conditions such as soil properties, climate, water availability, altitude, and aspect.

Table 3 A comparison of the relationship between actual evapotranspiration (AET) and foliar litter fall for Scots pine and Norway spruce separately and litter fall for the two species combined[a]

	R	R^2_{adj}	n
Norway spruce	0.891	0.778	16
Scots pine	0.868	0.746	38
Data combined	0.877	0.766	54

[a]The geographical extension ranged from the Arctic Circle (66°57′N) to the Alps (47– 48°N).

Thus, Berg and Johansson (1994) made such a comparison of Norway spruce and Scots pine in paired stands at eight sites across Sweden and found that Scots pine produced more litter than Norway spruce (measured as "total" litter fall) and that Norway spruce produces more needle litter than Scots pine. Other studies revealed that Norway spruce produced more litter than common beech and lodgepole pine more litter than Scots pine. Still, we have to keep in mind that the litter-fall pattern may vary with stand age. Thus, if one species sheds more litter than another one at a certain age, this difference does not necessarily hold later at a higher stand age. In the examples already given, the litter production was measured over shorter periods, not for whole stand ages.

In a review, Liu *et al.* (2003) compared litter fall in 30-year-old stands of Chinese cork oak and Chinese pine in a temperate forest in China and found an approximately 50% higher litter fall for the former. For the broadleaf species *Castanopsis kawakamii* and quarantine weed, annual litter fall was 13,000 and 7160 kg ha^{-1}, respectively, compared to that of Chinese fir with 4800 kg ha^{-1}, all in paired stands. Thus, the two broadleaf tree species produced more litter than did the coniferous species at the same site. Still, comparisons like these often reflect the conditions for growth for the different species and may depend on factors such as climate and soil fertility. In a critical approach, it would be reasonable to relate litter fall not just to stand age but to a parameter for stand development, for example, basal area.

G. Litter Fall on a Continental to Semiglobal Scale

1. General Patterns and Amounts

At regional to global scales, the variation in litter fall is well explained by climate variables such as actual evapotranspiration (AET), annual average temperature and annual precipitation, or climate-related variables such as latitude. In the global model of Meentemeyer *et al.* (1982), AET was used as a predictive variable for total litter fall, with an R^2 value of 0.77 ($n = 81$) thus "explaining"approximately 77% of the variation in litter fall. In another approach, models were established with latitude alone as the independent variable ($R^2 = 0.35$, $n = 242$), or with both latitude and altitude ($R^2 = 0.63$, $n = 181$) (Lonsdale, 1988). However, as already mentioned, latitude is not a causal variable. Using a considerably larger database and a multiple regression model including both coniferous and broadleaf litter with temperature and precipitation as prediction variables, Liu *et al.* (2003) obtained an R^2_{adj} value of 0.53 ($n = 439$) on a Eurasian basis.

In a study covering Europe and Asia, Liu *et al.* (2003) compared broadleaf and coniferous trees and found that broadleaf forests have a higher average total litter fall than do coniferous ones in five biomes out of six (Table 4). Thus, there is a general tendency to higher average litter fall in broadleaf forests except for the boreal ones, where total litter fall in the coniferous forests was about 15% higher than that of the broadleaf ones (Table 4). In four climatic zones, foliar litter fall was higher in broadleaf than in coniferous forests (Table 4). However, this difference was significant ($p < 0.05$ to $p < 0.01$) only for the Asian and European temperate zones and the Asian subtropical and tropical zones. In warm and wet climates, broadleaf forests tend to have a larger variation in both total litter fall and leaf litter fall than do coniferous ones (Fig. 6).

2. Comparison of the Effects of Temperature and Precipitation

In the largest study yet done on litter fall, Liu *et al.* (2004) evaluated litter fall for over 400 stands in Europe and Asia. In the boreal zone, with low average temperature and low precipitation, they did not find any significant difference between coniferous and broadleaf forests in regard to the amounts of foliar and total litter fall, although the average litter fall was higher in the coniferous forests (Table 4). With increasing temperature and precipitation, the total litter fall in broadleaf forests increases faster than that in coniferous ones and gradually a significant difference develops.

3. Litter Fall in Broadleaf Forests Appears to Increase Even when Annual Average Temperature Approaches 30°C

In a comparison on the effects of temperature and precipitation on total litter fall, Liu *et al.* (2003) found that simple linear relationships provide significant models for total litter fall versus average temperature and annual precipitation. They found that a change in temperature of a standardized unit (see Textbox 2) has a greater impact on total litter fall than a standardized-unit change in precipitation within the observed ranges for the variables, namely, annual average temperature from about −7 to 30°C and, for annual precipitation, from about 350 to 4000 mm. To compare the effects of temperature and precipitation on litter fall, Liu *et al.* (2003) used a logarithmic transformation of data since their data did not have a normal distribution. With temperature as the independent variable, the model for broadleaf litter fall had a significantly higher coefficient for Ln(Temp), showing a faster increase in total litter fall with increasing temperature for broadleaf

Table 4 Annual litter fall, both foliar and "total" litter in coniferous and broadleaf forests in the main climatic zones of Europe and Asia[a]

Forest	Leaf litterfall				Total litter fall			
	Mean value	SE	Range	n	Mean value	SE	Range	n
Boreal forest								
Coniferous	1840	100	320–3300	63	2690	120	580–5080	87
Broadleaf	1930	220	230–3740	17	2260	170	270–5200	28
European temperate forest								
Coniferous	2860[a]	170	1160–4400	26	3470[c]	150	2100–6800	41
Broadleaf	3440[a]	170	2360–5200	20	4420[c]	210	1340–6710	34
European subtropical								
Coniferous	3020	350	1210–5010	11	4090	620	1740–7700	11
Broadleaf	3140	530	800–5300	8	4770	620	2320–6700	8
Asian temperate								
Coniferous	2070[b]	190	790–3340	21	2980[b]	200	910–4990	28
Broadleaf	3320[b]	430	2190–5670	7	4340[b]	440	3000–6670	8
Asian subtropical								
Coniferous	3310[a]	250	940–7040	32	4940	290	1670–9670	32
Broadleaf	4240[a]	210	840–9100	65	5620	300	1010–13,000	69
Asian tropical								
Coniferous	2340[a]	890	1450–3230	2	5010[a]	1350	3000–9000	4
Broadleaf	5400[a]	230	2300–10,750	79	8520[a]	290	3260–15,100	121

[a]Significant differences for pair-wise comparisons between forest types in a climatic zone marked as: *$p < 0.05$.
[b]$p < 0.01$.
[c]$p < 0.001$. From Liu *et al.* (2004).

Textbox 2 Standardized climatic indices

To compare the effects of two variables such as "annual average temperature" and "annual precipitation" on foliar and total litter fall, these may be transformed to standardized units. The standardized temperature and precipitation are dimensionless with a mean of zero and a standard deviation of one. Thus, the values of the coefficients for temperature and precipitation in a multiple regression equation indicate their contributions to the model explaining the variation in foliar and total litterfall in terms of a relative unit change. Most statistical software packages can make such transformations, and some even calculate standardized regression coefficients by default. Using standardized temperature and precipitation in a multiple regression (Table 5) resulted in a significantly larger coefficient (steeper slope) for temperature than for precipitation in the model for total litter fall in broadleaf forests. This indicates that for broadleaf forests, temperature has a stronger effect on total litter fall than precipitation on a relative basis and within the present ranges.

forests than for coniferous forests. This relationship was generally valid over all the biomes (Table 5).

Further, the total litter fall in broadleaf forests tends to decrease at a precipitation above about 2500 mm (Fig. 6). The negative effect of high precipitation on litter production is possibly due to a higher number of cloudy days and lower solar radiation, which can reduce tree photosynthesis and result in lower productivity and litter fall. For the relationships between leaf litter fall and climatic factors, the pattern was generally similar to that of total litter fall.

V. THE FIBER STRUCTURE AND ORGANIC–CHEMICAL COMPONENTS OF PLANT LITTER

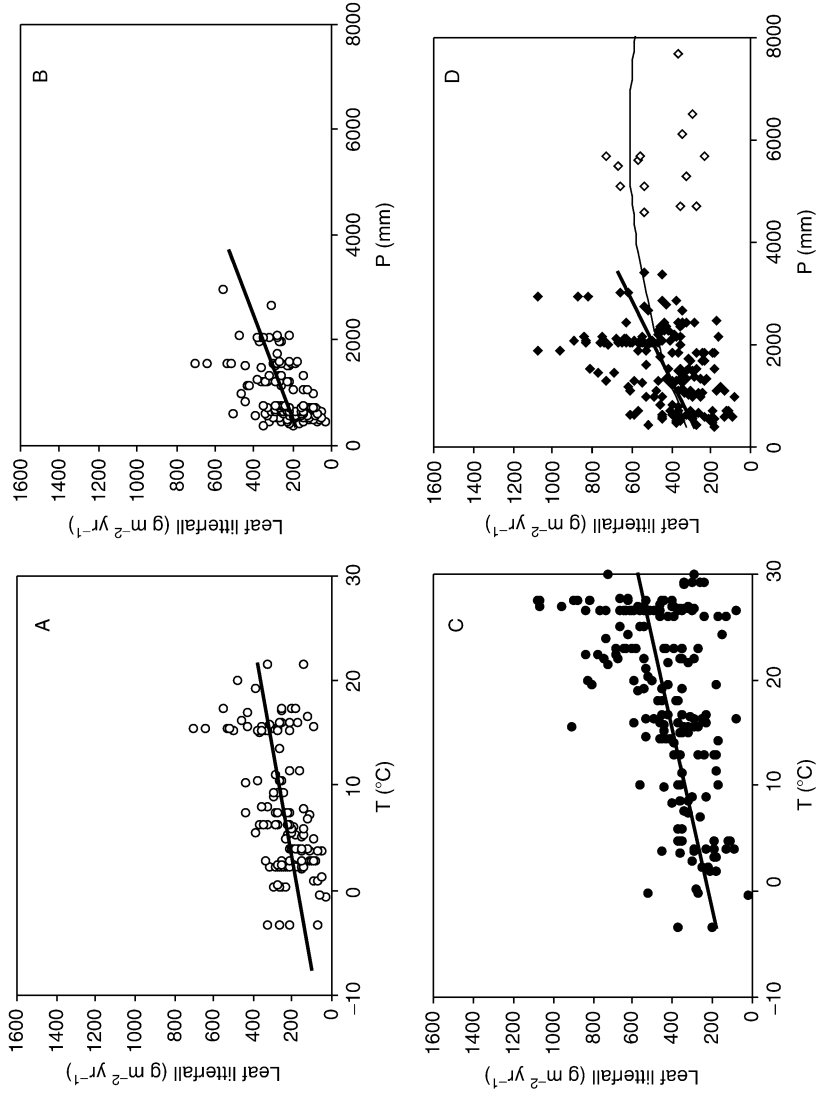
A. The Fiber

In the plant fibers, the cellulose, the hemicellulose (together called holocellulose), and the lignin molecule are not only combined physically but normally more or less encrusted. The formation of lignin in the fibers (lignification) of the live plant is a slower process than the formation of cellulose and hemicelluloses and the result is that the last formed parts of the fiber structure may be very low in lignin or not lignified at all and the older parts richer, thus causing a lignin "cover" for part of the holocelluloses.

Table 5 Multiple linear regressions relating the logarithms for total litter fall ln(ltotal) to standardized ln(temp) and ln(precip)[a]

Forest type	Constant		ln(Temp)		ln(Precip)		n	R^2_{adj}
	Intercept	p	Slope	p	Slope	p		
Broadleaf	6.3	<0.001	0.298	<0.001	0.11	<0.005	240	0.498
Coniferous	5.71	<0.001	0.169	<0.001	0.116	<0.002	199	0.272
Broadleaf and coniferous	6.032	<0.001	0.331	<0.001	0.13	<0.001	439	0.535

[a]The litter fall data originating from Europe and Asia covered the latitudes from ca. 7°S to 69°N, a temperature range from ca. −7°C to 30°C, and a precipitation range from approximately 350 to 10,400 mm. Intercepts between broadleaf and coniferous litter fall were significantly different, as were the coefficients for temperature between broadleaf and coniferous litter fall. Data from Liu *et al.* (2004).


A
B
C
D
Leaf litterfall (g m⁻² yr⁻¹)
T (°C)
P (mm)
0
200
400
600
800
1000
1200
1400
1600
−10
0
10
20
30
2000
4000
6000
8000

The wood cell is composed of various layers (Fig. 7) of cells combined into tissue. In the wood cell, the middle lamella and the primary wall make up the compound middle lamella, which is located between the secondary walls of adjacent cells (Core *et al.*, 1979). The cell wall is made up of a primary wall (P) and a secondary wall (S), which has three layers designated S1, S2, and S3 (Fig. 7). The S3 layer is located closest to the lumen (L). Normally, the thickest layer is the middle layer (S2), and S1 is the outermost layer of the secondary wall. These layers are distinct from each other because the cellulose occurs in different microfibrillar orientations.

In the wood, lignin is distributed throughout the secondary (S) wall and the compound middle lamella, with the highest concentration in the middle lamella. The secondary wall makes up a large part of the total cell wall area and most of the cell wall lignin (60–80%) is located in this region (Saka and Thomas, 1982a,b). The hemicelluloses are distributed parallel to the lignin within the wall (Parameswaran and Liese, 1982) and surround the cellulose microfibrils, which, in their turn, occupy spaces between the fibrils. Within the cell wall, cellulose forms microfibrils, which are organized into bigger fibrils.

There is a tremendous diversity in wood structure among tree species that grow in the boreal and temperate zones of the world (Panshin and de Zeeuw, 1980) and the example of a wood cell given in Fig. 7 is thus not general. Still, our purpose is to give an overview of the environment for the microbial decomposers.

B. The Organic–Chemical Components

Together with lignin, which is a complex polymer formed mainly by aromatic rings, the polymer carbohydrates form the plant fiber structures. The most common organic components in plant litter are such polymer carbohydrates as cellulose and hemicelluloses. The quantitatively most common among them, the cellulose, is made up of glucose units connected 1–4 bonds, forming long straight chains of molecules (Fig. 8) with the chains, in their turn, organized into fibers. Cellulose may constitute between 20 and 30% of the litter mass (Table 6).

Figure 6 Variation of foliar litter fall with mean annual temperature (°C) and annual precipitation (mm) in coniferous (A, B) and broadleaf forests (C, D). For precipitation (D) leaf litter fall in broadleaf forests had a non-linear relationship when including all data. However, when stands with precipitation >4000 mm were excluded, a linear relationship held on (from Liu *et al.*, 2004).

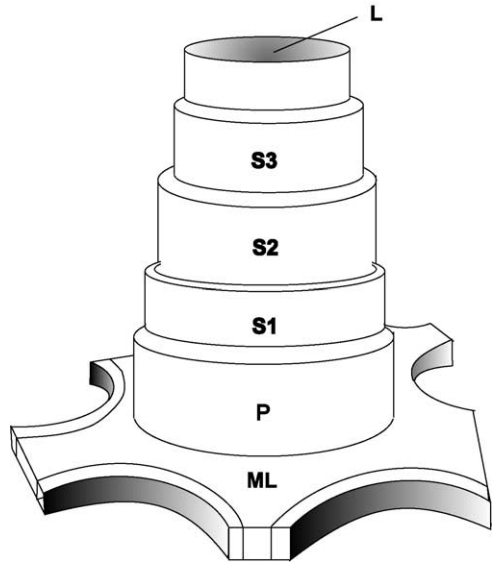


Figure 7 A model for a cell wall and the arrangement of cellulose, hemicelluloses, and lignin in the secondary wall. ML, middle lamella; P, primary wall; S1, S2, and S3, layers of the secondary wall; L, lumen. Each layer has a different microfibrillar orientation and thickness. Based on Eriksson *et al.* (1990).

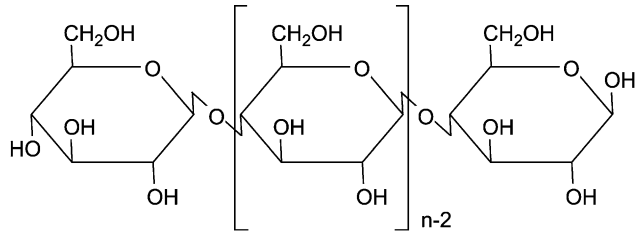


Figure 8 The cellulose made of glucose units form long chains of *n* identical molecules. Carbon atom numbers 1 and 4 are connected with an oxygen bridge giving a 1 to 4 bond.

The hemicelluloses are polymers of sugars other than glucose which form long chains of molecules, which are built into the fiber with names related to the corresponding simple sugars, namely mannan, galactan, arabinan, xylan, and others. Together, they may make up as much as 30 to 40% of the fiber, and are normally present in the range between 1 and 10% each (Table 6). It appears that the molecules of the different sugars are mixed and thus the chains are not always homogeneous. The chains may also be branched.

Lignin often makes up between 15 and 40% of the litter mass, but, in some extreme cases, we may find foliar litter with very low lignin contents (e.g., 4%

Table 6 Comparison of the major organic–chemical compounds in a few boreal litter types[a]

Litter type	Concentration of compound (mg g^{-1})									Ratio hemicellulose to cellulose
	Water soluble	Ethanol soluble	Lignin	Cellulose	Mannans	Xylans	Galactans	Arabinans	Rhamnans	
Deciduous										
Leaf litter										
Silver birch	241	57	330	166	14	77	44	49	16	1.2
Grey alder	254	39	264	116	10	30	32	44	9	1.08
Wood										
Silver birch			217	351	9	207				
Trembling aspen			220	462	16	189				
Red alder			246	470	4	176				
Coniferous										
Needle litter										
Scots pine	164	113	231	245	75	23	32	36	3	0.69
Lodgepole pine	103	42	381	254	90	34	46	48	6	0.88
Norway spruce	32	48	318	288	105	33	28	40	7	0.74
Wood										
Scots pine			300	383	111	65				
Red pine			279	449	123	84				
Norway spruce			271	416	136	52				

[a]Foliar litter data from Berg and Ekbohm (1991), wood data from Eriksson *et al.* (1990).

in leaf litter of flowering dogwood) and values as high as 50% have been recorded for leaves of common beech from temperate forests. The structure of lignin molecules varies among plant species, and one example is illustrated in Fig. 9. Even if some basic structural elements are common across species, probably each plant species has its own variety of lignin, with varying amounts of smaller groups, such as the methoxyl groups and other substituents (Fig. 9), located at different sites in the molecule.

The terminology pertaining to lignin and its transformation products is not always clear. Different analytical methods may produce different results. The name of the analytical method is important since it specifies more exactly what "kind" of lignin was analyzed. Furthermore, the native lignin of different species may be specified by the name of the plant species, for example, Norway spruce lignin. Another complicating factor is that when the lignin molecules start decomposing, the structure changes and the term "lignin" has been questioned for such modified lignin (see Textbox 3).

The lignin content of hardwoods is generally lower than that of softwoods, although the range is wide in both groups. Generally, the types of lignin formed in coniferous trees and in deciduous trees are different. Whereas the deciduous lignin contains varying ratios of syringyl and guaiacyl units (Fig. 10), the coniferous ones have mainly guaiacyl lignin (Fengel and Wegener, 1983). These components, being important building units, have properties that affect the basic structure of lignin, which may be of importance for the microbial attack on lignin and thus on the litter as a whole (see Chapter 3).

Litter contains quantitatively large groups of more low-molecular substances too, such as amino acids, simple sugars, lower fatty acids, and lower phenolic substances. More complex compounds, such as high-molecular fatty acids and phenolic compounds, are also found and probably some hundred different molecules can be distinguished within these groups. Often, they are analyzed as water-solubles for the former group and ethanol or acetone solubles for the latter. Although many of these have been identified and described, no clear functional roles can be seen for particular compounds in the decomposition process. One notable exception is the large group of phenolics of different kinds (for example, benzoic acid) which suppress microbial activity.

VI. NUTRIENTS

A. General Features

The chemical composition of live leaves and needles is also reflected in the litter formed. This applies to several compounds, such as the relative composition of hemicelluloses, cellulose, and lignin, as well as to chemical

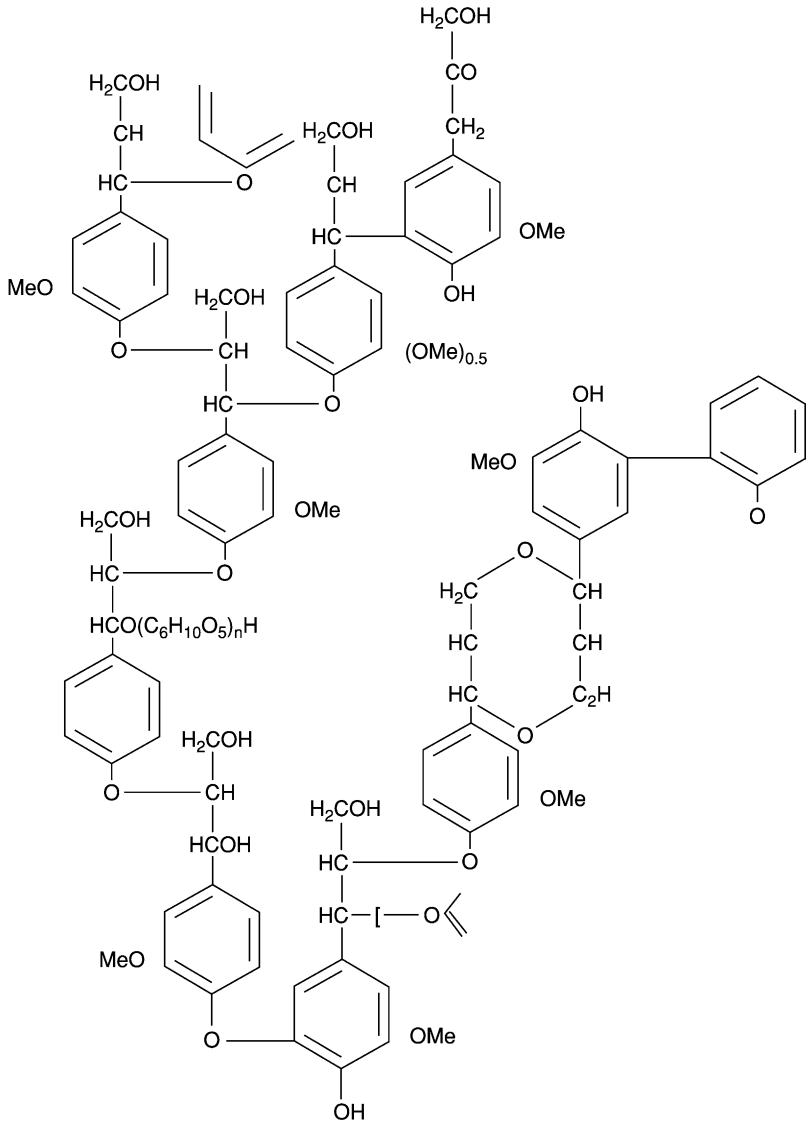


Figure 9 Lignin molecule from Norway spruce.

elements. The nutrients found in newly shed plant litter have their origin in the strictly controlled structures of live plant parts, and a nutrient such as nitrogen could be found, for example, in membranes, nucleic acids, and proteins. When a leaf starts dying and turns into litter, these structures

Textbox 3 Different lignin names and the terminology of lignins

Lignin is rather a group of compounds than a single specific one. The methods to determine lignins as a group of compounds are numerous. Most of these methods have been intended to determine lignin in fresh plant matter (e.g. newly harvested wood or fresh fodder). That was the original intention, and there are several gravimetric methods that are based on hydrolysis of the polymer carbohydrates, normally with sulfuric acid. Some examples are sulfuric-acid lignin (Klason lignin), Effland lignin or acid-detergent lignin, often called ADL. There are also other methods, such as milled wood lignin based on, among others, numerous extractions with dioxan. Further methods based on extensive oxidation, using for example CuO, hydrolyze the lignin further to more basic units. However, we have to keep in mind that the gravimetric lignin may also contain ''ash'', which can consist of, for example, silicates that are not hydrolyzed in the sulfuric acid and whose contents increases during decomposition.

The authors have compared some of the gravimetric methods using the same substrate—Scots pine needle litter—and found about the same lignin concentration for Klason lignin, Effland lignin, ADL, and milled-wood lignin. Thus these methods were rather compatible.

If we apply these methods to newly shed litter the term *lignin* is correct. Considering the number of methods it may be better, though, to use the method's name (e.g. Effland lignin or Klason lignin). For the ''lignin'' in partly decomposed litter we do not have any generally accepted terminology and it appears that when we use the gravimetric methods more compounds than native (original) lignin are included in the fraction determined that way. Of course the ''ash'' fraction mentioned above can increase in concentration, but also products of the humification process may be included, and the concentration of N increases in the gravimetric lignins as the decomposition process proceeds. So far determination of this combined fraction of lignin plus humification products has been useful in decomposition studies, in spite of the fact that the terminology is controversial. We have suggested as a provisional term ''the NIT–Lignin complex'' for this fraction in decomposing litter, a term that indicates the inclusion of newly formed humic substances.

break up, at least in part, and some part of each nutrient is retrieved to the live plant while another part remains in the newly dead material. What is often measured as just a mineral nutrient, say, nitrogen, is thus bound in different chemical structures in the litter, such as partly decomposed proteins and nucleic acids. In part, it becomes tied to lignin, which has started to be modified as the humification process has begun. Thus, it is found in compounds with different properties. In foliar litter, nitrogen can be found in

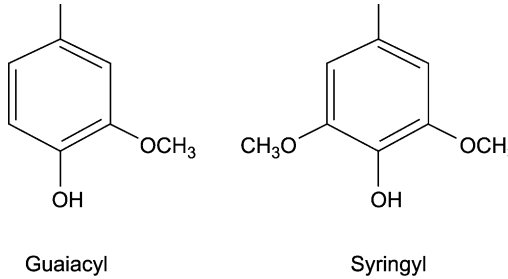


Figure 10 Guaiacyl and syringyl, the important structural units of lignin.

amounts between around 2 and 30 mg g^{-1} (Table 7). In woody structures, such as that in branches, the concentration may be as low as 0.4 mg g^{-1} (Table 8). Phosphorus is bound in nucleic acids, and sulfur is found in proteins, among other molecules (for phosphorus and sulfur see, for example, Stevenson, 1994).

When the microbial ingrowth and the decomposition have started, the distribution of nutrients in different compounds as well as their concentrations will be very different from that of the original material. In this chapter, we will not discuss the nutrients in the form of their structural origin but rather as just chemical elements.

B. The Trees Withdraw Nutrients before Shedding their Foliar Litter

Many genera, such as pine, growing on relatively nutrient-poor soils, which, in addition, often are drained from nutrients by repeated wildfires, retrieve the main part of nutrients before shedding the foliar litter. This ''inner circulation'' is a conserving mechanism for nutrients. This withdrawal differs among nutrients as well as among species. Extreme examples are the N_2-fixing genera such as alder and locust producing leaf litter that has as high a concentration of nitrogen as the live leaves.

In the case of Scots pine, silver birch, and trembling aspen, the concentration of N may decrease to about one-third of that in live leaves when the leaves and needles are shed in the autumn. For example, for Scots pine, the concentration may decrease from about 12 to 14 mg g^{-1} to about 3 to 4 mg g^{-1} (Table 9; Fig. 11). This retrieval process may, of course, be disturbed, possibly by an early frost, which occasionally would give extreme levels of

Table 7 Concentrations of some major nutrients, ash, and lignin in some selected boreal and temperate foliar litter species

Litter type	Concentration of nutrient (mg g^{-1})									Reference
	N	P	S	K	Ca	Mg	Mn	Ash	Lignin	
Deciduous leaf litter										
Grey alder	30.7	1.37	6.12	15.6	12.3	2.32	0.1	42.4	–	(1)
Silver birch	7.7	1.05	0.8	4.66	11.8	3.3	1.23	22.4	294	(2)
Ash	8.63	1.96	–	15.3	33.2	2.28	0.03	12.2	–	
Mountain ash	7.12	0.31	–	10.8	12.4	2.86	0.3	5.5	–	
Trembling aspen	8.15	0.93	–	5.09	29.9	4.69	0.53	9.3	–	(3)
European maple	5.07	3.15	–	13.1	20.4	1.46	0.12	11.9	–	(5)
Common beech	9.5	1.4	1.3	2.3	7.4	1.2	1.9	n.d.	–	(4)
Coniferous needle litter										
Spruce										
Norway spruce	4.9	0.45	0.73	0.72	17.9	0.65	–	–	–	(6)
Pines										
Scots pine	4.8	0.33	0.55	1.07	4.42	0.49	0.79	10.5	261	(2)
Lodgepole pine	3.9	0.34	0.62	0.56	6.35	0.95	1.79	13.6	–	(2)
Maritime pine	6.8	0.54	1.01	1.95	3.1	1.9	0.59	22	–	(4)
Red pine	6	0.36	0.73	1.4	8.9	2	0.73	36	–	(4)
White pine	5.9	0.21	0.68	0.7	7.2	1.1	0.8	28	–	(4)
Jack pine	7.8	0.64	0.77	2.3	4	2.1	0.25	23	–	(4)
Limber pine	4.3	0.43	0.52	1.1	5.3	1.1	0.21	24	–	(4)

(1) Berg and Ekbohm (1991), (2) Reurslag and Berg (1993), (3) Berg *et al.* (2003), (4) B. Berg and C. McClaugherty (unpublished), (5) Bogatyrev *et al.* (1983), (6) Berg and Tamm (1991).

Table 8 Concentrations of nitrogen, water soluble compounds, and sulfuric-acid lignin in wood from some tree species[a]

Species	Concentration (mg g^{-1})		
	N	Water solubles	Lignin
Norway spruce	0.39	37	271
Common beech	0.92	35	228
Silver birch	0.64	26	195
Trembling aspen	0.55	39	197

[a]Data in part from Staaf and Berg (1989) and Eriksson *et al.* (1991).

N (Table 10). Norway spruce appears to differ from the Scots pine with N concentrations often decreasing to about 50% of that in live needles.

The range in concentrations of remaining P is wider than for N, from 15 to 50%, and in the case of S, the concentration in litter is approximately 38 to 73% of that in the original green needles. For K, there is a difference between coniferous and deciduous trees, with the latter having clearly higher proportions of original contents when shed, that is, concentrations have decreased to a range of 40 to 50% as compared to less than 25% on average for the spruce group, and for pines even less.

Trees not only withdraw part of the nutrients before shedding leaves. At the same time, different soluble carbon components, such as sugars and phenolics, are withdrawn. As a result, the total leaf mass decreases, and as a consequence, the basis for calculation of concentrations changes. This may result in an increase in concentration for those nutrients that are withdrawn only to a low extent (e.g., Ca) and a decrease for those that have been withdrawn to a higher extent. There may also be an influence of soil type, and low pH has been found to have a negative effect on Ca withdrawal. Thus, at sites with a lower soil pH, there is a lower withdrawal, an effect seen only for Ca though (Staaf, 1982).

A study on leaves of common beech (Staaf, 1982) indicates that the withdrawal of nutrients is positively related to the concentration of the element in green leaves (Fig. 12). This relationship was especially steep for N (Fig. 12A), indicating a high withdrawal, while for Ca, the relationship was rather flat (Fig. 12E), indicating lower withdrawal. Thus, calcium was retrieved in relatively small amounts and the net result was an increase in concentration in all cases (to 115–220% of the initial concentration). In the same study, magnesium concentrations ranged from 43 to 113% of the initial concentrations, indicating a high variability in relative withdrawal (Fig. 12F).

The few data on heavy metals indicate that their concentrations increase in senescing leaves before these are shed. Storage of metals in senescent tissues is

Table 9 Concentrations of some nutrients and heavy metals in green leaves collected in July and the corresponding "brown" litter shed some months later (B. Berg, unpublished)[a]

Litter species (type) and % change in concentration from green to brown leaves	Concentration of a nutrient									
	mg g^{-1}							mg kg^{-1}		
	N	P	S	K	Ca	Mg	Mn	Fe	Zn	Cd
Scots pine (green)	12.1	1.36	0.809	5.9	3.9	0.79	0.53	64	49.4	0.1
Scots pine (brown)	3.6	0.2	0.444	0.5	5.6	0.34	1.19	79	48.3	0.1
Concentration change (%)	−70	−85	−45	−92	+44	−57	+125	+23	−2	0
Lodgepole pine (green)	10.5	0.82	1.17	3.84	3.99	0.93	0.82	–	–	–
Lodgepole pine (brown)	3.1	0.29	0.441	0.5	8.7	1.06	2.03	–	–	–
Concentration change (%)	−70	−65	−62	−87	+118	+14	+148	–	–	–
Norway spruce (green)	8.5	1.32	–	4.01	11.3	1.22	1.07	–	–	–
Norway spruce (brown)	4.2	0.41	–	0.97	13.1	0.89	1.32	–	–	–
Concentration change (%)	−51	−69	–	−76	+16	−27	+23	–	–	–
Silver birch (green)	24.3	1.96	1.535	9	9.5	3.37	0.76	53	140	0.2
Silver birch (brown)	7.7	1.05	0.8	4.66	11.8	3.3	1.23	61	340	0.8
Concentration change (%)	−68	−46	−48	−48	+24	−2	+62	+15	+143	+300
Trembling aspen (green)	24.2	2.12	1.87	14.2	8.4	2.29	0.1	44	107.1	0.3
Trembling aspen (brown)	6.8	0.63	1.369	6.3	17.1	2.13	0.15	46.4	126.1	0.5
Concentration change (%)	−72	−70	−27	−56	+104	−7	+50	+5	+18	+67
Common beech (green)	22.6	1.44	1.18	5.42	7.7	1.67	–	–	–	–
Common beech (brown)	9.1	0.63	1.21	2.7	10	1.7	–	–	–	–
Concentration change (%)[b]	−60	−56	+3	−50	30	+2	–	–	–	–

[a]The difference between green and brown leaves in their chemical composition is also reported as the percentage concentration change.
[b]Data for common beech from Staaf (1982).

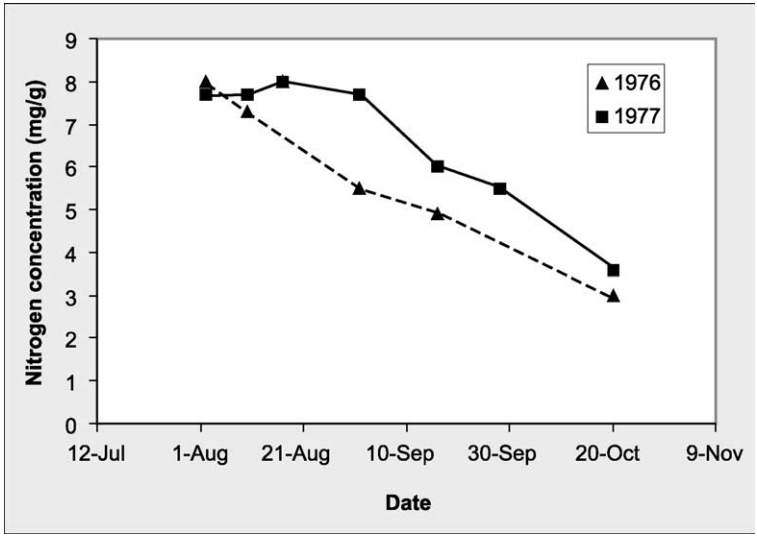


Figure 11 The withdrawal of nutrients for the major nutrients normally results in a decrease in concentration. The figure shows the change in concentration of N in Scots pine needles during the months before shedding.

interpreted sometimes as a "detoxification mechanism" (Ernst, 1998). For example, Dahmani-Muller *et al.* (2000) found that Zn, Cd, Pb, and Cu concentrations in brown leaves of Sea Pink growing near a former metal smelter were 3 to 8 times higher than those in green leaves.

C. Scots Pine—A Case Study

1. Annual Variation in Chemical Composition at One Site

Even in a given stand, there is a clear variation in the chemical composition of the newly shed needle litter among years. This is illustrated in an investigation in which some nutrients in Scots pine needle litter were followed for 17 consecutive years (Table 10). A clear difference may be seen among years, but still no pattern in the variation in concentrations could be distinguished. A trend analysis did not reveal any significant change in nutrient concentrations over time.

At the site of our case study, the average concentration for nitrogen in needle litter was 4.2 mg g^{-1}, varying between years from 3.8 mg g^{-1} up to an exceptionally high value of 10.4 mg g^{-1} (Table 10). Compared with other years, such a value is disproportionately high also in relation to concentrations of other elements, such as phosphorus and sulfur, in the same year. The

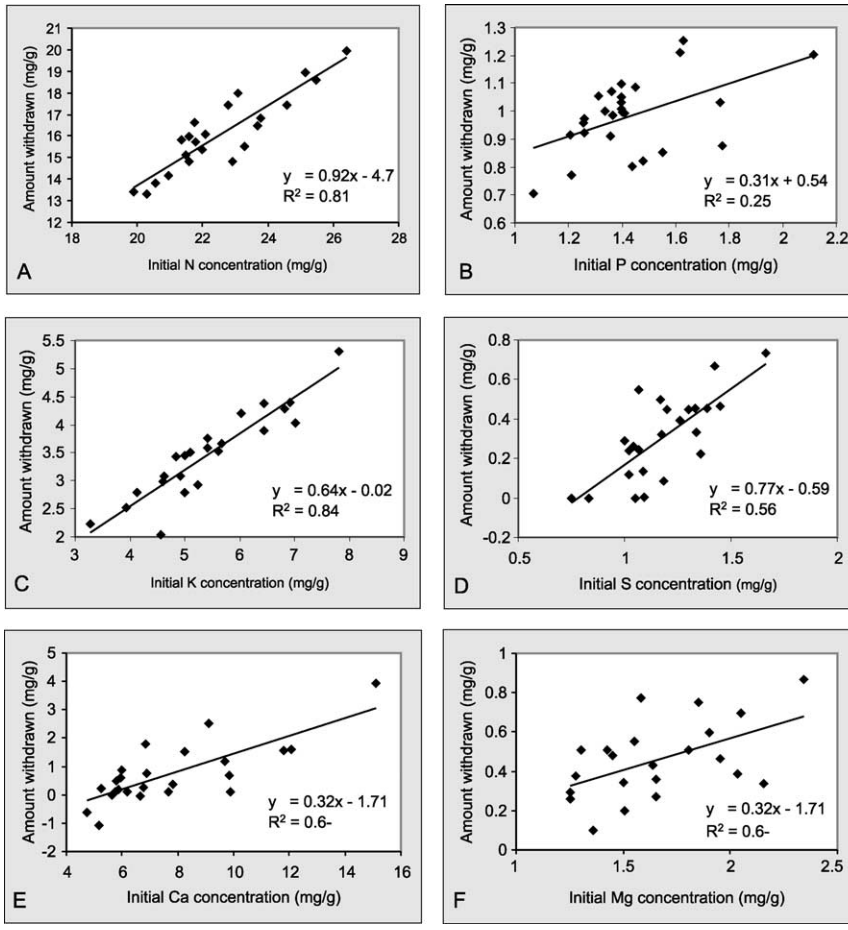


Figure 12 The linear relationships between concentrations of nutrients (N, P, K, S, Ca, and Mg) in green leaves of common beech and the amount of nutrients withdrawn from the leaves during senescence. Each dot represents a sampling in a separate forest (from Staaf, 1982).

frequency of occurrence of such high values has not been established and may be regarded as a consequence of an unknown extreme event. Even excluding that extreme value, with the next highest value being 4.8 mg g^{-1}, there is still a considerable year-to-year variation (a range factor of 1.3) in nitrogen concentration. The reason for this variation is not yet known.

The concentration of phosphorus varied between 0.17 and 0.33 mg g^{-1}, with a factor of 2.5. For sulfur, the range was from 0.29 to 0.78 mg g^{-1}, also with a factor of 2.5. Within the same site, the annual variation for calcium

Table 10 Annual variation in concentrations of solubles, lignin, and nutrients of Scots pine needle litter (in part, from Berg *et al.*, 1993)[a]

	Concentration (mg g^{-1})											
Sampling year	Water solubles	Ethanol solubles	Lignin	N	P	S	Ca	K	Mg	Mn	Ash	N:P:S
1973	92	120	223	3.8	0.19	0.42	6.5	0.73	0.38	1.55	23	1:0.050:0.111
1974	145	84	276	4.2	0.22	0.29	5.4	0.71	0.49	n.d.	24	1:0.052:0.069
1975	172	107	238	3.4	0.2	0.32	4.7	0.61	0.39	n.d.	19	1:0.048:0.094
1976	151	89	255	4	0.21	0.36	4.9	0.53	0.42	n.d.	n.d.	1:0.053:0.090
1977	202	102	224	4.1	0.19	0.38	6	0.87	0.42	1.02	n.d.	1:0.046:0.093
1978	164	96	257	3.8	0.21	0.33	5.5	0.62	0.55	1	20	1:0.055:0.087
1979	129	95	288	10.4	0.29	0.78	2.3	0.97	0.39	0.31	12	1:0.028:0.078
1980	180	102	246	3.8	0.18	0.5	6.1	1.72	0.53	0.77	17	1:0.047:0.132
1981	213	94	231	3.9	0.28	0.61	7.1	1.02	0.58	1.17	23	1:0.072:0.152
1982	164	113	231	4.8	0.33	0.55	4.4	1.07	0.49	0.79	19	1:0.069:0.115
1983	178	112	229	3.8	0.3	0.45	5.9	0.9	0.39	1.08	26	1:0.079:0.118
1984	82	116	288	3.7	0.21	0.47	6.3	0.82	0.44	1.12	22	1:0.057:0.127
1985	182	94	241	3	0.19	0.45	4.8	0.52	0.38	1.24	18	1:0.063:0.150
1986	170	89	257	4	0.23	0.44	5.6	0.58	0.57	1.13	20	1:0.058:0.110
1987	162	100	250	3.8	0.21	0.42	4.9	0.55	0.41	1.18	18	1:0.055:0.111
1988	165	94	247	3.8	0.21	0.39	5	0.67	0.38	1.18	19	1:0.055:0.106
1989	n.d.	n.d.	n.d.	3.6	0.17	0.38	4	0.59	0.42	0.92	n.d.	1:0.047:0.106
Mean:	159	100	249	4.2	0.23	0.44	5.3	0.79	0.45	1.03	20	1:0.055:0.105
S.D.:	35	11	21	1.6	0.05	0.12	1.1	0.29	0.07	0.27	3.5	

[a]The data show a certain interannual variation. A value for N as high as 10.4 mg g^{-1} probably should be regarded as caused by an event disturbing the retrieval process.

concentrations ranged from 2.3 to 7.1 mg g^{-1}, with a factor of 3.1, a relatively large variation, considering several investigations indicating that Ca concentration in leaves is strongly dependent on soil properties. For potassium, the mean value was 0.79 mg g^{-1} and the range from 0.52 to 1.72 mg g^{-1}, giving a factor of 3. For magnesium, the mean was 0.45 mg g^{-1}, and the range from 0.38 to 0.58 mg g^{-1}—a factor of 1.5. The highest variability, with a factor of 5, was found for manganese: the mean value was 1.03 mg g^{-1} and the range was from 0.31 to 1.55 mg g^{-1}.

The concentrations of the main nutrients, N, P, and S, were in the average proportions of 1:0.055:0.105. As we will see later, especially N and P have been ascribed the role of being rate limiting for decomposition (Chapter 4). When we relate both P and S to N, the relative proportions are seen to vary considerably—for P from 0.028 to 0.079 and for S from 0.069 to 0.156 (Table 10). This variation in relative proportions between years may decide which nutrient is rate regulating in a particular year (see Chapter 4).

Ash content in the collections of Scots pine needle litter, with an average of 20 mg g^{-1}, was relatively low as compared with those of other tree species (Bogatyrev *et al.*, 1983). Concentrations of water-soluble substances ranged from 82 to 213 mg g^{-1}, with the average value of 159 mg g^{-1}, and lignin concentrations ranged from 223 to 288 mg g^{-1} with an average value of 249 mg g^{-1}, a range factor of about 1.2.

2. *Variation among Scots Pine Stands and in a Transect of Forests*

In Europe, Scots pine grows mainly from Barents Sea in the north to the Mediterranean in the south, although it forms forests to about the latitude of the Alps and the Carpathians. Scots pine may grow on nutrient-poor granite sand and on clayey soil. On a European scale, the magnitude and pattern of litter fall varies with the geographical position and climate (see Section IV.C.). The chemical composition of foliar litter varies also with the site's geographical position and climate (Berg *et al.*, 1995a). A study along a transect ranging from Barents Sea in the north to about the Carpathian Mountains in the south, encompassing half the length of Europe, shows a clear trend in chemical composition with climate (Fig. 13). Along this climatic gradient, concentrations of nitrogen, phosphorus, sulfur, and potassium are positively related to AET. This behavior appears to be general over the genus *Pinus* and has been found also when different pine species were combined in a regression. Nitrogen levels range from about 3 mg g^{-1} close to Barents Sea to about 9 mg g^{-1} at the more southern locations (Fig. 13). In contrast, for manganese, a weak relationship is negative, meaning that the highest manganese concentrations were found at low AET values in the north, and the lowest at the southern sites with high AET. Whereas there may be an

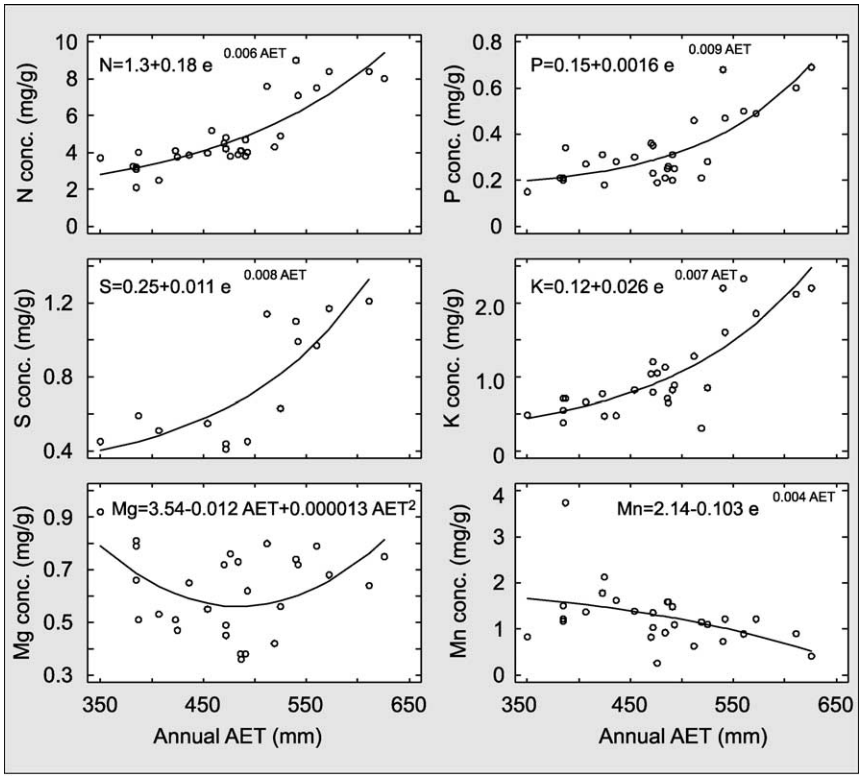


Figure 13 Relationships between actual evapotranspiration (AET) and concentrations of N, P, S, K, Mg, and Mn in newly shed Scots pine needle litter collected in a transect from Barents Sea to the Alps and the Carpathians in the south (from Berg *et al.*, 1995).

explanation related to climate for nitrogen and, consequently, also for phosphorus and sulfur, an explanation related to manganese may be less evident and possibly AET is just an indirect index. The warmer sites with higher precipitation, having higher AET values, thus produced litter rich in nitrogen, phosphorus, sulfur, and potassium and poor in manganese.

These increases in concentrations of N, P, S, and K in litter with increasing AET and decreasing latitude may very well reflect a direct or an indirect effect of climate on litter quality. Direct effects may be related to differences in physiological requirements for these nutrients in live leaves and possibilities of allocating them in larger quantities due to, for example, warmer and wetter growing seasons in the southern end of the Scots pine area.

Calcium and magnesium did not exhibit any correlation with latitude or with other nutrients within Scots pine. The lack of any relationship for calcium and magnesium to AET indicates that factors other than climate

affect the concentrations of these constituents. Concentrations of magnesium and calcium, in contrast to those of nitrogen, phosphorus, sulfur, and potassium, depend more on site-specific factors, mainly, the bedrock type.

The concentrations of major nutrients in fresh litter fall (nitrogen, phosphorus, sulfur, and potassium) were highly intercorrelated, which can be attributed to their property of being main constituents of proteins and nucleic acids, etc. (see previous text).

D. Foliar Litter N Concentration in a Trans-European Transect, Several Species

In a trans-European study Berg and Meentemeyer (2001) compared all data for N concentration in foliar litter against the climatic index AET. First they compared N concentration in pine needle litter using available data for Scots pine, lodgepole pine, stone pine, maritime pine, Corsican pine, and Monterey pine with average annual AET resulting in a highly significant linear relationship ($R^2_{adj} = 0.536$; $n = 40$). In this data set there was no relationship with latitude. To avoid areas with N deposition they selected sites with clearly very low or no N deposition, namely forest stands in northern Scandinavia and stands in coastal areas on the Iberian peninsula, still sites with varying AET values and found that litter N concentration still was related to AET ($R^2_{adj} = 0.749$: $n = 19$).

In another step they compared all available data for coniferous foliar litter for Europe to AET and with 60 data sets they obtained a highly significant relationship with $R^2_{adj} = 0.370$. In addition to the above pine species this data set included Norway spruce, Sitka spruce, silver fir, grand fir, and Douglas fir. Adding available data for deciduous foliar litter did not change the relationship ($R^2_{adj} = 0.344$; $n = 68$; Fig. 14) and the data for deciduous litter alone formed a significant relationship ($R^2_{adj} = 0.800$; $n = 8$) between N and AET although based on a small number of samples.

It thus appears that there may be a certain generality to the relationship between climate and litter N concentration at least for the boreal, temperate and Mediterranean climatic zones.

E. Several Deciduous and Coniferous Leaf Litters

1. Nutrients in Litter Fall—Similarities and Differences among Species

To make a thorough overview of the chemical composition of the most common litter types in a given ecosystem is not yet possible due to the lack of basic information. We may distinguish some main patterns,

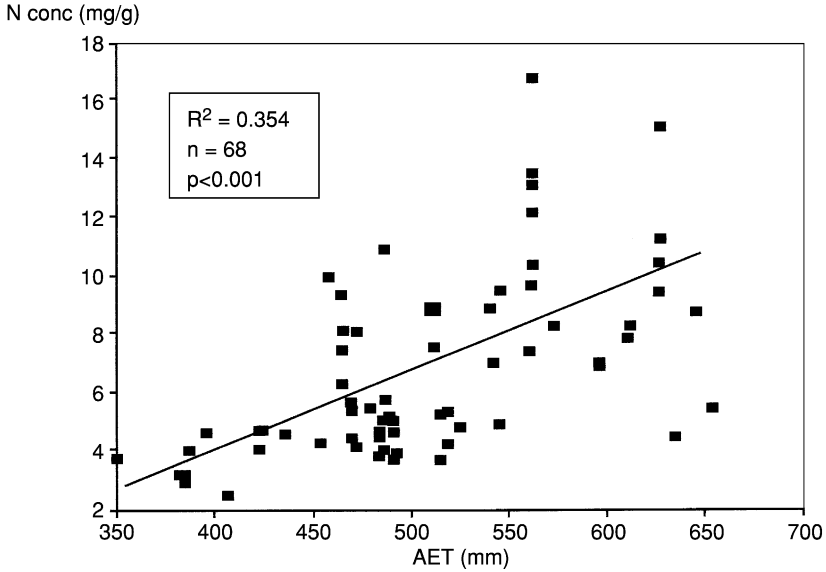


Figure 14 A linear relationship between climate as indexed by actual evapotranspiration (AET) and N concentration in foliar litter. All available data on coniferous and deciduous litter across Europe from Barents Sea to the Mediterranean area were used. Included in the data set is foliar litter from Scots pine, lodgepole pine, maritime pine, stone pine, Monterey pine, Norway spruce, Sitka spruce, silver fir, grand fir, Douglas fir as well as leaf litter of common beech, and silver birch. From Berg and Meentemeyer (2001).

though, which we may relate to tree genera/species and their nutritional patterns.

Litter chemical composition may be related to a few factors such as soil nutrient supply, climate, and tree species, and a set of data covering some north European tree species will illustrate some basic differences. Although there are general differences between the groups of deciduous and coniferous trees (Table 7), one difference being the contents of hemicelluloses and lignin (Table 6), there are also clear differences among species within each of these main groups.

Average values from a large set of data for some major boreal tree species indicate a clear tendency in nutrient richness among genera/species. Generally, leaves of silver birch are more nutrient-rich than those of common beech, followed by those of Norway spruce. The most nutrient-poor are Scots pine needles (Table 7), which are close to those of lodgepole pine. This picture applies to most of the measured nutrients (N, Mg, K, Mn). Regarding nitrogen, birch and beech leaf litter have similar levels, and for phosphorus, spruce and beech have similar levels. This set of data originates from stands

growing on soils and at climates representative for the species but is confirmed by pair-wise comparisons made on the same soil and climate where needles of Scots pine generally were more nutrient poor than those of Norway spruce and a tendency was seen for spruce needles to be less nutrient rich than leaf litter from silver birch. That means that, aside from differences in foliar nutrient concentrations that are caused by climatic or site-specific factors, clear between-species differences also exist. The results demonstrate the inherent tendency of some species to produce more nutrient-rich litters than others, even under identical edaphic and climatic conditions.

The coniferous foliar litter, on the whole, appears poorer in nutrients such as N, P, Ca, and K than do the deciduous litters (see Table 7). The coniferous litter species, in general, had nitrogen levels under 7 mg g^{-1}, whereas the deciduous levels were higher and the groups differed in phosphorus levels by a factor of at least 3. Calcium concentration was exceptionally low in pine needles, and Norway spruce had a higher value, whereas the deciduous trees had concentrations that, in general, were at least 5 to 6 times higher than the average for coniferous litter. In contrast, concentrations of magnesium and manganese were more similar in coniferous and deciduous foliar litter. There was even a tendency for Mn to be lower in the deciduous leaves as compared to pine needle litter.

2. Chemical Composition across Climatic Transects

Not only Scots pine appears to exhibit variation in litter chemical composition with climate. For other pine species, available data for nitrogen in foliar litter indicate that they follow the same pattern as Scots pine and all available data for AET and foliar litter including pine, spruce, and deciduous trees manifest the same pattern. Thus, the finding that N concentration in litter fall can be related to climate has a higher generality (Fig. 13). In that comparison, N_2-fixing species were excluded. For Mn, there was a general negative relationship to AET, also similar to Scots pine. However, no such general relationships have yet been found for other nutrients, such as P, S, and K.

3. Chemical Composition as Influenced by Soil Properties

The influence of soil chemical composition and nutrient availability on litter chemical composition is well illustrated by a study on common beech leaves in 24 stands in a climatologically homogeneous area. Ten plots with mull soils had significantly higher humus pH, and the shed litter had higher concentrations of Ca and Mg than litter at those with a mor soil. In contrast, the concentrations of N, P, S, and K were not affected by soil type (Table 11). The author (Staaf, 1982) did not mention the chemical composition of the mineral soil.

Table 11 Variation in nutrients composition for leaf litter of common beech[a]

	Concentration (mg g^{-1})					
Plot no.	N	P	S	Ca	Mg	K
Mor humus						
15	9.1	0.49	0.98	10.13	1.9	2.3
19	9.4	0.41	0.98	8.01	1.35	1.38
23	9.2	0.41	1.26	8	1.83	2.9
14	9.9	0.54	1.24	9.82	1.98	2.22
6	8	1.42	1.19	9.63	1.45	2.56
20	9.2	0.56	1.13	7.69	1.23	1.96
21	9.2	0.4	1.09	7.63	1.3	3.34
9	8.7	0.56	1.3	8.19	1.23	2.16
18	9.7	0.54	1.3	7.5	1.5	2.4
24	8.6	0.36	1.04	7.69	1.57	2.26
10	10.1	0.82	1.33	8	1.14	2.92
8	9.2	1.16	1.32	9.63	1.65	2.38
5	8.7	0.54	1.25	8.88	1.47	3.36
7	7.8	1.01	1.09	8.75	1.38	4.18
Average	9.06	0.66	1.18	8.54	1.5	2.59
SD	0.43	0.1	0.02	0.85	0.04	0.49
Mull humus						
3	8.3	0.49	1.06	14.82	2.08	2.46
1	9.1	0.45	1.27	16.38	2.39	3.6
2	9.9	0.56	1.34	12.63	1.9	3.2
4	8.1	0.58	0.77	12.88	1.99	3.84
13	8.6	0.42	1.17	11.69	2.17	2.48
12	8.9	0.82	1.41	13.26	1.89	2.84
11	9.3	0.56	1.46	9.63	1.92	2.1
16	9.6	0.45	1.55	10.25	1.9	2.74
17	9.5	1.03	1.36	9.88	1.7	2.38
22	9.1	0.44	1.2	8.32	1.78	2.78
Average	9.04	0.58	1.26	11.97	1.97	2.84
SD	0.33	0.04	0.05	6.3	0.04	0.31
t-test (p value)	>0.05	>0.05	>0.05	<0.0001	<0.0001	>0.05

[a]The litter was sampled from stands within a limited geographical region. Significance level for differences between the mor and mull humus types is also reported for each nutrient. Data from Staaf (1982) and from H. Staaf, personal communication.

The effect related to by humus type (directly or indirectly) was apparently small, with mean Ca concentrations of 12.0 mg g^{-1} (mull soil) and 8.5 mg g^{-1} (mor soil) and for Mg 2.0 versus 1.5 mg^{-1}, respectively. Nevertheless, these differences were statistically significant. Still, when comparing to Scots pine litter (Table 10), the annual variation at the Scots pine stand was as large as the range between litter from the two previously mentioned soils.

4. A Case Study on K Concentrations in Foliar Litter

In a large study on K concentrations in boreal and temperate foliar litter fall, a statistically significant ($p < 0.0001$) difference in average initial K concentrations between coniferous and deciduous litters was seen (1.03 versus 4.52 mg g^{-1}, respectively; Berg *et al.*, 1995). The litter types investigated covered the most common litter types found in forests of Northern and Central Europe and some major North American species. Of investigated boreal species, lodgepole pine needle litter had the lowest initial concentrations followed by those of Scots pine. Both these litter types had lower initial K concentrations than those found in the leaf litter of Norway spruce, oak–hornbeam, and silver birch. The highest average value was that for grey alder leaves (8.3 mg g^{-1}) followed by that for silver birch leaves (5.0 mg g^{-1}). In contrast, leaves of common beech with 1.7 mg g^{-1} were in the same range as the coniferous litter.

5. Some Types of Woody Litter

Wood is largely made up of cellulose, lignin, and hemicelluloses in different proportions (Table 6). As a whole, the woody parts of the tree are poorer in nutrients than the photosynthesizing parts. We may see (see Tables 7 and 8) that nitrogen concentrations in woody parts may be lower than those in foliar litter by a factor of at least 10 within the species, for example, Norway spruce, trembling aspen, silver birch, and common beech.

VII. ANTHROPOGENIC INFLUENCES

In this section, we compare the effects on litter chemical composition of modified soils with artificially raised levels of nitrogen and soils with increased levels of heavy metals. We have used examples which are applicable to deposition of nitrogen as well as sulfur and several heavy metals.

A. Nitrogen-Fertilized Scots Pine and Norway Spruce Monocultures

Fertilization of forest soils as well as deposition of nitrogen add significant amounts of nitrogen to the ground, resulting in higher concentrations as compared to those in the original soil. In the examples reported in the following text, the trees have simply taken up more of both nitrogen and some other nutrients with a high availability, resulting in higher concentrations in the foliage. At retrieval, before the needles are shed, a certain fraction of the

needles' nutrients is retrieved and a certain fraction is left, resulting in higher concentrations in the foliar litter as compared to the natural system.

For both Scots pine and Norway spruce there was a clear trend in chemical composition of needle litter with increasing fertilizer doses (see Textbox 4; Fig. 15). In general, the concentrations of nitrogen, phosphorus, sulfur, and potassium increased as a consequence of nitrogen fertilization, and the effect on the concentration of nitrogen was most pronounced. In contrast, the concentration of calcium decreased in litter produced by both species (Fig. 15), and, for magnesium, no significant relationship was found for Scots pine while its concentration increased in Norway spruce litter.

Increased uptake of nitrogen in N-fertilized plots and resulting enhanced concentrations of nitrogen in the freshly formed litter were the most obvious phenomena, observed in a number of studies (Berg and Staaf, 1980a; Miller and Miller, 1976). The former authors, using Scots pine needle litter from a fertilization experiment (dosage details given by Tamm, 1991) found that nitrogen additions at an annual dosage of 80 kg N ha^{-1} resulted in a statistically significant increase in litter-N concentrations, whereas a dosage of 40 kg ha^{-1} yr^{-1} did not have any significant effect, even after 10 years of additions. The range of the increase measured over several years at one experimental site was from about 3.6 to 8.5 mg N g^{-1} needle litter. The variation in N concentration was accompanied by a variation in concentrations of other nutrients as well, to some extent producing a balanced nutrient composition.

Norway spruce needle litter followed a similar pattern as that of Scots pine, although the needle litter had significantly higher concentrations of all measured nutrients throughout the whole gradient of fertilizer doses. Also, the rate of concentration change (regression slope) differed between

Textbox 4 Nitrogen fertilization experiments

The fertilization experiments were performed on Norway spruce (started 1967, needle litter fall sampled in 1983 and 1984) and Scots pine stands (started 1969, litter fall sampled in 1975 and 1976) in boreal forests in central Sweden. The plots were fertilized annually with doses of 60 and 90 kg N ha^{-1} for Norway spruce and 40, 80, and 120 kg ha^{-1} for Scots pine, in both cases given as ammonium nitrate. Chemical composition of foliar litter fall was analyzed for during the two consecutive years at experimental and control plots. In the experiment with Norway spruce there were five replicate plots for each N dose, while only one replicate per dose was used for the Scots pine stands. For the analysis presented (Fig. 15) the average values of the second year data for the Norway spruce plots were used.

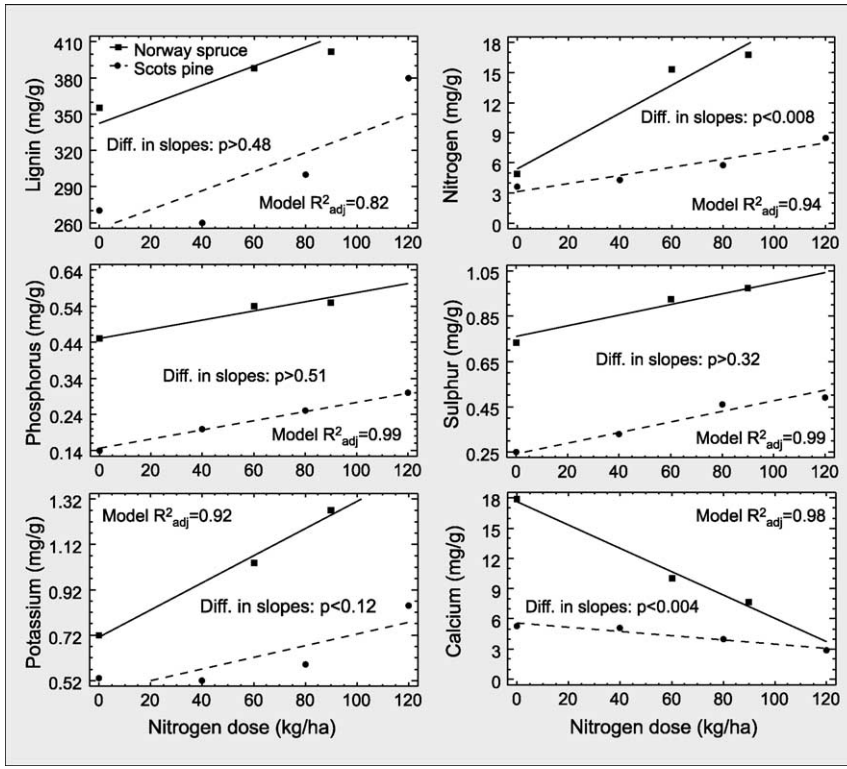


Figure 15 Relationships between annual doses of nitrogen fertilizer given as ammonium nitrate and concentrations of lignin, nitrogen, phosphorus, sulfur, potassium, and calcium in newly shed litter of Norway spruce and Scots pine (Norway spruce, [■] and full line; Scots pine, [●] and dashed line). All models are significant; the p-values indicate the significance level for the difference in slopes between Scots pine and Norway spruce. Despite a nonsignificant difference for potassium, regression lines with different slopes are shown because of the higher R^2 (see text for more information).

the species for some nutrients (see Textbox 5). Thus, in Norway spruce litter, nitrogen concentration increased significantly faster than in Scots pine, while calcium concentration decreased significantly faster. For potassium, statistical tests did not detect significant difference in slopes. However, a due to substantially higher R^2_{adj} for the model with different slopes, a low number of data points, and still quite low p value for the difference in slopes, we may expect that the rates of increase in potassium concentration are rather different among the species (see Fig. 15). A substantial difference was also noted for magnesium; its concentration

Textbox 5 Comparing regression lines

Regression analysis is a powerful tool allowing us to describe mathematically the relationship between one dependent variable and one or more independent variables. Specific tests have been developed to test the significance of the model as a whole as well as of its particular parameters. In this book regression analysis is used frequently to describe such phenomena as, for example, relationship between accumulated mass loss and lignin concentration, nutrient contents or pollution level. However, finding such a relationship and describing it by a mathematical function is often only a first step in data analysis. If a significant relationship is found, the next obvious question is whether the same relationship applies over a broad range of systems. In our case these could be represented by different forest types (e.g., deciduous vs. coniferous) or species (e.g., Scots pine vs. silver birch). In statistical terms such a question is equivalent to asking if regression parameters can be considered the same over the systems (species) studied, or the if difference between them is large enough to be considered significant. The latter case means that a common regression does not describe the systems (species) studied adequately, and the regression parameters should be estimated for each case separately. The central question here is when the regression parameters should be considered significantly different.

The method to test for significance is the regression analysis with so-called "dummy variables" (D), sometimes called also "indicator variables" as their only purpose is to indicate separate categories that we are comparing in the analysis. For the sake of simplicity, we will describe the concept using a simple linear regression as an example. In litter decomposition studies such a regression may describe, for example, how the concentration of nitrogen (Y) depends on litter accumulated mass loss (x):

$$Y = a + bx$$

where a is the regression intercept and b is the slope (rate of concentration change). If we make similar studies on a number of species named 1, 2, ..., n, we would obtain n regressions:

$$\begin{aligned} Y_1 &= a_1 + b_1 x \\ Y_2 &= a_2 + b_2 x \\ &\ldots \\ Y_n &= a_n + b_n x \end{aligned}$$

Having n such equations, we want to know whether the estimated regressions are really different or are similar enough to be combined into one common model for all species studied. We thus need a statistical tool that would let us separate the models if they are significantly different, and combine them to a common model if differences are nonsignificant.

With the dummy variable method, we start with adding additional n (or n–1, depending on details of the method) variables that consist only from 1s and 0s. Thus, using as an example the set of linear regressions as above, the first

dummy variable (D1) has 1s for species 1 and 0s for all other species, the second dummy variable (D2) has 1s for the species 2 only, and 0s for the remaining species, and so on up to the last species (n) taken into account in the comparison. Now, we construct a common linear regression model which distinguishes the species thanks to the dummy variables created:

$$Y = a + bx + D_1a_1 + D_1b_1x + D_2a_2 + D_2b_2x + ... + D_na_n + D_nb_nx$$

The reasoning in interpreting results of such a regression analysis is quite straightforward: if a common model (the first part of the equation, $Y = a + bx$) describes the relationship adequately, then all remaining terms in the equation will be nonsignificant because none of them introduces significant information to the model. Thus, if the only significant parameters in the regression above are a and b, then we conclude that a common model is sufficient and no significant differences among species exist. If, however, any other parameter appears significant, then the common model cannot be used—in our example that would mean that nitrogen dynamics differs significantly between species. Note that we have separate parameters for each species, thus looking at significance levels for each case, we may distinguish the species that do not fit to the common model from those that do. Thus, the dummy variable regression is a powerful method, allowing to test for differences between different groups of data (populations) in their relation to some independent variable(s). The method can be extended also to nonlinear models, but the interpretation of the results gets more complicated.

increased in Norway spruce litter, whereas no fertilization effect was found in Scots pine.

It is noteworthy also that concentrations of lignin increased with dosage of N fertilizer both for Scots pine and Norway spruce. For Scots pine, the lignin concentrations increased with those of N from 270 to 380 mg g^{-1}. For Norway spruce, the increase was of a similar rate (Fig. 15) with the range from 242 to 407 mg g^{-1}. This kind of effect seems to vary with the type of system and appears to be indirect. This may be related to deficiency of boron in the soil, a phenomenon that may be of interest, though not being a direct causal relationship. It is possible that the high dosage of nitrogen fertilizer forced the trees to grow so quickly that the supply of some essential nutrients became insufficient as their mobile pool in the soil became exhausted. The weathering apparently could not provide a good enough supply and therefore some nutrients became limiting. Boron has an important role for the formation of an enzyme transporting phenols out from the needles. The lack of boron probably resulted in accumulation of phenolics in the needles and thus caused a higher synthesis of lignin.

B. The Effect of Heavy Metal Pollution

Scots pine needle litter has been investigated as regards pollution in a transect from a smelter. The chemical composition of newly shed, locally collected needles in the pollution transect varied with the distance from the smelter (Fig. 16; Table 12). A significant positive relationship ($p < 0.05$) was found between the distance from the smelter and Mg concentrations in the fresh litter and the same tendency was also observed for Mn (Fig. 16) meaning that concentrations of these nutrients increased with the distance from the smelter. Of the pollutants, Pb and Zn concentrations showed a strong decrease with distance from the smelter ($p < 0.01$). The same trend was noted for Fe and Cu ($p < 0.05$; Fig. 16) and also, although less marked, for S and Cd ($p < 0.1$; Fig. 16). The concentrations of organic compounds, on the other hand, seemed largely unaffected. The completely unpolluted litter (Table 12) had somewhat lower lignin and higher N and P concentrations than the needles (Berg *et al.*, 1991).

In the case of metals originating from industrial activity, the majority of their contents in foliage can be deposited as particles on leaf surfaces. For example, according to Kozlov *et al.* (2000), as much as about 80% of nickel and copper in leaves of mountain birch, growing in the area polluted by a nickel-and-copper smelter, were found as dust particles on the leaf surface.

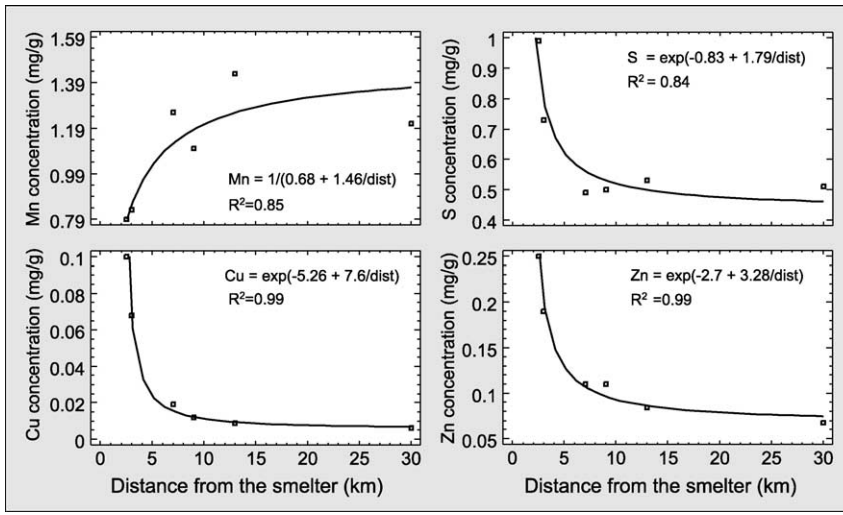


Figure 16 Concentrations of manganese (Mn), sulfur (S), copper (Cu), and zinc (Zn) in Scots pine needle litter collected at different distances from a smelter.

Table 12 Concentrations of plant nutrients, and heavy metals in fresh needle litter of Scots pine sampled at six study plots in a smelter pollution transect in Northern Sweden (local litter) and needle litter sampled at an unpolluted site[a]

Distance from the smelter (km)	Chemical element (mg g^{-1})										
	N	P	S	K	Ca	Mg	Mn	Fe	Zn	Cu	Pb
Local litter from a transect											
2.5	3.78	0.26	0.99	1.43	5.23	0.47	0.79	0.38	0.25	0.1	0.311
3	3.73	0.24	0.73	1.01	5.7	0.53	0.83	0.36	0.19	0.068	0.191
7	3.25	0.19	0.49	0.7	6.11	0.46	1.26	0.14	0.11	0.019	0.044
9	3.71	0.26	0.5	1.08	4.65	0.56	1.1	0.27	0.11	0.012	0.034
13	3.66	0.25	0.53	1.23	5.65	0.66	1.43	0.12	0.084	0.009	0.022
30	4.4	0.22	0.51	0.98	5.7	0.67	1.21	0.11	0.068	0.006	0.012
Litter from a clean area											
	4.8	0.35	0.41	1.2	5.26	0.49	1.35	0.06	0.051	0.002	0.0011

[a]Concentrations of Na, Al, B, Ni, Mo, Sr, and Cd did not exhibit any trend along the transect. From Berg *et al.* (1991).

It seems that metals available through soil do not necessarily affect internal chemical composition of live leaves significantly. For example, Bargali *et al.* (2003) found no increase in concentration of most metals in leaves of downy oak growing in a district of centuries-long mining of Fe, Ag, Cu, Pb, and Zn. Arsenic was the only element exhibiting increased concentrations in leaves from sites with deposits of metal sulfide ores or As-polluted soils around abandoned smelting plants. It has to be stressed, however, that incorporation of heavy metals into live plant tissues may depend heavily on soil properties, the acidity (pH) being the most important factor in addition to metal concentration. Thus, in forest stands with approximately neutral soil reaction, where only minor fractions of metals accumulated in soil are bioavailable, leaves may not accumulate significant concentrations of metals. However, at acidic stands, the situation may be quite different. For example, Blake and Goulding (2002) found that oak leaves in moderately contaminated areas contained ten times more Mn, four times more Ni, and three times more Cd at pH 4 than at pH 7. The latter results indicate clearly that concentrations of metals in leaves and, consequently, in leaf litter fall depend not only directly on pollution level but also on site-specific properties, such as soil pH in particular, and possibly indirectly also on other pollution effects, such as acidification caused by SO_2 and NO_x emissions.

VIII. METHODS FOR LITTER COLLECTION

A. Quantities

A common method to sample litter fall is to use circular litter traps, often of 0.25 m^2, mounted at an height of ca 1 m above the ground, with the collector bag being a loosely hanging net on a metal or wooden frame. Such traps were recommended already in the International Biolpgical Programme (IBP; Newbould 1967). Although in the literature different numbers of such traps are suggested per plot, it appears that in many recent studies a common number is between 10 and 20 replicate traps per stand, with plot sizes ranging between 2500 m^2 and a hectare.

With needle and leaf litter being rather evenly distributed over a stand, litter traps intended to collect foliar litter can be placed randomly over the plot. The net mesh size should be considered with respect to the litter type that is collected. For example, for litter types such as needles of spruce or larch the mesh size should preferably be less than ca 0.2×0.2 mm whereas for e.g. beech and oak leaves a mesh size of 1 cm could do.

Other litter components such as twigs, branches and most fruiting bodies like cones or acorns have no even distribution over the ground but fall

directly below the canopy. Thus, traps for these components could ideally be placed to reflect the canopy projections on the ground. This means either randomly, depending on canopy density, or directly under the canopies. Of course, a high enough number of traps randomly placed and reflecting also the canopy distribution can be used. For cones and nuts an often used type of a seed trap measures 1 × 1 m.

For twigs and large branches a successful approach was made using low "bed-like" traps with a crude steel net, measuring at least 1 × 1m (Flower-Ellis, 1985). In that case the mesh size should be selected to let finer material out and retain twigs of the wanted size. Also the sides need to have a fence or net structure to prevent falling branches from bouncing off.

Sampling periods and frequency vary according to the literature and may be adapted to whether foliar litter only or other, additional litter components should be sampled. For foliar litter from conifers or evergreens, e.g., needle litter from pine and spruce, with litter fall distributed over the whole year, a sampling frequency of every one to three weeks is often used throughout the year. In contrast, for those deciduous species that shed the main part of their foliar litter during a shorter period only, e.g., aspen, birch, chestnut in central Europe between July and December, and birch in Scandinavia from August through October, samplings may be carried out during a more limited period. The sampling frequency is important from both the point of view of quality and quantity since, e.g., nutrients and soluble compounds may be leached out by rain and a wet litter may start decomposing and thus lose mass.

Regarding collection of woody components in litter fall the sampling may continue over the whole year since twigs and branches rather fall in connection to events such as storms, snowfall or heavy rains.

There is also a considerable variation among years and samplings should never be made for one year only, even in mature stands in which litter fall often is considered to be "constant". Even if the tree biomass is actually more or less constant in mature stands, there is still a considerable between-year variation in the litter fall. There does not seem to be any general recommendation about the duration of a measurement and we refer to a ten-year long measurement in a mature Scots pine stand, in which the litter fall was considered to be constant. Over the ten years the ratios between highest and lowest amount of needle litter fall was considerable, with 1.9 for needle litter, 5.0 for cones, 2.4 for twigs and 1.5 for total. The only general recommendation we can make is to continue with the sampling for as long as possible, keeping in mind that just one or two years measurements may give values that are distant from a long-term average.

B. Qualitative Sampling

As seen in Fig. 11, the chemical composition of the leaves or needles to be shed do change with time before abscission takes place. A too early sampling may thus result in a litter sample that is not representative. The ideal representation is thus the litter that has been shed naturally, namely that has fallen itself and not been picked from the trees.

Still, such collections are not always possible to do and we may therefore suggest two alternative approaches. In both cases we suggest that for a sample representative of the selected stand at least 20 trees are used. Today we still do not know the variation in chemical composition of litter fall among individual trees so this number is selected out of a general statistical principle.

In the case of natural litter fall, sheets of plastic or cloth are spread under the 20 or more trees and the shed litter is collected daily. As an alternative, limbs of the trees are shaken gently and the shed leaves are collected on sheets. Often part of the shed needles would be green, a phenomenon often seen for spruce, for example. We cannot give advice about that here but a decision about what to include in the samples in terms of green litter is up to the investigator.

Decomposers: Soil Microorganisms and Animals

I. INTRODUCTION

There is an unfortunate tradition ascribing to soil animals a large role in the decomposition of organic matter, leaving a minor role to the soil microorganisms. Since 1980, an increasing number of studies and calculations have shown that the relative roles are reversed. Thus, it has been found that in, for example, boreal forests, the soil microbial population transforms more than 95% of the plant litter carbon, leaving a maximum of 5% to soil animals. The dominating 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, hemicelluloses, and various lignins (Textbox 3 in Chapter 2).

In this chapter, we emphasize the functional roles of microorganisms (e.g., cellulolytic and lignolytic) rather than their taxonomy. The concepts of white-rot, brown-rot, and soft-rot and what they functionally stand for in terms of degradation processes will be presented. We use these functional concepts as a basis to discuss the degradation of litter tissues. Although the terms originally referred to visually different types of lignin degradation, it now appears that the degradation of not only lignin but also cellulose and

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hemicellulose is different among the taxonomic groups of microorganisms (Worrall *et al.*, 1997). The terms, however, relate to the type of rot rather than to the group of organisms, namely, rots giving the wood a white or brown color. In the following text, we adopt the common use of the terms and refer to fungi when using the terms white-rot, brown-rot, and soft-rot. Regarding degradation by bacteria, it is described and discussed as such.

Many microorganisms in nature degrade cellulose and hemicellulose. 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. Thus, the first steps in their degradation activity take place outside the cells. Some polymer carbohydrates may be degraded by both aerobic and anaerobic microorganisms, 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 be carried out also by anaerobic bacteria but is mainly found among fungi and aerobic bacteria.

The species composition of the microbial community (as regards cellulolytic and lignolytic species) may vary with the general properties of the soil/litter subecosystem, such as nutrient status and pH. A specific functional property that may discriminate among soil systems in terms of their microbial community structure is, for example, differentiated sensitivity of species to concentrations of nitrogen in litter and humus, which may be either stimulating or suppressing for particular species. Such a suppressing effect of nitrogen is not general, but is common in species of both white-rot and brown-rot organisms as regards their lignin degradation.

By tradition, soil animals have been considered important for litter decomposition; such groups as springtails, mites, and earthworms, among others, have been ascribed different roles in decomposition, although the roles are not always clear and not always proven. The decomposition by free-living microorganisms has also been considered important but the relative influences of the two main groups, namely, soil animals and soil microorganisms, have not been apparent. It has become increasingly clear, however, that for some systems, at least boreal and temperate coniferous ones, the microbial component is of absolute dominance, with more than 95% of the energy going through the microbial community. The implications of such a finding and of such a proportion are considerable. As the book focuses on boreal and temperate systems, with an evident dominance of microorganisms in the decomposition process, we have given special attention to microbial communities (Section II.A.) and the enzymatic degradation mechanisms (Section III.) for the polymer carbohydrates and lignin. This chapter thus presents basic properties of microorganisms, as regards degradation of cellulose, hemicellulose, and lignin. Although presented on

the basis of studies carried out in boreal and temperate forest systems, these decay mechanisms should be similar across ecosystems and climatic zones. What may differ among systems and climates is the relative interaction between microorganisms and litter chemical composition and the influence of microorganisms versus soil animals.

For those microorganisms that decompose plant litter structures, the term "decomposer" is sometimes used. The structure and development of decomposer communities can influence the pattern of decay. Also, structural changes in the community and its function during the decay process will be addressed. The effects of moisture and temperature on the activity of the microbiological decomposition are presented later, in Chapter 7.

II. COMMUNITIES OF SOIL MICROORGANISMS AND ANIMALS

A. Soil Microorganisms

The two main systematic groups of litter decomposers are bacteria and fungi. Both groups include some of the same basic physiological properties when it comes to degradation of the fresh litter polymers. Generally, the fungi are considered the more important group, which means that we know more about their litter-degrading properties and enzyme systems. Each of these two groups may be subdivided into functional subgroups with different properties and the ability to degrade the main groups of chemical components. We will discuss them shortly.

The systematics of both fungi and bacteria encompass numerous genera and subgroups, the description of which is beyond the scope of this book. The bacterial group also includes both aerobic and anaerobic organisms, which makes them differ from the exclusively aerobic fungi. Further, among bacteria belongs an important group of lignin degraders, namely the filamentous bacteria that earlier were called Actinomycetes. Both fungi and bacteria include organisms able to degrade all the main plant litter polymers: lignins, cellulose, and hemicelluloses. There are also organisms able to degrade woody tissue containing all the components combined into fibers. Still, a complete degradation of lignin appears to be carried out only by some of the fungi and some of the filamentous, aerobic bacteria. Some main properties are collected in Table 1.

Bacteria may be immobile or mobile, with one or more flagella, a whiplike structure. Fungal mycelia are mobile in another way since they simply grow in one direction and thus move their protoplasm, leaving an empty cell-wall structure behind.

Table 1 Some general properties of the 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	?	+
Species without N repression of the ligninase system	?	+

[a]Incomplete degradation to be compared to the brown-rot type. With kind permission of Springer Science and Business Media.

The diameter of most bacteria range from 0.1 to 2 μm, and filamentous fungi from approximately 1 to 20 μm. Whereas the lengths of rod-shaped bacteria, in general, are less than, say, 20 μm, those of the fungal mycelia are more undetermined. The size of a large part of the microorganisms is generally on the level of 1 μm in diameter, which gives them access to different parts of the fibers and tissues.

The numbers of soil microorganisms and the general biological diversity of the soil microbial community can be considered very high. We may see the potential species diversity just by using crude numbers of identifiable species within, for example, one square meter. The number of fungal species for a natural and unpolluted soil may be estimated to approximately 100 dominant species, and for bacteria, the number may be more than 5000.

The high density of microorganisms in an organic soil creates a high potential for invading new substrates, such as newly shed litter. Estimates of 10^9 bacterial cells per gram organic soil, either active or in a resting stage, for example, as spores, are common when made by direct light microscopy counting. However, there are numerous bacteria that are simply too thin to be seen in a light microscope and have to be counted using electron microscopy. This figure is, thus, rather conservative. In similar soils, total mycelial lengths have been estimated to reach approximately 2000 km per liter of humus, of which perhaps 10% would be live.

Only those microorganisms for which the environmental conditions are suitable for growth are active whereas the others remain in some kind of dormant stage. Further, fungal spores are easily transported by wind and animals, and this means that they may be transplanted among ecosystems. These two factors mean that an ecosystem may have a passive species bank, with microorganisms able to be revived when the conditions allow and to attack a variety of litter types, including those containing chemical components that are unknown in a particular environment.

Mycorrhizal fungi have been found to turn into aggressive decomposers under certain circumstances and may decompose humus that has been considered stabilized, and such a degradation can take place at a high rate. This phenomenon may be related to nutrient stress of the growing trees. The role of mycorrhiza in decomposition is still under dispute and we set forward observations without taking part in that dispute (Section VI.G.) Chapter 3 focuses 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, only partly degraded molecules.

B. Soil Animals

Detailed descriptions of soil fauna communities exceed the scope of this book, and separate handbooks are devoted solely to this topic. A good overview of soil organisms, including microorganisms, and their ecology can be found in "Soil Ecology" by P. Lavelle and A. V. Spain (2001).

Soil, being the most complicated subecosystem on earth, offers extremely diversified environments to organisms: it is rich in different food resources, both as dead organic matter and as numerous live microorganisms and invertebrates; it normally consists of microenvironments of very diversified humidity and different chemical properties. Further, soil pores can actually represent a freshwater environment rather than a terrestrial one. Due to this diversity, most of the invertebrate taxonomic groups can be found in soil. The soil system is also probably the environment richest in different ecological groups of animals: hydrobionts are actually aquatic organisms which occupy the smallest soil pores, more or less permanently filled with water; hygrobionts still require high moisture and, frequently, available free water, but are typical terrestrial animals; the driest parts of soil systems are occupied by xerobionts—animals preferring dry conditions.

Traditionally, soil fauna is divided into three major classes, depending simply on the size criterion: the *microfauna* covers a size range up to 0.2 mm, approximately 100 to 2000 times larger than the main groups of bacteria; larger animals up to 10 mm belong to *mesofauna*, and still larger ones comprise the last group of *macrofauna* (Lavalle and Spain, 2001). Some authors adopt slightly different size criteria and also recognize yet another group of *megafauna* for animals such as the largest earthworms, slugs, and snails as well as all soil-living vertebrates (Górny, 1975). The general classification of major groups of soil fauna is presented in Fig. 1. Although this might seem like a very artificial grouping, there is some deeper sense behind the size classes recognized. The microfauna representatives live mainly in the water-filled and small soil pores and belong chiefly to hydrobionts. Due to their small size, their effect on soil structure is very limited or

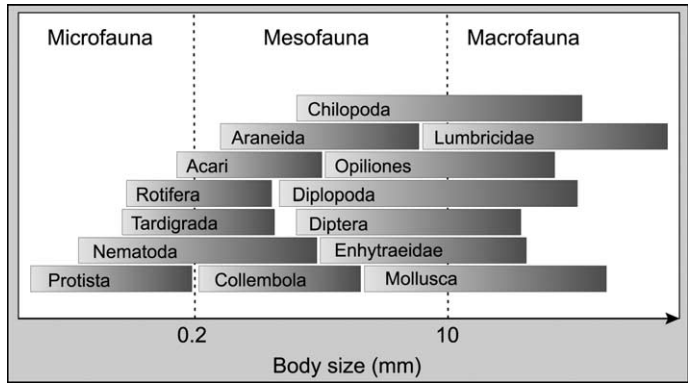

Figure 1 Size-classified major groups of soil invertebrates.

none. Mesofauna inhabits larger soil pores with no free water but filled with water vapor—they generally belong to hygrobionts. Through deposition of fecal pellets and limited possibilities to burrow in soil, they may affect soil structure to some extent. In contrast to microfauna, generally, they are not able to decompose organic matter by themselves. Finally, macrofauna is the group of free-moving animals, large enough to actively burrow in soil and mix organic and mineral layers. Their effect on soil structure is, by far, the largest among all soil-living organisms. As they represent a huge variability of taxonomic groups and ecological niches, one may find in this group both hygrobionts and xerobionts. In spite of their decisive effect on soil structure, their capabilities for direct primary decomposition of dead organic matter is limited or nil. Their effect on organic matter decomposition may be through mixing organic matter with mineral soil (see Section VI. G.).

Yet another classification of soil fauna, introduced by Van der Drift (1951), is based on an association of a species with specific compartments of soil environment. Thus, *euedaphic* species live in deeper soil layers. Most microfauna and some mesofauna belong here. Surface layers of soil, such as humus and litter, are inhabited by *hemiedaphic* species; most meso- and macrofauna can be classified as such. Animals that generally live on the litter surface but temporarily may live in the litter layer, such as numerous beetles, spiders, snails, or slugs, form a third group of *epedaphic* species. Finally, some species can be found on the soil or litter surface, although they are in no way connected to the soil environment— such species have been classified as *atmobionts*.

Obviously, no single classification is perfect. Many animals spend only part of their life cycle in soil or litter, and later have no connection with it. For example, a number of insects, such as butterflies or dipterans, spend their larval and/or pupal stages in soil, but adults can hardly be named "soil

animals.'' As can be seen from Fig. 1, size-based classification is also far from perfect since a number of taxonomic groups spread over a few orders of magnitude in size. Moreover, animals do grow and, during that process, even a single species can pass from one size class to another. Still, classification is helpful and, as we have indicated, usually there is some biological or ecological meaning behind even the simplest grouping system.

III. THE DEGRADATION OF THE MAIN POLYMERS IN PLANT FIBERS

In Chapter 2, we described the main polymer litter chemical components, namely, cellulose, hemicellulose(s), and lignins, the latter represented by spruce lignin. In this chapter, we focus on the main groups of organisms degrading these polymers.

A. Degradation of Cellulose

Cellulose is degraded by numerous species of both fungi and bacteria. These organisms rely on extracellular enzymes that either are located on the cell surface or secreted into the organisms' immediate surroundings. A common property of all cellulose-degrading organisms is that they produce extracellular hydrolytic enzymes that attack the cellulose structure. Due to the fiber size, the main part of the degradation of cellulose must take place outside the microbial cell (Fig. 2). Part of the cellulose in the plant fiber is arranged in a way that makes it harder for enzymes to degrade—it has a crystalline form and not all of the cellulolytic organisms have the necessary complete set of enzymes to degrade that structure. Several microorganisms, on the other hand, are able to degrade the kind of cellulose that is arranged in a more amorphous way (see, e.g., Eriksson *et al*., 1990). In the first steps of degradation, the insoluble macromolecules are degraded stepwise to oligomers (chains of different lengths) and finally to the dimer cellobiose with just two glucose units (Fig. 3), which is taken up by the cell and metabolized.

The most studied group of cellulose-degrading organisms is the fungi. No fewer than 74 species (Eriksson *et al.*, 1990) have been studied in detail and clear differences have been observed among species.

Probably the best studied wood decay fungus is the white-rot basidiomycete *Phanerochaete chrysosporium* Burdsall (previously called *Sporotrichum pulvurolentum* Novabranova). Much of our knowledge about the decay of cellulose and lignin in nature is based on studies of this fungus (Eriksson *et al.*, 1990) and we may use it as an example. Three main enzymes are involved in cellulose degradation: one type of enzyme (endo-1,4-β-glucanase) covers the

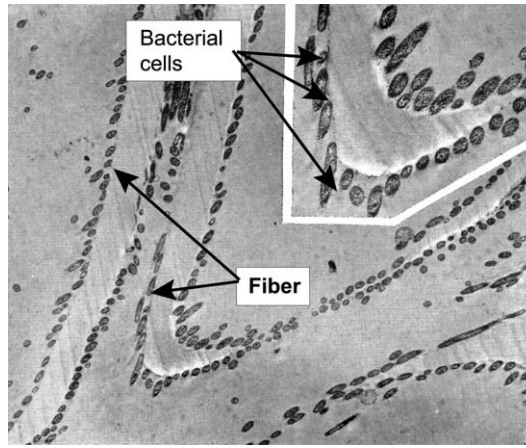

Figure 2 Electron microscopic photo of the cellulose degrading bacterium *Cellvibrio fulvus* growing on a fiber, in this case, of pure cellulose. Note the close contact between the bacterium and the cellulose. From Berg *et al.* (1972).

cellulose chain and splits the glucosidic linkages in a random way (Fig. 3). In this case, ''randomly'' means that oligosaccharide units of different lengths are formed in this first degradation step, although they may still be attached to the microfibril structure. Another enzyme, an exo-1,4-β-glucanase, splits off either glucose or cellobiose from the nonreducing end of the cellulose chain. Finally, a 1,4-β-glucanase hydrolyzes cellobiose and other water-soluble oligosaccharides, such as triose and tetraose, to glucose. This latter enzyme is located in the cell in contrast to the two cellulases (endo- and exo-) that are located on the outside of the cell wall. One important aspect of this enzyme system is that the two cellulases with different specificities (the endo- and exoglucanases) exert a synergistic action that enables them to degrade both crystalline and amorphous cellulose.

The soft-rot fungi, as a group, generally appear to have a cellulose-degrading enzyme system similar to that of the white-rots. On the other hand, in contrast to white-rot and soft-rot fungi, brown-rots have not been found to have the cellulases with the synergistic effects that are found in white-rots and they appear not to have the exocellulase previously mentioned. However, Highley (1988) found several species of brown-rots that were able to solubilize microcrystalline cellulose. Thus, the generally held conclusion that brown-rot fungi seem merely to depolymerize cellulose without producing soluble glucose of cellobiose may not be entirely correct. Still, no other enzyme has been found to substitute for the missing exocellulase that splits off soluble units, such as glucose or cellobiose (cf. Fig. 3). This has led Eriksson *et al.* (1990) to conclude that there may be a nonenzymatic mechanism involved in the brown-rot degradation of cellulose.

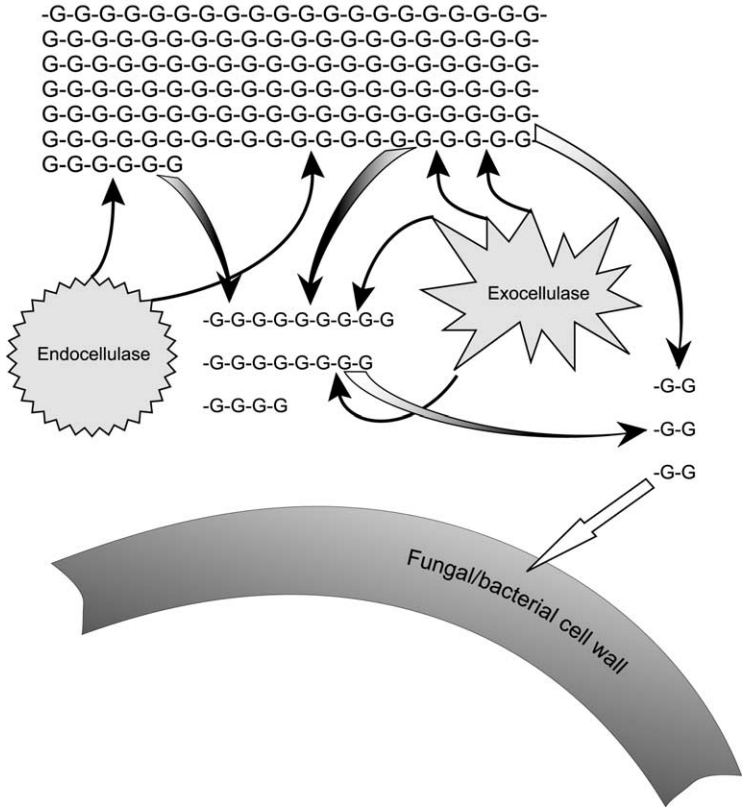

Figure 3 Part of a cellulose microfibril is attacked by an endo-1,4-β-glucanase, also called endocellulase, splitting off oligosaccharides in a random manner, thus producing chains of different lengths. An exo-1,4-β-glucanase, also called exocellulase, splits off cellobiose units from the nonreducing end of the carbohydrate chains. The letter G symbolizes a glucose unit.

An observation that hemicelluloses are 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) suggests that, at least for some brown-rot species, a less specific or multifunctional enzyme that can degrade several different polysaccharides was active.

Also, in many bacteria, we can find the ability to degrade crystalline cellulose. Detailed studies on the anaerobic *Clostridium cellulolyticum* show that the organism produces at least six different cellulases, each with slightly different structural and catalytic properties. The cellulases and the xylanases are held together in a large structure, the cellulosome, by a scaffolding

protein (see Bélaich *et al.*, 1997), largely as was predicted by Eriksson *et al.* (1990). Already in the very early work of Viljoen *et al.* (1926) on the anaerobic bacterium *Clostridium thermocellum*, a multicomponent complex of cellulolytic enzymes was named "cellulosome." Close contact between the cellulose substrate and the organism often appears to be necessary. Such contact may be illustrated by an electron microscopic picture (Fig. 2) of bacteria growing in contact with a cellulose fiber.

The degradation of cellulose by bacteria has been suggested to be carried out by hydrolytic enzymes; still, the mechanisms seem to be different from those of the investigated fungi. For bacteria, the cellulolytic enzymes are arranged in clusters and act in a combined way, as has been described. This property seems today to be widely recognized (Wiegel and Dykstra, 1984). The few groups of cellulolytic bacteria that have been studied include *Cytophaga*, *Cellulomonas*, *Pseudomonas*, *Cellvibrio*, and *Clostridium*. 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; see Fig. 2). Actinomycetes, in contrast to some other bacterial groups, appear to degrade cellulose in a manner similar to that of fungi and can also degrade the crystalline form. Several strains even have the ability to degrade the lignocellulose complex. The "fungal model" for enzymatic degradation of the cellulose molecule, namely that an endo- and an exocellulase act synergistically, appears to be valid also for Actinomycetes, supporting their similarity to white-rot and soft-rot fungi in this respect.

We know that the synthesis of cellulases is induced by cellulose, cellobiose, sophorose, and lactose. As cellulose is a large and nonsoluble molecule, it cannot be transported into the microbial cell and exert a direct inducing effect. However, the presence of cellulose appears to be the best induction agent and just the presence of the cellulose outside the cell appears to cause an induction. Today, the accepted theory is that the microorganisms 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 the formation of cellulase. It is likely that both the type of a compound, for example, cellobiose or cellotriose, and a low concentration of these compounds influence the synthesis of cellulase. There are also theories that transfer products of glucose, for example, glucosyl, are active, one of these being the sugar species sophorose (cf. Eriksson *et al.*, 1990). On the other hand, the cultivation of bacteria and fungi using glucose as the sole carbon seems to repress the synthesis of the cellulase system.

B. Degradation of Hemicelluloses

We mentioned in Chapter 2 that 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 ("heteropolymers" meaning that the chains are built up of different species of simple sugars). The individual sugars may be methylated or acetylated, and most hemicellulose chains contain between two and six different kinds of sugars. This structural complexity means that the degradation of hemicelluloses requires more complex enzyme systems than are needed for the hydrolysis of cellulose. We may illustrate this with the possible structure of such a xylan-dominated hemicellulose with both 1,4-β-linkages and branched hetero-poly-saccharides, which require a complex set of enzymes for degradation (see Dekker, 1985) (Fig. 4). The xylan backbone is made up of both acetylated and nonacetylated sugar units. On the branches, there are units of methylated glucose and arabinose. The degradation of such a complex molecule requires the concerted action of several different hydrolytic enzymes (Eriksson *et al.*, 1990).

C. Effects of N, Mn, and C Sources on the Degradation of Lignin

1. 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 has been mentioned, Kirk (1980) described N-regulated effects on lignin degradation for *P. chrysosporium* and that lignin degrading enzymes were synthesized under conditions of N starvation. In the first experiments on this effect, Keyser *et al.* (1978) found a drastic effect of N on lignin degradation rate when the N concentration in the culture medium was increased from 2.6 to 5.6 mM. The lignolytic activity (measured as transformation of ^{14}C-lignin to $^{14}CO_2$) was repressed by 83% at the higher concentration. This property has 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*, significant decrease in lignin degradation rate was found at 7.8 and 34 mM N in the culture, but not at 2.6 mM N. The magnitude of the effect caused by 20 mM N varied from an almost complete repression in *P. chrysosporium* to about a 50% repression in *P. mutabilis* when using ^{14}C-labeled lignin from red maple wood. Table 2 lists a number of species investigated for this property.

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. We may speculate about the ecological significance of that. It may be so that in N-rich environments

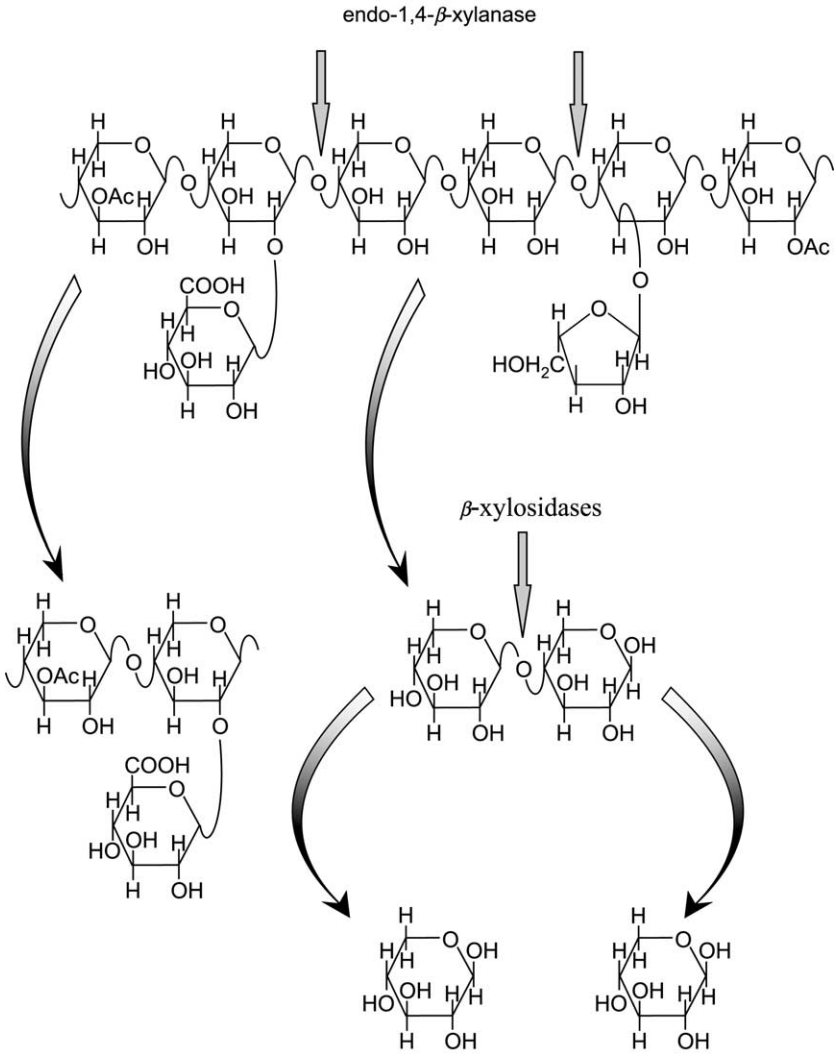

Figure 4 Degradation of part of a xylan molecule. The main enzyme attacking the unbranched part of the chain would be an endo-1,4-β-xylanase, producing oligosaccharides of different lengths, such as dimers and trimers. Part of these may have a short side chain with, for example, a uronic acid or an arabinofuranolsyl unit. To split off the side chains, other enzymes are necessary as well as for splitting off, for example, the acetyl substituent which may occur in a xylose unit. β-xylosidases split the oligomers into simple xylose units. From Eriksson *et al.* (1990). With kind permission of Springer Science and Business Media.

Table 2 Some fungal species for which raised N concentrations have, or alternatively, have not elicited a repressing effect on lignin degradation

Species	Comments	Literature 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

there is a dominance of white-rot fungi that are not sensitive to high litter N concentrations as regards lignin degradation.

The results until today suggest that N repression of lignin degradation is common but not always the rule. The addition of N to fungal cultures may, in certain cases, even increase their efficiency to utilize lignin. We would expect that such fungi whose lignin degradation is stimulated by N, and N-tolerant fungi in general, would be found in environments with high N concentrations, as in the example previously given 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 N.

2. *Effect of Manganese*

Manganese is essential for the activity of Mn-peroxidase, a lignin-degrading enzyme with Mn as part of the functioning enzyme, and high Mn levels enhance its production (Perez and Jeffries, 1992). Manganese-peroxidase belongs to the group of enzymes that are classified as phenoloxidases, enzymes that oxidize and open aromatic ring structures in lignin. Although not much was published on this enzyme before 1983, Lindeberg (1944) discovered in the 1930s that *Marasmius* spp. in culture were dependent on the Mn concentration for their growth and that a low level of Mn in a substrate may hamper the degradation of lignin. This finding was not pursued and not until the 1980s did additional detailed studies follow.

The role of Mn-peroxidase in lignin degradation is not clear, although one of its roles may be to form H_2O_2 (see Textbox 1). The enzyme itself shows no affinity to nonphenolic compounds, which, on the other hand, are readily

Textbox 1 Manganese peroxidase, an enzyme in the lignin-degrading enzyme system

Manganese peroxidase was discovered in 1985 as an enzyme in the lignolytic enzyme system. The enzyme is dependent on Mn^{2+} as a component, a so-called coenzyme. The Mn is essential for the activity of the enzyme. Mn-peroxidase is the most common lignin-modifying peroxidase produced by almost all wood-colonizing basidiomycetes causing white-rot and various soil litter-decomposing fungi. Multiple forms of this enzyme are secreted by ligninolytic fungi into their microenvironment, where the enzyme can dissolve parts of the lignin in wood to be released in soluble form. The enzyme is not only active against different lignin species but can also participate in the degradation of, for example, humic acids.

When degrading a substrate, the Mn-peroxidase preferentially oxidizes manganese(II) ions (Mn^{2+}), which always are present in wood and soil, into the highly reactive Mn^{3+} ion, which is stabilized by, among other substances, oxalic acid, and sometimes precipitated. Such oxalic-acid chelated Mn^{3+}, which has a low molecular weight and is diffusible, acts, in its turn, as a redox-mediator that attacks phenolic lignin structures, resulting in the formation of unstable free radicals. Mn-peroxidase is capable of oxidizing and depolymerizing natural and synthetic lignins as well as entire lignocelluloses, for example, in milled straw or wood in cell-free systems. Depolymerization is enhanced in the presence of co-oxidants such as unsaturated fatty acids.

attacked by ligninase. It has been found that MnO_2 stabilizes lignin peroxidase and may accumulate in wood attacked by white-rots (Blanchette *et al.*, 1984). Manganese is also involved in the regulation of other lignolytic enzymes, including laccase (Archibald and Roy, 1992) and lignin peroxidase (Perez and Jeffries, 1992).

3. Effect of the C Source on Lignin Degradation

It appears that the presence of a carbon source other than lignin stimulates the lignin degradation for several white-rot species, including *P. chrysosporium*, *Coriolus versicolor*, *Coriolus hirsutus*, *Polyporus* spp., and *Lentinus edodes*. It has been also found that cellulose has a stronger stimulating effect on lignin degradation than, for example, glucose, an

observation that was ascribed to its lower availability, thus an influence of catabolite repression could be expected (cf. Section C.1.). The major organic compounds in litter are normally the insoluble ones, such as lignin, cellulose, and hemicelluloses, and the latter ones normally supply the lignin-degrading organisms with alternative C sources.

A large group of the white-rots may degrade lignin preferentially to cellulose (Hatakka, 2001). Although almost all white-rot fungi produce Mn-peroxidase, this enzyme appears to be the most important lignolytic enzyme for those fungi that prefer lignin to cellulose.

D. Degradation of Lignin

Lignin degradation is a process that differs among three general groups of decomposers called white-rot, soft-rot, and brown-rot. Although the names are old and refer to characteristics easily seen by the eye, there are also functional differences in the enzymatic degradation mechanisms, which motivate continued use of the terminology. The names often are used in connection with fungi, although bacteria also can degrade lignin and be classified according to this terminology. Some characteristics for the lignin degradation of each of these groups are given in the following text, starting with white-rots, which probably are the best-investigated lignin degraders known.

1. Lignin Degradation by White-Rot Fungi

There is a large number of different enzymatic mechanisms for lignin degradation in white rots, but only one is well described so far, namely that for *Phanerochaete chrysosporium*. White-rot organisms possess the ability to completely mineralize lignin to CO_2 and H_2O. The attack on the lignin structure has long been considered to start with the removal of the methoxyl group (Fig. 5A,B). More recent research has shown that a first step is a combination of demethylation and hydroxylation, resulting in adjacent OH groups on the aromatic ring, creating a starting point for the next step, which is an oxidative attack on the aromatic ring (Eriksson *et al.*, 1990), resulting in ring cleavage and the creation of carboxyl groups. This cleavage of the aromatic ring (Fig. 5) is an oxygen-demanding step and experiments in an atmosphere of ambient air and pure oxygen (Table 3) illustrate a higher mass loss from decomposing lignin in the pure O_2. In the following steps, parts of the former aromatic ring are broken off and larger units are also broken off from the main lignin structure.

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) (see following text). Comparisons of the lignolytic system of *P. chrysosporium* to those of other white-rot fungi indicate that several different lignolytic enzyme systems exist. It has even been suggested that the lignolytic systems could be species-specific, which would mean that, for example, each fungal species would have its own lignolytic enzyme system and be the basis for a special ecological niche (Hatakka, 2001). A good example of such a relation to ecological niche is that of the white-rot *Ganoderma lucidum*, which produces Mn peroxidase in a medium with poplar wood but not in one with pine wood (D'Souza *et al.*, 1999). This observation may help to explain why white-rot fungi are more commonly found on angiosperm than on gymnosperm wood (Gilbertson, 1980).

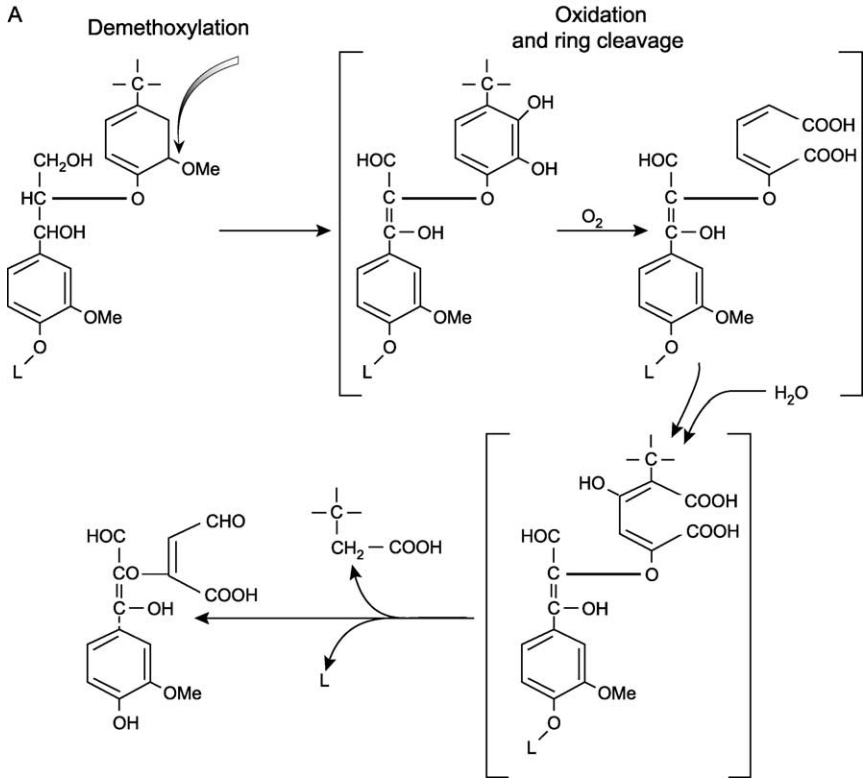

Figure 5 (*continued*)

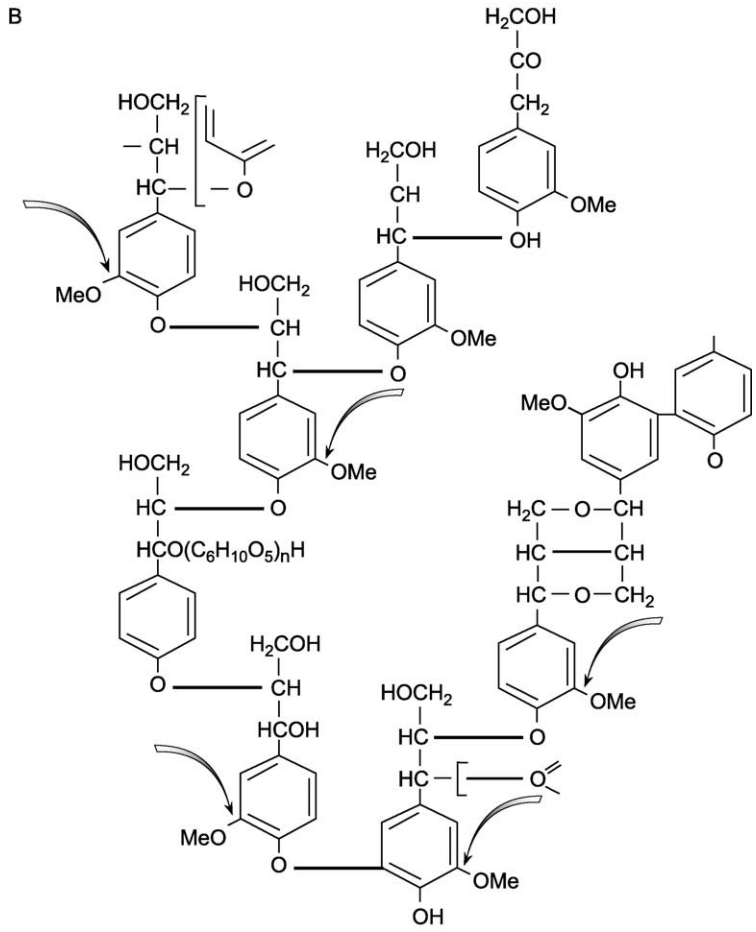

Figure 5 Part of a lignin molecule of spruce during degradation. (A) In the degradation by white-rots (from Kirk, 1984), a demethoxylation and hydroxylation are followed by an oxidative step leading to ring cleavage. (B) The same molecule under attack by brown-rot fungi. In this case, only methoxyl groups are removed by the enzyme.

2. Lignin Degradation by Soft-Rot Fungi

Today, it has been well confirmed that soft-rot fungi do degrade lignin and, in laboratory experiments using pure cultures and whole wood, up to 44% of the lignin was degraded at a wood mass loss of 77% (Nilsson, 1989). In general, soft rots are considered to degrade lignin, at least to some extent—less than white-rots but clearly more than brown-rots. An observation made

Table 3 Degradation of aspen wood lignin by different white-rot fungi in the presence of air or pure oxygen[a]

	$^{14}CO_2$ evolution [%]		Klason lignin loss [%]	
Fungal species	Air	O_2	Air	O_2
Phanaerochaete chrysosporium	10.8	35.2	13	40
Coriolus versicolor	14.6	35.5	24	46
Gloeoporus dichrous	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

[a]Determinations were made as $^{14}CO_2$ evolution and as Klason lignin. From Reid and Seifert (1982). With kind permission of Springer Science and Business Media.

Textbox 2 Syringyl and guaiacyl units versus lignin degradation

We may speculate that since softwood lignin has a high level of guaiacyl units (see following text), at least soft-rots have less potential to degrade lignin from conifers. In contrast, the syringyl units of deciduous species have been observed to be more readily oxidized by soft-rots.
This might be of importance for the fungal populations of different ecosystems, and could be an important factor for a difference in lignin (and litter) degradation between coniferous and deciduous forest floors.

on the fungus *Daldinia concentrica* may explain why these fungi prefer to degrade lignin of hardwood species to that of softwoods. This fungus degraded birch wood efficiently but not that of pine (Nilsson, 1989) and an explanation can be that the lignolytic peroxdidases of soft-rot fungi have less potential to oxidize the softwood lignin with a high level of guaiacyl units. In contrast, the syringyl lignin in hardwoods is readily oxidized by soft-rot fungi (Nilsson *et al*., 1989) (Textbox 2).

3. *Lignin Degradation by Brown-Rot Fungi*

Brown-rot fungi decompose mainly the cellulose and hemicellulose components in wood and, although they have the ability to significantly modify the lignin molecule, they are not able to completely mineralize lignin. They can degrade cellulose and hemicellulose in a fiber with a relatively small loss of lignin.

Brown-rot fungi are considered to have some similarities in their degradation mechanisms to those of white-rot fungi. In both cases, the formation of hydroxyl radicals (see Textbox 3) that attack wood components is important and high oxygen tensions support the degradation (Hatakka, 2001). The radicals formed by brown-rot fungi can remove methoxyl groups from lignin, produce methanol, and leave residues of modified lignin (Eriksson *et al.*, 1990). It was assumed earlier that all brown-rot fungi use the same mechanism for wood decay. However, newer research has indicated that similarly to white-rots, brown-rot fungi have a number of different mechanisms. The initiation of the degradation of both lignin and cellulose appears to be by diffusible small molecules that can penetrate the fiber cell wall. In contrast to white-rots, only one brown-rot fungus has been found to produce Mn-peroxidase.

Relative to native lignin, brown-rotted lignins are structurally modified and the aromatic rings have decreased numbers of methoxyl groups and increased numbers of hydroxyl groups (Fig. 5) (Crawford, 1981). It has been observed that also carbonyl and carboxyl groups are formed (Jin *et al.*,

Textbox 3 A hydroxyl radical participates in the degradation of lignin

Part of the degradation of lignin is carried out through non-enzymatic processes. In one of these, the so-called hydroxyl radical plays an important part. Although not all steps in lignin degradation are understood, we mention the concept here.

When oxygen is reduced, hydrogen peroxide is formed, which in its turn is split in a reaction. Below we have given a general chemical reaction. So far it is not known how fungi carry out the reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$

It seems clear, though, that the highly mobile radical ($^{\bullet}OH$) is produced by fungal enzymes, among others, a cellobiase oxidase and laccase. Hydroxyl radicals may cause an oxidation of lignin to quinines.

1990). Brown-rotted lignin is more reactive than native lignin due to the increased content of phenolic hydroxyl groups.

IV. DEGRADATION OF FIBERS

Previously, we have described the degradation of the single compounds that build up the fibers and how the compounds are arranged. Still, when lignin, cellulose, and hemicelluloses are combined into a fiber structure (see Chapter 2, Fig. 7), new effects appear due to the increased complexity of the substrate and so different decomposer groups follow different organic matter decomposition pathways.

A. Fungi

White-rot fungi carry out two different types of fiber degradation, namely, simultaneous rot and selective lignin degradation. Some species can carry out both types (Blanchette, 1991). In simultaneous rot, both lignin and the carbohydrates are degraded simultaneously. The fungi 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 of degradation, selective delignification, often results in cell separation as well as overall thinning of the cell walls.

White-rots sometimes seem to have a delay or lag time, with relatively slow mass loss before a period of mass loss that is more rapid. 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, into solutions containing proteins of known sizes. 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 with a higher rate of mass loss.

Soft-rots generally develop and grow under conditions that are not favorable for Basidiomycetes. However, a key for good growth of soft-rots is 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 ligninlike materials accumulate on the edge of the cavities. Type II causes cell-wall erosion, but unlike white-rot, soft-rot does not degrade the middle lamella (Fig. 7, Chapter 2). It is possible that the middle lamella is resistant to this group of fungi because its lignin contains more guiacylpropane units. Type II is more common in angiosperms.

Brown-rot fungi have the ability to degrade holocellulose in plant cell walls without first removing lignin and apparently begin their attack on fibers by degrading the hemicellulose matrix. A support for this theory is that xylans begin to disappear before cellulose (Highley, 1987). The first step is a rapid decrease in the degree of polymerization of the holocellulose polymers. In wood, the result is a rapid loss of fiber strength when the large polymers are fractured. These two factors suggest that agents smaller than enzymes are involved (Green and Highley, 1997). This initial degradation step is generally accompanied by a relatively low mass loss.

In fiber degradation, brown-rot fungi appear first to attack the S2 layer, leaving the S3 layer until later (see Fig. 7, Chapter 2; Highley *et al.*, 1985). Although the reason for this is not known, a proposed mechanism that agrees with observations was given by Hirano *et al.* (1997). They suggest that the brown-rot fungus grows into the cell lumen and releases a low molecular mass substance (molecular weight 1000–5000) that probably diffuses into the S2 layer. Fe(III) is then reduced to Fe(II) and becomes chelated by this substance. 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 (Textbox 3). Of course, more work is needed to validate this mechanism and to identify the unknown substances required for its operation.

B. Bacteria

Though bacteria have long been known to be involved in decomposition of litter, they have received far less attention and have been less studied than fungi in regards to the enzymatic mechanisms. In most cases, bacteria coexist with fungi, and their presence has been shown to increase and even double the rate of fungal growth on wood and increase the overall rate of decay (Blanchette and Shaw, 1978). Although bacteria once were considered not capable of degrading lignified cell walls without some type of pretreatment, a variety of fiber-degrading bacteria has now been identified. Three types of bacterial degradation have been recognized, the types based on the manner in which they degrade the cell walls of the substrate, namely tunnelling, erosion, and cavitation (Blanchette, 1995). Bacterial decomposition seems to be more common in situations where fungi are under stress, which means that they live under suboptimal conditions.

Bacteria have also been found to degrade substrates, especially wood, that resistant to fungal decay (Singh *et al.*, 1987).

V. MICROBIAL COMMUNITIES AND THE INFLUENCE OF SOIL ANIMALS

A. Microbial Succession and Competition

The composition of the microbial community that invades newly shed litter and litter in late decomposition stages depends on the initial properties of the litter and the changes in litter properties over time. Decomposer communities undergo many of the same processes as do communities of primary producers. These processes include succession and competition, and the pathway of plant litter decay may be influenced by modifications in these processes.

The change in microbial communities composition over time (microbial succession) is related to the change in quality of the decomposing substrate, but it also occurs because different organisms invade substrates at different rates. An example is taken from a study on the fungal community on common ash, common oak, and European beech twigs, where the succession of species was followed (Griffith and Boddy, 1990). The primary colonizers included endophytes, that is, fungal species that were present on the twigs already while they were still alive. Secondary invaders did not show up in appreciable numbers until about 11 months after twig death. This group did not include endophytic species. Griffith and Boddy (1990) identified a third type of colonizer, which they called "the superficial," which appeared on the surface rather early when decay had started. Still, these species were not present on the living twig. It is probable that this pattern is similar for all litter types, though, of course, the species and the timing may differ. As an example, spruce needles normally persist on twigs for some time after death but decomposition can begin when needles ultimately fall onto the forest floor and 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 microbial succession that occurs along with decomposition, there are seasonal changes in the microbial community reflecting the seasonal changes in temperature and moisture. For example, Kayang (2001) followed fungi, bacteria, and selected enzyme activities in newly shed leaves on Nepalese alder in India under a climate that was described as subtropical monsoon. Frosts occur there during December and January, and the dry season lasts from November through March. The fungal and bacterial propagule numbers varied by a factor of nearly five between winter and

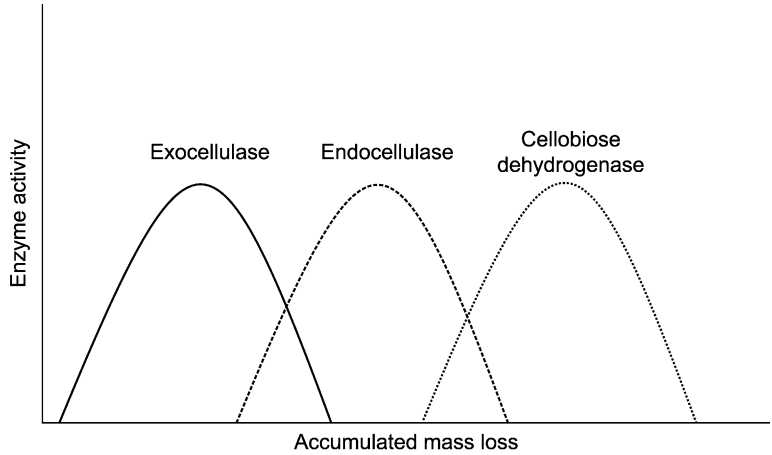

Figure 6 The three main enzymes in the cellulolytic system appear in a sequence in the substrate being decomposed exocellulase, endocellulase, cellobiose dehydrogenase. General pattern based on data from Linkins *et al.* (1990).

summer. Activity of different enzymes such as invertase, cellulase, and amylase reached their peaks, in that order, before microbial numbers, namely between April and June, and then fell slowly. The sequence of peaks shows a succession of enzyme activities reflecting a succession of microorganisms.

When investigating the activity of cellulases and cellobiose dehydrogenase on leaf litter in laboratory microcosms, Linkins *et al.* (1990) observed similar patterns for three different litter species. The litter originating from red maple, flowering dogwood, and chestnut oak differed in decay rates and in concentrations of lignin. 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. When cellulase activity began to decline, the cellobiose dehydrogenase activity started to increase (Fig. 6).

As fungal communities are changing, so are the enzyme activities. Osono and Takeda (2001) investigated the fungal populations on Japanese beech leaves as they decomposed in a cool temperate deciduous forest. Both total and living fungal biomass increased during the first year of decay and then fluctuated for the remainder of the study period. The percentage of fungi belonging to Basidiomycetes increased for the first 21 months of the study, and reached a maximum of 25 to 35% of the total living fungal biomass. The authors noted that the relative abundance of Basidiomycetes was linearly and negatively related to the lignocellulose index (cf. Section IV.B.2, an index of litter quality equal to the fraction of holocellulose in the lignocellulose complex. As part of their study, they identified over 100 fungal taxa on

the beech leaves and distinguished three groups: (i) an early-appearing group, (ii) a late-appearing group, and (iii) a group of species constantly present. 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 (see Chapter 5).

Decomposer populations may work synergistically or in competition. Competition is visible in, for example, decaying logs where clear and discrete zones of decay caused by different organisms can be easily distinguished. There are examples where the organisms define their boundaries with black zone-lines, which make them very clear. The interactions may change as decomposition proceeds. For example, Bengtsson (1992) found a synergism with no evidence of competition between fungi and bacteria on leaves of common beech during their first year of decay in stream microcosms. In comparison, Miller *et al.* (1999) found clear evidence of competition between fungi and bacteria on one-year-old beech leaf litter, and also in a microcosm study. This difference may relate to the litter age, and hence the state of decomposition, the litter quality, and the combination of species.

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

There are many interactions among the microorganisms involved in decomposition of litter and these interactions change over time. These dynamic systems are complex and 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 test the hypotheses about litter decomposition precisely. 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.

B. Effects of Soil Animals on the Decomposition Process

Although for tropical forests, some authors report litter decomposition by soil animals to be twice as high as that performed by microorganisms (Swift *et al.*, 1981), in the light of newer findings, it is very doubtful that animals are able to decompose the polymer organic compounds in litter, in the strict meaning of the term. Complex organic polymers, such as lignin, can be degraded solely by microorganisms. Invertebrates able to digest such polymers do so through symbiotic microorganisms inhabiting their digestive tracts; also, in such cases, there are the microorganisms that are ultimately

responsible for organic matter degradation. This, by no means, should be understood as neglecting animals' role in organic matter decay. Even if the biochemical/enzymatic degradation is performed by microorganisms, soil fauna plays an important role in many ecosystems, even in the temperate climate and boreal zones. In general, we may consider their role to be such that they increase litter palatability to microorganisms through mechanical transformation of freshly shed litter, for example, by comminution of leaves or needles and thus opening new surfaces for microbial attack.

Soil animals, by grazing either directly on microorganisms (e.g., fungi-feeding springtails) or on dead organic matter inhabited by bacteria and fungi, can also spread their populations and increase the turnover rate, thus enlarging microbial productivity and, in consequence, the amount of organic matter transformed. Mixing organic matter with mineral soil and digging activity improves soil aeration and creates more favorable conditions for aerobic microorganisms, such as lignin-degrading fungi. Thus, even if a direct participation of soil animals in organic matter decomposition is minor, their overall influence cannot be underestimated, especially in warmer climates. For example, in Mediterranean forests, just one species of millipede, *Glomeris marginata*, can consume as much as 8 to 11% of the annual leaf litter fall (Bertrand *et al.*, 1987). A population of another diplopod, *Cylindroiulus nitidus*, in an oak forest in southern France was estimated to consume as much as 10 to 14 g litter per square meter yearly, also a substantial amount (David, 1987). Couteaux *et al.* (2002) studied the effect of temperature and presence of *G. marginata* on litter decomposition rate. Although the studies were carried out over a broad range of temperatures (4, 8, 15, 23, and 30°C), a significant increase in decomposition rate attributable to the presence of *G. marginata* was detected only at 15 and 23°C (Table 4). More detailed studies allowed the authors to hypothesize that the animals affected litter decomposition by increasing the decomposition asymptotic limit value (cf. Section IV.F, Chapter 4) rather than increasing the decomposition rate itself (Table 4; Couteaux *et al.*, 2002).

Other groups of soil animals besides arthropods, which are important for decomposition through their effect on fungal and bacterial populations, are protozoans, nematodes, enchytraeids, and earthworms. The first two groups, inhabiting the smallest soil cavities and pores and living in the thin water film covering soil aggregates, graze on bacteria and fungi, causing a release of soluble nutrients and affecting microbial populations' growth rates (Bamforth, 1988). In an experiment with metal-polluted soil, adding enchytraeids and microarthropods to soil columns increased leaching of dissolved carbon and nutrients by 20 to 30% (Bengtsson *et al.*, 1988). Komulainen and Mikola (1995) found a significant increase in mineral nitrogen release from microcosms containing the enchytraeid *Cognetia sphagnetorum* in a comparison between an enchytraeid–microorganism system and one with

Table 4 Remaining mass, out of original 5 grams, after 198 days incubation of Aleppo pine litter at different temperatures in the absence or presence of *Glomeris marginata* (averages ± standard deviations) and calculated decomposition limit values—asymptotes for carbon mineralization estimated with asymptotic regression model for CO_2 release from litter during experimental incubation (Couteaux *et al.*, 2002)

	Without *G. marginata*		With *G. marginata*	
Temperature (°C)	Remaining mass (mg dry mass)	Limit value (mg C released)	Remaining mass (mg dry mass)	Limit value (mg C released)
4	3.47 ± 0.01	1719	3.45 ± 0.06	1720
8	3.29 ± 0.01	1293	3.26 ± 0.03	1370
15	3.14 ± 0.08	1098	2.98 ± 0.08	1283
23	3.10 ± 0.04	1002	2.93 ± 0.12	1131
30	2.99 ± 0.04	1126	2.83 ± 0.03	1204

microorganisms only. Raised CO_2 evolution and mineralization of nitrogen and phosphorus from litter and organic soil as the effect of the presence of soil fauna was also found by Huhta *et al.* (1991). As microorganisms may be limited by nutrient availability in litter and humus, at least in some ecosystems and decomposition stages, any activity increasing nutrient accessibility would promote microbial population growth and, in consequence, decomposition rate. As discussed previously, this is definitely one of the results of faunal activity in soil. Teuben and Verhoef (1992) calculated that Collembola alone increase NO_3 availability by 2.4 times through its production of feces.

Although a number of studies, such as those already cited, indicate the importance of faunal activity for mineralization rates, for microbial activity, and for biomass development, the present state of knowledge is not clear enough to take a general influence of soil fauna for granted (see also the introductory part of this chapter). In some studies, the overall effect of soil invertebrates on organic matter mineralization was found to be small or even negligible. For example, Kandeler *et al.* (1994) did not find any influence of mesofauna on microbial biomass under field conditions. Further, they found that activities of extractable enzymes in soil (xylanase, cellulase, and beta-glucosidase) were not affected by exclusion of meso- and macrofauna, indicating that the fauna did not influence the microbial population.

The presence of soil fauna may also exert different influences on microbial biomass and CO_2 release rate, as in the study by Forster *et al.* (1995). These authors, studying interactions between microorganisms and enchytraeids in grassland soil and litter, found that the worms did not affect microbial

biomass but increased soil respiration rate. In a more recent study on effect of species richness and density of soil mesofauna on nutrient mineralization in an Italian ryegrass field, Cole *et al.* (2004) found, in turn, that soil respiration decreased with increasing density of microarthropods, while the biomass of microorganisms was not affected. Despite that, concentrations of total nitrogen and NO_3–N in soil leachate increased with increasing faunal density, indicating an enhancing effect of microarthropod abundance on nutrient release rate. Species richness had, however, the opposite effect in regard to the respiration rate and nitrogen concentration in leachate. Such results indicate an indirect influence of faunal activity, probably by stimulating microbial population turnover rates.

We have seen several studies in the literature involving adding different biocides to soil with the intention to eliminate part of the fauna. We have avoided presenting the results of such studies since they are difficult to interpret. It is known that biocides may affect microbial communities directly, which means that a selective effect is not achieved. Furthermore, sometimes biocides may even serve as a carbon source for microorganisms, confusing the results.

Yet another way in which mesofauna may affect litter decomposition rate and nutrient turnover in ecosystems was described by Chapman *et al*. (2003), who studied effects of arthropod herbivores on litter quality in a semiarid forest of pinyon pine. Although these effects are obviously secondary and do not even relate to soil fauna, they are certainly worth mentioning when discussing the role of fauna on litter decomposition. The authors found that both species of herbivores studied significantly increased N concentration and decreased the lignin: N ratios of aboveground litter. Also, litter phosphorus concentration and annual needle litter-fall mass increased due to herbivory. Thus, herbivory produced litter that was richer in nutrients and decomposed more rapidly. Chapman *et al.* conclude that ''herbivory may increase nutrient cycling rates in this system by altering the chemical quality of litter.''

As we have mentioned, the effect of faunal activity on litter decomposition seems larger in tropical ecosystems than in more northern, that is, boreal ones. However, even this difference is not that straightforward. For example, Gonzalez and Seastedt (2001) found higher faunal effects on litter decomposition in tropical wet forests than in subalpine forests, but also in tropical dry forests, effects of fauna on decomposition was lower than in the wet tropical forests. As a result, no general difference in effect of fauna on annual decay rates between tropical and subalpine forests was found. Although these results may seem contradictory at first glance, we may recall that litter decomposition rates are strongly dependent on both temperature and soil/litter moisture. Gonzalez and Seastedt (2001) found that the total density of soil fauna was highest in wet tropical forests, followed by the subalpine

forests, and the lowest densities were found in dry tropical forest. They summarize their finding by stating that soil fauna has a disproportionately large effect on litter-decay rate in tropical wet forests as compared to the tropical dry forest or a subalpine forest.

Besides climatic effects on soil fauna activity, the effect of forest floor type (humus type: mull, moder, or mor) is another obvious line of inquiry. The results, however, are not as clear as might be expected. Bocock *et al.* (1960) incubated European ash and durmast oak leaf litter in nets with 1 cm mesh on mull and moder sites. Oak litter decay rates were independent of the forest floor type, but ash leaves disappeared much more rapidly on mull sites. It is important to note that there was significant earthworm (*Lumbricus terrestris* L.) activity on the mull site and that disappearance may be greater than actual decomposition because material could be easily moved out of the coarse mesh nets.

As can be seen from the examples presented, there is no general agreement about the role of soil animals in litter decomposition. Advances in this area of soil research are hampered by a number of technical complications. For example, allowing access of soil invertebrates, especially meso- and macrofauna, to litterbags or field micro/mesocosms makes it impossible to distinguish any actual effect on litter disappearance due to mechanical removal of the material. Similarly, distinguishing direct faunal decomposition of organic matter from that due to activities of symbiotic microorganisms inhabiting digestive tracts of many soil invertebrates is next to impossible at the present stage of knowledge. We may state that effects of soil fauna on litter decomposition, and soil structure in particular, are manifold and comprise such processes as mechanical shredding of litter material, mixing organic matter with mineral soil, distributing soil microorganisms and grazing on them, and increasing palatability of dead organic matter and nutrient availability to bacteria and fungi. Further, soil fauna may structure soil through digging activity and deposition of fecal pellets as well as having a more direct participation in decomposition either through their own digestive systems or due to activity of symbiotic microorganisms. Thus, even if direct litter decomposition through soil fauna might be negligible, the overall effect on organic matter fate and soil properties may be significant. The prime example is formation of mull-type soils, whose properties are largely determined by effective mixing of dead organic matter with mineral soil—a process performed almost exclusively by soil meso- and macrofauna. In the absence of these two groups of soil fauna, a completely different soil type is formed, with separate, thick layers of less decomposed organic matter (mor-type soils).

Changes in Substrate Composition and Rate-Regulating Factors during Decomposition

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I. INTRODUCTORY COMMENTS

In the course of decomposition, the litter is subject to considerable chemical changes when being converted from fresh litter to humus. Only some of these chemical changes are known; most remain to be discovered. Those chemical changes that have been described are known for only a few species of foliar litter and a few ecosystems and, even today, we can not say that the chemical changes described in this chapter have general validity. Regarding the dynamics of nutrients and metals, these have been studied mainly for nutrient release and cycling on the ecosystem level (Anderson and Macfadyen, 1976; O'Neill *et al.*, 1975) and apparently less to reveal the finer details of the chemical composition of litter, such as when it approaches humus, or details in quantitative uptake or release. Still, several studies also provide concentration changes during decomposition (Dwyer and Merriam, 1983; Dziadowiec, 1987) of the major plant nutrients (Berg and Staaf, 1981; Blair, 1988a,b; Laskowski *et al.*, 1995; Rashid and Schaefer, 1988).

Although a number of scientists focus their studies either on major plant nutrients or on "heavy metals," the distinction between these two groups is not clear. The term *heavy metals* is often used for pollutants, although a number of elements from this group also belong to nutrients (such as Zn and Cu). In this chapter, we treat selected heavy metals as nutrients in unpolluted systems and discuss their dynamics in that context.

The microbial decomposers of litter organic components are selective toward different compounds, which results in clear patterns in chemical changes in the course of litter decomposition. Each such pattern may be related to the initial chemical composition of a given litter type. In this chapter, we describe detailed chemical changes for Scots pine needle litter as a case study and, in applicable parts, we also present data from other boreal and temperate species. The patterns discussed here have been found mainly in boreal systems but probably have higher generality and even such different systems as decomposing chaparral shrubs show similar decomposition patterns as litter from boreal tree species (Schlesinger and Hasey, 1981).

The chemical changes taking place during initial decomposition stages expose compounds of different kinds and different biological degradability to further decomposition. The decomposition dynamics in most so-far-investigated needle and leaf litter species follow the model presented in Fig. 1. In fact, it seems that the model covers not only different types of foliar litter, but probably also, to some extent, root litter, as well as litter from grass and herbs. Thus, the model may have relatively broad generality. On the other hand, some litter types show specific behaviors, and, for example, spruce needle litter deviates from the model. A possible explanation to that differing decomposition pattern is that spruce trees produce

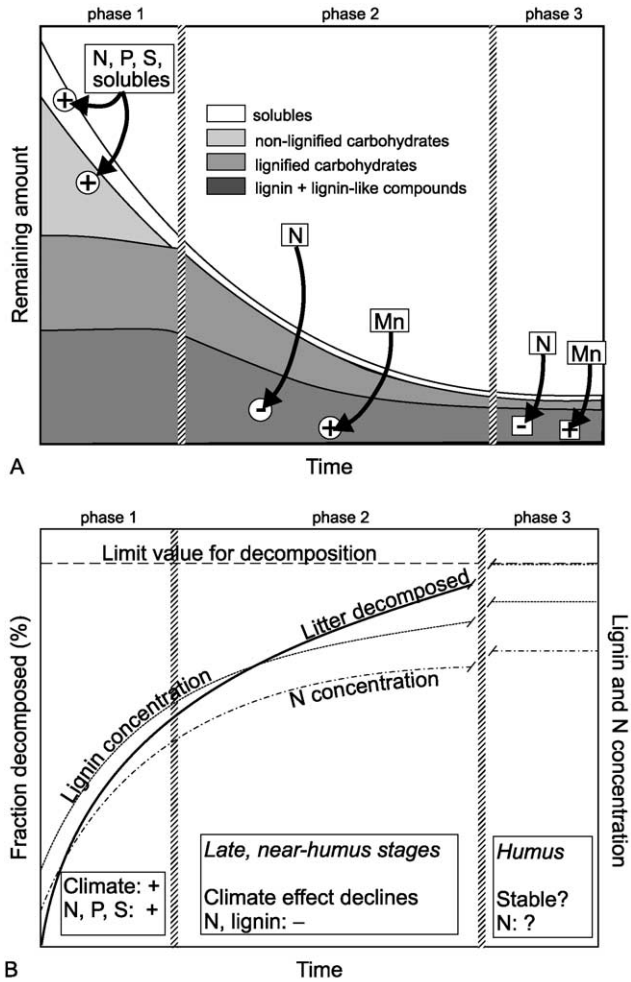

Figure 1 (A) Model for chemical changes and rate-regulating factors during decomposition, modified from Berg and Matzner (1997). The decomposition of water-soluble substances and unshielded cellulose/hemicellulose is stimulated by high levels of nutrients such as N, P, and S (early stage, phase 1). When all unshielded holocellulose is decomposed, only lignin-encrusted holocellulose and lignin remain. In this late stage (phase 2), the degradation of lignin rules the litter decomposition rate. The degradation of lignin is hampered by N, and higher N levels suppress its decomposition whereas Mn has a stimulating effect on the degradation of lignin. Finally, in the humus-near stage (phase 3), the lignin level is about constant, the litter decomposition rate approaches zero, and the accumulated mass loss reaches its limit value. (B) Lignin concentration increases up to a level of 50 to 55%, N concentrations increase, and the litter decomposition rate approaches zero as the accumulated mass loss approaches a limit value (Section IV.F).

more heterogeneous foliar litter which, in addition, is in a late decomposition stage (Section IV.C already when shed, as a consequence of an advanced decomposition of the needles while still attached dead to the twigs.

The decomposition process normally reaches a final stage at which it almost stops or goes so slowly that this stage may be approximately described mathematically by an asymptote. We have considered this to be a limit value for decomposition, which for foliar litter of different species normally ranges from 50 to 100% mass loss (Section IV.F). The level of this limit value has been negatively related to initial litter N levels, which means that the richer the litter is in N, the less it will decompose under comparable conditions. This relationship, which has been generalized for foliar litter types, is developed and discussed in this chapter as well as in Chapter 6.

Most litter species leach carbon compounds to differing extents. Such leaching may start in the early phase (Section IV.B) and continue throughout the following decomposition stages. Recent findings have indicated that raised N concentrations in foliar litter may support the leaching process of carbon compounds. The reaction mechanisms are still unknown. When litter is transformed to humus, this property of the litter/humus remains and it has been observed that, under some circumstances, the release of C compounds can be emphasized and accelerated. There are actually extreme cases reported with a very high reaction rate, causing an actual disintegration of very N-rich humus with a very fast degradation and leaching of N-rich compounds taking place. It has been speculated that this could be due to changes in the microflora. These findings will be further discussed in Chapter 6. The intention of this chapter is to demonstrate and systemize decomposition patterns as well as the effects of several chemical components and the chemically changing litter substrate on decomposition rates.

II. ORGANIC–CHEMICAL CHANGES DURING LITTER DECOMPOSITION

A. Decomposition of Single Chemical Components and Groups of Compounds

Microorganisms start degrading plant litter as soon as it has fallen to the ground and been invaded by decomposers, that is, by fungal mycelium and bacteria. The microorganisms that can utilize the soluble components start degrading them first and normally at a relatively high rate. The reason is that normally small soluble molecules are more easily available to microorganisms since they may be transported directly into the cell and metabolized. There is thus no need for the additional enzymes that are used to

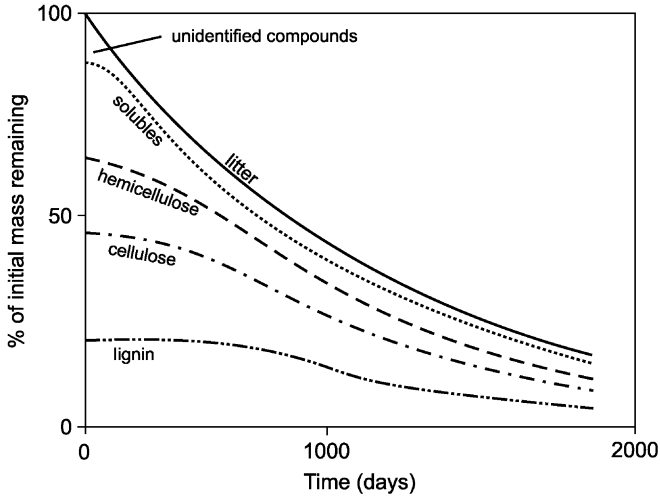

Figure 2 Degradation pattern of Scots pine needle litter. Remaining amounts of litter (upper full line) solubles, cellulose, hemicellulose, and lignin are given (from Berg *et al*., 1982). We see that the degradation of solubles and hemicellulose start in the first year, whereas a net loss of the sulfuric-acid lignin fraction does not start until later, in this case, the end of the second year.

depolymerize the larger molecules. The degradation of hemicelluloses, cellulose, and lignin starts later. We describe the process for Scots pine needle litter in more detail and comment on other litter species. Figure 2 provides an overview to the main decomposition pattern, including some main groups of compounds.

1. Water Solubles

The fraction of water solubles, being chemically complex, is far from a homogeneous substrate and the degradability of different components varies a great deal. Generally, in newly formed foliar litter, this fraction contains high levels of compounds such as simple sugars, lower fatty acids, and protein remains, such as amino acids and peptides. Such simple molecules can easily be taken up by microorganisms and metabolized. The fraction of water solubles thus should, at least in part, decompose rather quickly and its concentration should decrease (Fig. 3). Leaching may play a role, too, decreasing the concentrations of water solubles in the litter. The extent of leaching may vary among litter species and may range from less than 1% in Scots pine needle litter to approximately 28 to 30% of the water solubles being leached from willow and maple leaf litter (Table 1). When the leaching is low, as in Scots pine litter (Table 1), we may assume that a large part of the soluble material is degraded within the litter structure.

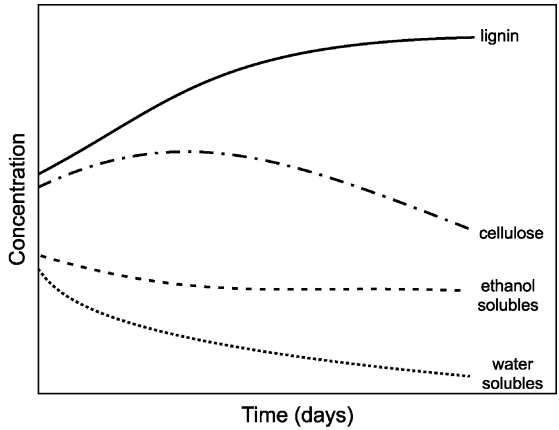

Figure 3 Changes in concentrations of water solubles, ethanol solubles, cellulose, hemicelluloses, and lignin in decomposing Scots pine needle litter.

Table 1 Leaching of water soluble substance from some leaf and needle litter species—laboratory measurements

Litter type	Potentially leachable water-soluble (% of d.w.)	Actually leached substance (% of d.w.)	Reference
Deciduous			
Ash	26.4	22.3	(2)
Ash	20.8	16.5	(3)
Black alder	12.2	12	(1)
Black alder	28.1	21.3	(2)
Common beech	6.2	3.8	(1)
Common oak	13.3	7.1	(1)
Downy birch	26.3	16.3	(2)
European maple	35	29.4	(2)
Mountain ash	26.9	22.8	(2)
Silver birch	13.7	10.7	(4)
Trembling aspen	27.7	25.2	(2)
Willow	31.4	27.9	(2)
Coniferous			
Norway spruce	12.5	1.1	(4)
Scots pine	9.2	<1	(5)
Scots pine	13.7	1.3	(2)
Scots pine	14.5	6.3	(2)
Scots pine	14.4	<1	(5)

References: (1) Nykvist (1962), (2) Bogatyrev *et al.* (1983), (3) Nykvist (1959), (4) Nykvist (1961a), (5) B. Berg, unpublished.

For our case study needle litter from Scots pine in a boreal system, the concentration of the water-soluble fraction was found to decrease from approximately 100 to 57 mg g^{-1} in about a year, whereas for the subfraction of simple sugars and glycosides alone, the concentration decreased from 31 mg g^{-1} to "not detectable" amounts in the same period. For some deciduous species that have been investigated, the decrease may be even more drastic (Table 1) and for silver birch leaf litter, the total water solubles decreased in one year from 321 to 45 mg g^{-1}, with part of the solubles being leached. Finally, the level of water solubles reached 40 mg g^{-1} after 4 years (Table 2). For Norway spruce needles, of which at least part is considered to start decomposing while still attached dead on the twigs, the concentration decreased from 114 to 38 mg g^{-1} (Table 2).

However, in the course of decomposition, new soluble compounds are formed during the decay of polymer compounds, such as holocellulose and lignin, and a low level of water-soluble compounds is almost always found in decomposing litter containing simple sugars from degrading polymer carbohydrates. In fact, even a compound as easily decomposable as glucose has been found in concentrations of up to 1% in Scots pine needle litter decomposing in the field for up to 5 years (Berg *et al*., 1982a).

2. *Ethanol Soluble Fraction*

In fresh litter, rather small molecules, not being water soluble, are often analyzed as ethanol solubles or acetone solubles. These solvents extract, among others, lower phenolics and higher fatty acids. This fraction sometimes contains compounds that suppress microbial growth, as seen for single fungal species (Berg *et al*., 1980), and we can expect also that mixed microbial cultures degrade these compounds more slowly than they degrade water solubles. All single components of this fraction have not yet been analyzed, not even for newly shed litter of one species (Chapter 2) and their degradability is thus not known.

The original components of this fraction are degraded but new compounds are added as the degradation of more complex compounds, such as lignin, proceeds and the concentration of ethanol solubles is often high even after some years of decomposition, as found, for example, for Scots pine and lodgepole pine (Table 2). For Scots pine, the concentration of ethanol solubles after 3 to 5 years' decomposition could be of a similar magnitude as in the initial litter. An example (Table 2) gives the concentration of 120 mg g^{-1} initially and 126 mg g^{-1} four years later. The same phenomenon was seen for decomposing needle litter of Norway spruce, lodgepole pine, silver birch, and grey alder. Although the total concentration of ethanol solubles does not change significantly in these litter species with

Table 2 Long-term organic chemical changes in some different decomposing litter types expressed as initial and final concentrations, that is, when the given mass-loss level was reached

Species	Water solubles (mg g^{-1})		Ethanol solubles (mg g^{-1})		Holocellulose (mg g^{-1})		Lignin concentration (mg g^{-1})		Final mass loss (%)	Reference
	Initial	Final	Initial	Final	Initial	Final	Initial	Final		
Scots pine	92	34	120	126	342	92	223	472	77.1	(1)
Lodgepole pine	109	44	42	53			366	482	75.3	(2)
Norway spruce	114	38	60	31			344	516	51.3	(1)
White pine	162	18	166	46	447	219	225	185	53.2	(4)
Silver birch	321	40	57	43			263	506	65.4	(2)
Grey alder	254	33	39	36			264	475	55.5	(2,3)

References: (1) Berg *et al.* (1982); (2) Berg and Ekbohm (1991); (3) Berg *et al.* (1991); (4) Aber *et al.* (1984).

time, particular compounds may differ in their degradability. Thus, after some years' decomposition of the litter, part of the chemical compounds making up this fraction are likely to be different from the initial ones.

3. *Cellulose*

The concentration of cellulose decreases, but only slowly (Fig 3). For example, in a study on Scots pine needle litter, the concentration decreased from 272 to 240 mg g^{-1} in two years, after which it remained rather constant (see also Section II.B). The changes in concentration are probably not independent of the litter's lignin. In a litter species with low lignin concentration, the concentration of cellulose is likely to change more drastically, whereas a high level of lignin means a higher level of cellulose encrusted in lignin and thus slower changes in its concentration. The same reasoning is likely to apply to the hemicelluloses.

4. *Hemicelluloses*

The most common hemicelluloses have similar behavior as regards their decomposition in litter. Largely, they behave similarly to cellulose, although they may occupy different positions in the fibers (Chapter 2, Section V.A). This means that the concentrations of, for example, xylan, mannan, arabinan, or galactan, decrease in the beginning of the decomposition process, becoming rather constant in the later stages. Considering the structure and chemical complexity of the hemicelluloses (Chapter 2, Section V.B), they could be combined and regarded as one group from the point of view of substrate for decomposition. Doing so and comparing the ratio between the sum of hemicelluloses and cellulose, we may see that it becomes rather constant as decomposition proceeds (Fig. 4).

5. *Lignin*

The concept of lignin in decomposing litter is not very clear (Textbox 1). Lignin, being defined through the analytical method applied, is rather unequivocal in, for example, pure wood or in fresh fodder, for which several of the existing analytical methods were developed. In decomposing plant litter, the lignin is modified by partial degradation by microorganisms as well as by humification processes such as condensation reactions (see Chapter 6). This raises the question whether "true" lignin is measured in the decomposing litter at all. In addition, the lignin fraction, as determined by gravimetric methods, also contains some other materials such as chitin from fungal

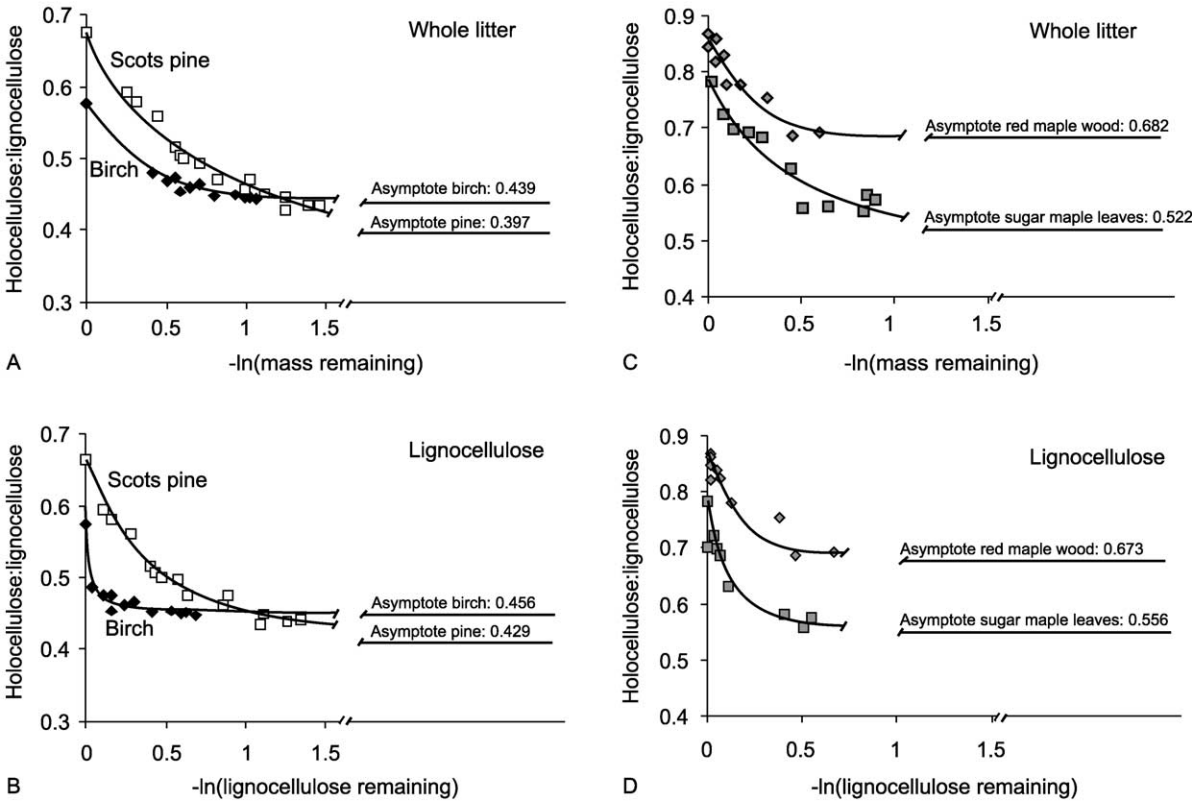

Figure 4 A fitted nonlinear model gives the decrease in the quotient holocellulose/ligno-cellulose as a function of litter mass loss (A,C) and mass loss of solid substance (B,D) as well as the asymptotic values that they approach. Scots pine needle litter and leaves of silver birch were incubated in a nutrient-poor Scots pine forest in central Sweden, sugar maple and red maple litter was incubated in a sugar maple forest in Wisconsin, USA. Redrawn from Berg *et al.* (1984).

Textbox 1 The Lignin Fraction

Several methods to determine lignin were originally intended for fresh wood (for the paper pulp industry, that is, Klason or sulfuric-acid lignin). The application of such methods on other substrates, such as different foliar litter species, both fresh and under decomposition, is not self-evident. The commonly used gravimetric determinations used in several methods may include components other than lignin, such as ash (Ca, Mg, and silicates) and also lignin recombination products. However, thus far, gravimetric determinations have been widely accepted, provided that they have been made correctly. Still, unexpected effects as regards the lignin fraction have been observed during decomposition and net mass increases in the lignin fraction have been reported (Berg and McClaugherty, 1988). For natural, unpolluted Scots pine needle litter, an increase in "lignin" mass up to 13% was observed. If humic acids, for example, are synthesized and recorded as Klason lignin, the measured process of lignin mass loss should be regarded as a net process.

Norden and Berg (1989) did not find any new peaks in the aromatic resonance region when applying high resolution 13C NMR to needle litter samples in decomposition stages from 0 to 70% accumulated mass loss, indicating that there does not appear to be any extensive synthesis of entirely new products. In addition, in their study, there was a clearly significant linear relationship between the lignin concentrations estimated using 13C NMR and sulfuric-acid lignin.

Compatibility among methods is not self-evident and Berg and McClaugherty (1988) compared lignin analysis according to Effland (1977) and to Klason (Bethge *et al.*, 1971) for fresh and decomposing litter and found no difference in concentrations, indicating a certain compatibility, at least from a quantitative point of view. The new analytical approach with near infrared reflectance spectroscopy (NIRS) (McTiernan *et al.*, 2003) is time-saving once a reference material has been stored. The spectra obtained with this method are often related to gravimetric measurements and the results thus are similar to the gravimetric measurements.

mycelium, an inorganic fraction (ash; Textbox 2), consisting of, among other elements, Si, Mg, and Ca. Although the ash fraction for Scots pine lignin normally is about 1%, it may reach as much as 10% for other plant species. The gravimetric lignin fraction should be additionally analyzed for ash to allow for comparative use of the analytical data (see also Chapter 9, Methods).

One may argue that although the analytical fraction determined with these traditional gravimetric methods is not truly native lignin, it may still be made up of a group of compounds derived from lignin, for example, by fixation of N compounds (Stevenson, 1994). Such partially modified lignin has, in part,

similarities to true lignin and may be degraded by lignolytic enzyme systems (Steffen, 2002). We may also keep in mind that structures of native lignin can differ vastly among litter species. As a consequence, in decomposition research, we need to consider that such defined lignin is not only modified due to decomposition but also highly variable among plant species as regards original, newly shed litter.

The nomenclature for lignin modified during decomposition remains problematic. Lignin and the term "lignins" is sometimes used and even the very incorrect "acid-insoluble substance" (AIS) is seen in the literature. The work presented in this book is based on sulfuric-acid lignin, and we use the term "lignin" for this analytical fraction in all stages of decomposition for the sake of convenience and identification (see also Textbox 3, Chapter 2).

During the course of decomposition, when the more easily degradable compounds are decomposed, lignin remains more or less intact for a long time (Fig. 2). This means that the litter becomes enriched in lignin and that its concentration increases (Figs. 1 and 3). Several studies using Scots pine needle litter have shown that the concentrations may reach up to approximately 500 mg g^{-1} (Table 2; Fig. 5). At a certain stage, when the more available and degradable holocellulose is decomposed, the remaining fiber will have lignin and its modified products as a protective barrier for its

Textbox 2 The Ash Fraction in Litter

Some foliar litter types may hold as much as 10% ash already when shed (Si, Ca, Mg, K), which affects the calculation of their levels of decomposition as well as levels of nutrients and other components. Also, litter that has been partly decomposed, especially when incubated on soil rich in mineral particles, may be contaminated with clay and fine mineral particles. The nutrient contents should thus be related to the litter organic matter, that is, the decomposable fraction rather than to the whole litter (see Chapter 9).

Textbox 3 The Lignin-Nitrogen Effect on Litter Decomposition Rate

The traditionally used concept about lignin retardation of litter decomposition rate may be questioned with the discovery that the rate-retarding effect may be due to a combined effect of nitrogen and lignin, with the latter as a mediator substance. This combined effect of nitrogen and lignin on litter decomposition rate has no name. The effect may be complex with an effect of N on lignin-degrading microorganisms (Section III.C, Chapter 3) and an effect through developing chemical barriers as part of the humification process (Sections IV. C and D, this Chapter). We suggest as a term"the nitrogen–lignin effect."

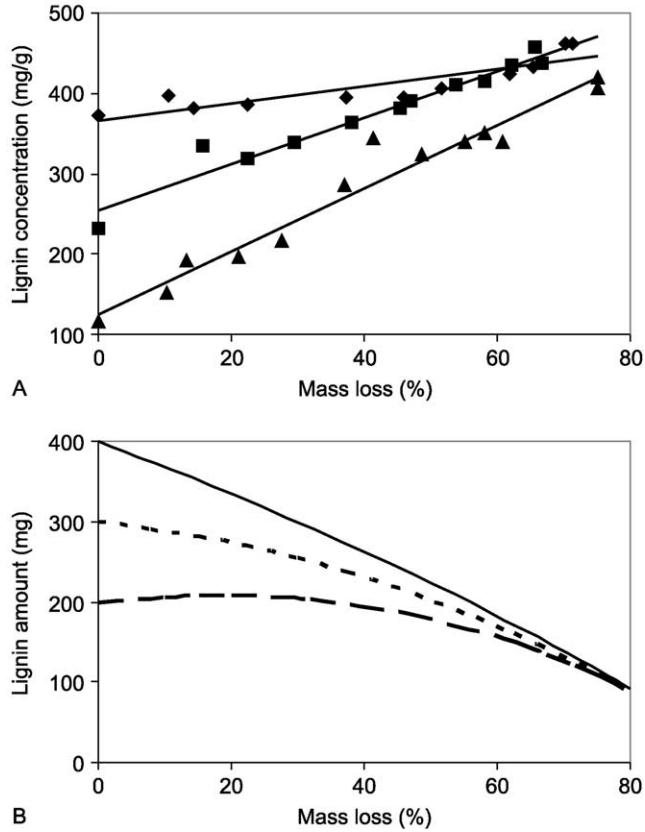

Figure 5 (A) Changes in lignin concentration during decomposition of needle litter of Scots pine (■), lodgepole pine (◆), and sugar maple (▲) with different initial lignin concentrations. Lignin concentration is plotted versus litter mass loss. (B) Onset of lignin degradation as compared to mass loss. The onset may be related to initial lignin concentration. We see that the degradation of lignin starts earlier in the lignin-rich litter. From Berg *et al.* (1997).

remaining holocellulose. This means that the degradation of holocellulose is dependent on that of lignin and lignin-like structures and when lignin and holocellulose are degraded further, the rates are similar and the concentration ratio of both groups of compounds remains about constant (see following text).

When different litter species have initially different lignin concentrations, these increase at different rates during the decomposition process: the higher the initial concentration, the lower the increase rate (Fig. 5). It also seems that irrespective of initial lignin concentration, the concentration reached

during decomposition approaches a similar maximum value. For example, in foliar litters, there appears to be a maximum concentration of lignin somewhere around 45 to 55%.

B. Relationships between Holocellulose and Lignin during Decomposition

Holocellulose and lignin differ substantially in their degradability, lignin being considered one of the most resistant components of foliar litter. As a result, the concentration of holocellulose decreases and that of lignin increases during decomposition, until a level is reached at which their proportions remain approximately constant. This proportion between the components has been described in the literature with two different quotients—the holocellulose-to-lignin quotient (HLQ) and lignin-to-cellulose index (LCI):

HLQ = holocellulose/(lignin + holocellulose) (Berg *et al*., 1984)
LCI = lignin/(lignin + holocellulose) (Melillo *et al.,* 1989)

The former quotient decreases as decomposition proceeds, and approaches asymptotically a minimum value, which may be different for different litter types (Fig. 4) and Berg *et al.* (1984) found a clear difference between the minimum HLQ values for Scots pine and silver birch. The latter quotient (LCI) increases and finally approaches a maximum value. After having been suggested, these two quotients have not been developed further or used as a substrate-quality tool. They may have a potential for calculations of litter degradability, though.

III. CONCENTRATIONS OF NUTRIENTS AND HEAVY METALS DURING LITTER DECAY

Again, we use studies on Scots pine needle litter as an example. The initial leaching of nutrients from Scots pine litter is generally low and, with the exception of potassium, often less than 1% of the whole amount of any given nutrient. Thus, the dynamics of nutrients is related rather to the microbial degradation.

The concentration dynamics of a number of nutrients presented in Fig. 6 is considered to be representative for pine litter in boreal forests. The patterns of particular nutrients are influenced by local environmental conditions, such as soil richness in different nutrients, which influences the microbial uptake of nutrients into the litter, and pH, which influences

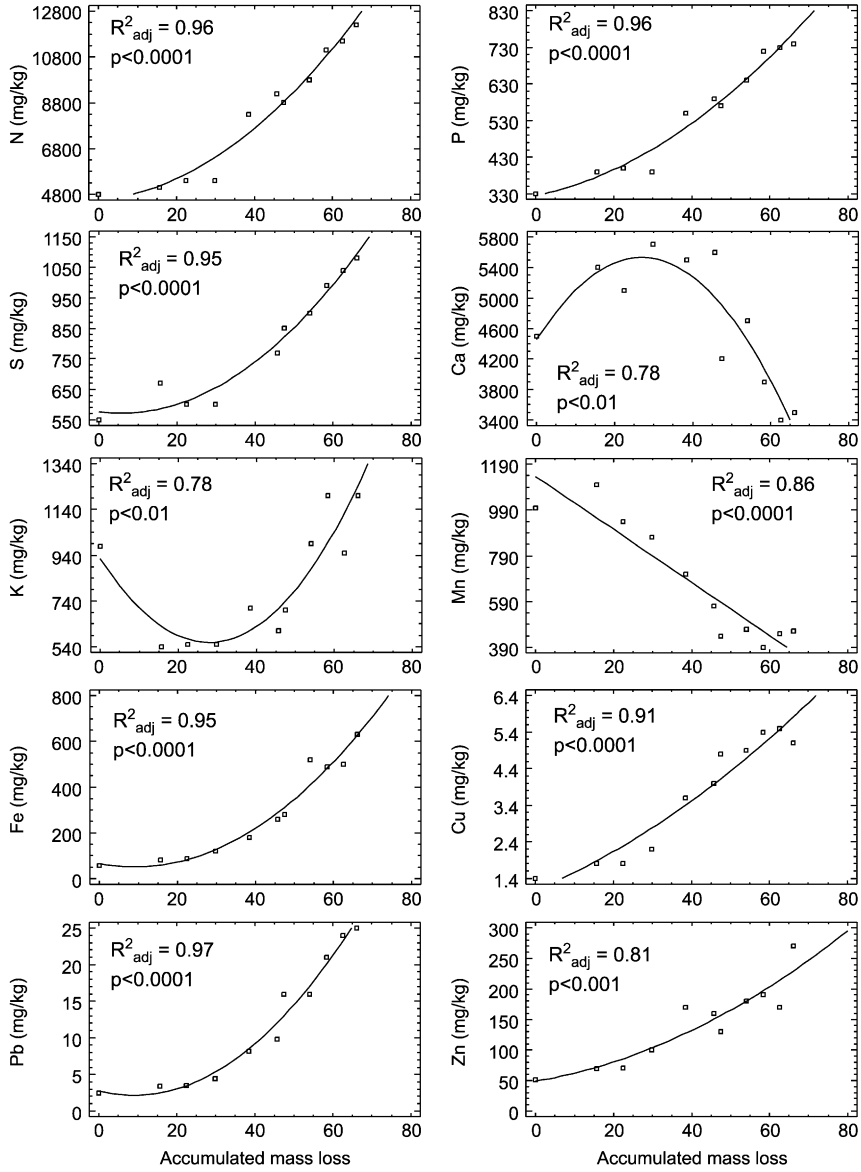

Figure 6 Concentration changes in N, P, S, Ca, K, Mn, Fe, Cu, Pb, and Zn during decomposition of Scots pine needle litter (B. Berg, unpublished). The concentration is plotted versus litter mass loss.

availability and mobility of several nutrients. Thus, with relatively few studies as a background, the observed patterns for concentration dynamics have clear uncertainties (Fig. 6).

A. Nitrogen (N)

The concentration of N in litter increases during decomposition. This increase may be described either versus time since incubation or as a function of litter mass loss. In the latter case, the decomposition process is regarded as a driving force for the change in N concentration. A positive, almost linear relationship of N concentration against litter mass loss results (Fig. 6) and allows for comparisons among different studies and treatments. This kind of relationship is purely empirical and has not been explained, although it normally results in R^2 values well above 0.9. It is limited to the mass loss interval from the start of the decomposition to the accumulated mass loss corresponding to the limit value. Different litter types have not only different initial N concentrations but also different increase rates, resulting in different final N concentrations (see Chapter 5).

For Scots pine needle litter, the N concentration may increase at least 3 times during decomposition: starting with approximately 4 mg g$-^{-1,}$ an increase up to approximately 12 mg g^{-1} has been recorded. In decomposing green Scots pine needles, N concentrations increased from 15.1 to about 32 mg g^{-1} and in grey alder leaves from about 30 to 51 mg g^{-1}.

B. Phosphorus (P)

As for nitrogen, the concentration of phosphorus in litter increases during decomposition and may be described as a positive function of litter mass loss, in which case, similarly to N concentration, the decomposition process of litter is regarded as a driving force for the concentration changes (Fig. 6). Initially, the concentration may decrease due to leaching. Also, for P, the relationship is empirical and no explanation has been found. For Scots pine needles, a four-fold concentration increase from approximately 0.2 to 0.8 mg g^{-1} has been observed (Staaf and Berg, 1982).

C. Sulfur (S)

Also, the concentration of S in litter increases during decomposition when related to accumulated litter mass loss and, similarly to nitrogen and phosphorus, it can stabilize or decrease at later stages. The positive exponential

relationship shown in Fig. 6 is purely empirical in this case. For Scots pine, an increase from 0.4 to 1.0 mg g^{-1} has been recorded (Staaf and Berg, 1982). A general observation is that, as with P, S often is leached initially, which means a decrease in concentration at the very beginning of the decomposition process.

D. Potassium (K)

This is probably the most mobile element among all plant nutrients, one reason being that it is present in leaf litter mostly in ionic form. Its leaching may start as soon as the litter has been shed. In decomposition studies, normally already at the first sampling, a heavy reduction in concentration is seen and a minimum value is reached, after which a slow increase starts. Due to potassium's high mobility, quick and large changes in concentrations may take place in the decomposing litter. A graphic representation of K concentration changes thus may result in very irregular patterns that may vary and change considerably among studies (Fig. 6). Some data suggest that in litter types with exceptionally low initial concentrations of K (below approximately 0.6 mg g^{-1}), an immobilization takes place from the very start of decomposition and, in that case, its concentration increases (Laskowski *et al.,* 1995).

E. Calcium (Ca)

Typically, Ca concentration initially increases in decomposing litter, reaching its peak, which is followed by a decrease (Fig. 6). The onset of a decrease has been related to the onset of lignin degradation (B. Berg, unpublished data) and a release mechanism described for N in Chapter 5, Section II.D may be applicable also in this case. Changes in Ca concentration often can be described by a negative quadratic equation and this main pattern is basically the same when concentrations are compared to time or to mass loss.

F. Magnesium (Mg)

Similarly to potassium, magnesium belongs to the rather mobile nutrients. However, its leaching is not as fast as that for K but its concentration normally decreases at a rather slow pace. Still, as for K, the decrease stops

at a certain concentration and a slow increase takes place as decomposition proceeds.

G. Other Metals and Heavy Metals in Natural Concentrations

Although there are a limited number of studies on the behavior of heavy metals during decomposition, virtually all studies indicate that the concentrations of most heavy metals increase as the litter decomposes and such concentration changes have been followed up to around 80% mass loss (Fig. 6). Their increase in concentration usually can be described by an exponential or a linear model. In most cases, this increase is faster than can be attributed just to conservation of the existing amount and suggests that an import takes place. The routes of this import are not fully recognized yet and at least two possibilities have been put forth: import from the soil with ingrowing fungal mycelia (Berg *et al.*, 1991; McBrayer and Cromack, 1980) and input with throughfall (Laskowski *et al.*, 1995; McBrayer and Cromack, 1980). For example, Laskowski *et al.* (1995), using a relatively unpolluted area in Poland for their studies in oak–hornbeam and pine–beech forests, showed that the input with throughfall is high enough to account for the increase in concentrations and amounts of cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). Iron (Fe) and Pb are known to be relatively immobile over a wide range of soil pH values (Bergkvist, 1986) and their dynamics are frequently characterized by high, exponential concentration increase rates. In a case study, the concentration of aluminum (Al) started at 280 mg kg^{-1} and ended at approximatelyh 900 mg kg^{-1} at about 65% mass loss. For Pb, the corresponding figures were 2.5 and 25 mg kg^{-1}, for Cu 1.4 and 5 mg kg^{-1}, for Fe 55 and 600 mg kg^{-1}, for barium (Ba) 4 and 28 mg kg^{-1}, and for strontium (Sr) about 5 and 10 mg kg^{-1}. The concentration of Cd increased from approximately 0.1 to 0.4 mg kg^{-1} at 65% mass loss.

Some of the heavy metals show high solubility at low pH values and their patterns of concentration change may differ among localities due to this factor. Thus, Mn, Cd, and Zn show increasing solubility and mobility with decreasing pH and thus often are leached out from litter. However, this relative mobility is not independent of the microbial population, and at low concentrations, a low pH does not necessarily mean a high net leaching since the microorganisms, such as fungal mycelium, would transport them into the litter. In contrast to most heavy metals, the typical pattern for Mn in decomposing Scots pine litter is a concentration decrease at a rate proportional to litter mass loss (Fig. 6).

IV. A THREE-PHASE MODEL APPLIED TO LITTER OF DIFFERENT INITIAL CHEMICAL COMPOSITION

A. Overview of the Model

When shed, different foliar litter species have different chemical composition (Chapter 2). These differences in chemical composition are reflected in the initial decomposition rate and some of them are reflected also in later decomposition stages. For example, initially higher concentrations of N and lignin result in relatively higher concentrations of both compounds during the whole decomposition process with consequences for the decomposition rate also in the late stage (Section IV.C and Fig. 1). In order to describe and systemize the decomposition process with respect to the variation in chemical composition and the chemical changes taking place, we present a three-stage model proposed earlier by Berg and Matzner (1997). This model was originally developed using field investigations and its validity has later been supported by other studies.

The three stages may be called an early stage, a late stage, and a near-humus stage and they each show different functional properties. In the early stage, the levels of the main nutrients have a positive influence on litter decomposition rate for a limited period and until a limited litter mass loss. The late decomposition stage, in this case, is generally a lignin-mediated suppression of the decomposition rate. In Chapter 3, we discussed the effect of N and Mn on the degradation of lignin. This part is now developed with respect to varying chemical composition of the initial litter, which also means a variation in the late-stage substrate.

Even if we can set a clear border between the early and the late stages, there is really no clear boundary between the late stage and what we call the ''near-humus'' or ''limit-value'' stage (described as final stages in Fig. 1). Several of the functional properties, such as the effect caused by N on decomposition rate of lignin and lignin-like compounds, appear to be shared for late and final stages. The effect of lignin, lignin-related compounds, and N may become so restricting on the decomposition process that it comes to a halt. This stage may be regarded as the stable stage of the humus. This is an important observation that helps us to interpret and predict properties of humus/SOM.

B. Initial Decomposition Rates for Newly Shed Litter—The Early Decomposition Stage

We start this section by describing a case study. For newly shed Scots pine needle litter with different nutrient levels, the initial decomposition rate was linearly related to initial concentrations of total N, P, and S, until an

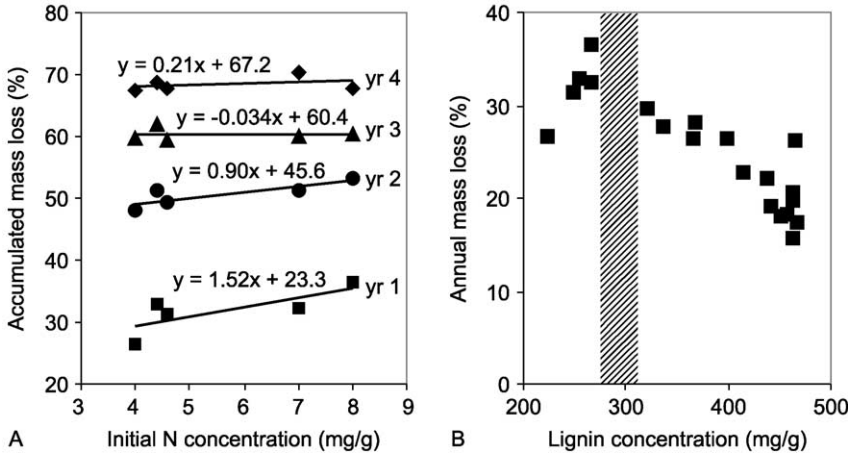

Figure 7 (A) Relationships between initial concentrations of N and mass loss of Scots pine needles. A set of five collections of Scots pine needle litter from N-fertilized plots was used (see Berg and Staaf, 1980a). We see that the slope coefficient decreases as the rate-stimulating effect of N decreases and that of other factors takes over. The litter P concentrations gave a very similar response pattern (Berg and McClaugherty, 2003). (B) Relationship between the increasing lignin concentration and annual mass loss for the same five Scots pine litter collections. Annual mass losses in the periods 12 to 24, 24 to 36, and 36 to 48 months were related to litter lignin concentration at the start of each 1-year period. To the left of the shaded area the early stage (1st year) and to the right of the shaded area mass loss and lignin concentration in the late stage.

accumulated mass loss of between 26 and 36% was reached (Fig. 7A). A linear relationship between the litter mass loss after one year and litter initial concentrations of N indicates that litter N concentration has a rate-promoting effect on the decomposition rate, at least up to a certain accumulated mass loss. Similar positive relationships were also seen for mass loss versus concentrations of P and S.

An early phase was identified by the procedure in part described in the legend to Fig. 7. Five preparations of Scots pine needle litter types were compared in a decomposition experiment. They originated from a fertilization experiment and had initial different concentrations of N, P, and S. After 10 months decomposition in the field, the accumulated mass loss was compared to the initial concentrations of N and P, both nutrients being limiting or close to limiting for the microbial decomposition of the litter. There was a positive relationship between N concentration and accumulated mass loss and, after 12 months decomposition, this relationship was even more pronounced. After 24 months, however, the relationship was weaker and apparently another rate-regulating factor had taken over. This is seen on the slope

of the regression line, which was shallower after 24 months (Fig. 7A). After 36 and 48 months of decomposition, no relationship is seen.

One way to analyze this result is to consider the partly decomposed litter, for example, after 12 months, as a new substrate, so that its chemical properties define the substrate quality. The mass loss in the period from 12 to 24 months is calculated, as is mass loss in the periods 24 to 36 and 36 to 48 months (Fig. 7B), and each time the new substrate quality is defined by chemical composition of the substrate decomposed during the last 12 months. Then, the mass loss during each 12-month period is plotted against selected substrate quality factor(s) which are expected to have rate-regulating effects. Lignin was suggested as such a factor since there is a probable causal relationship between lignin concentration and decomposition rate. We used the lignin concentrations at the start of each 12-month period (after 12, 24, and 36 months) and obtained the negative relationship to lignin concentrations, in this case, higher than about 300 mg g^{-1}, as seen in Fig. 7B.

To determine rate-regulating factors in the initial decomposition stage, studies are normally designed so that a range of, say, foliar litter types with different contents as regards nutrients and lignin are compared regarding mass loss during a year or even a shorter incubation period. When evaluating data, the decomposition rates obtained (e.g., mass loss) are regressed against a set of independent variables which potentially may control the decomposition rate, for example, concentrations of major nutrients and contents of different organic compounds, and those significant in the calculated multiple regression are considered the ones important for decomposition rate. By standardizing the regression coefficients, one may also rank the variables (the factors affecting decomposition rate) from most to least important. An alternative approach is to calculate a set of simple regressions, each time comparing the decomposition rate against a single factor (e.g., N, P, S), and ranking the significant regressions according to the R^2 values obtained. The best linear relationship, that is, that with the highest R^2, is supposed to show the most limiting factor.

The former method is more correct from a statistical point of view. Whatever the statistical method, not all foliar litter types should be compared in this way or should be part of our investigation over litter species, since they appear to behave according to different patterns. We will discuss in Section IV.E in Chapter 4 the decomposition pattern for Norway spruce needle litter, a litter type that appears to be in a late stage of decomposition already when it is shed. Considering the few litter types and species investigated so far, we can expect that such deviations from the described three-phase model are not uncommon. In the model, not only concentrations of N, P, and S show a positive influence in the early stage. The concentrations of water-soluble substances have also sometimes been related to initial decomposition rate.

A majority of studies on litter decomposition found in the literature, especially for slowly decomposing litter species, are relatively short-term in respect to decomposition rates. This has resulted in an overrepresentation of data on the early stage, sometimes leading to false interpretations about regulating factors for later stages. These studies present results from the early decay phase only, and in this stage, usually positive relationships are seen between litter concentrations of N, P, or S and the mass-loss rate or CO_2 evolution from the litter.

There are different ways of expressing the decomposition rate in the early stage and defining the concept ''decomposition'' will be useful for further discussion. Litter mass loss for a certain period usually means microbial decomposition and mineralization combined with leaching of water-soluble compounds. Depending on the litter species/type, the process of leaching may be more or less important for the overall mass loss, but it is always responsible for at least some mass loss. In several deciduous foliar litter types, leaching adds significantly to the initial mass-loss, while for a number of coniferous litter species, leaching is less important. Furthermore, we describe decomposition as mass loss, keeping in mind that part of the mass loss is due to leaching in the very early stage, and not to actual microbial degradation.

The amount of mass loss that can attributed to this initial leaching may be estimated simply by soaking the newly shed litter in water. Although, for example, Scots pine needle litter may lose just a few percent of mass in such an experiment, deciduous litter species may leach considerably more (Table 1), even as much as 30%. The most important factors determining the extent of initial leaching are (i) the litter type or species itself, including coniferous versus deciduous and differences between particular species, (ii) concentrations of solubles, (iii) freeze–thaw cycles, and (iv) amount of precipitation. It was suggested by Fog (1988) that litter N levels should also influence the magnitude of the leaching of the organic matter. However, this may be related to leaching in the late stage. Berg and Matzner (1997) presented data for coniferous needle litter showing a negative relationship between initial levels of N and of water-soluble substances.

The simplest model possible used to describe the decomposition rate is the exponential model, the same as for radioactive decay, often called Olson's model (Olson, 1963) for litter decomposition. It assumes that litter decomposition rate, that is, the change of litter mass W in time t, $\mathrm{d}W/\mathrm{d}t$, is linearly proportional to time:

$$\frac{dW}{dt} = kW \tag{1}$$

where k is the decomposition constant (rate constant). Thus, the mass W_t at time t is expressed by the exponential equation:

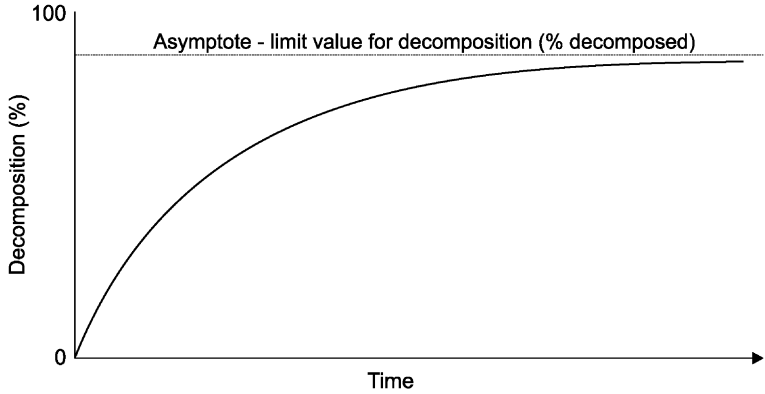

Figure 8 The type graph for an asymptotic function (Eq. 3). The limit value indicates a recalcitrant fraction of the litter. Adapted with permission from the Scandinavian Journal of Forest Research.

$$W_t = W_0 e^{kt} \tag{2}$$

Although the equation describes the general trend in organic matter decomposition, it misses some important phenomena—such as the initial leaching of soluble compounds, which makes the initial decomposition rate higher than the average, or lignin content, which slows down the decomposition in the late stage (cf. Section II.A., Chapter 9). Therefore, we introduce here the asymptotic equation for calculating limit values for decomposition and describe its use (Fig. 8):

$$AML_t = m \cdot (1 - e^{-kt/m}) \tag{3}$$

where AML_t is the accumulated mass loss (in %) at time t, and t is time in days. The parameter m represents the asymptotic level, which the accumulated mass loss will ultimately reach, and the parameter k represents the decomposition rate at the beginning of the decay, in this case. This equation will be discussed further in Section IV.F., and we will present it as a means to calculate limit values. In this context, we discuss it only from the point of view of calculating the initial rate indicated by k.

With Eq. 3, the initial rate can be estimated using the mass-loss data from a whole study (see Chapter 9), that is, from the first sampling of litter bags to the very last one after several years. The whole set of data, from 10 to 15 samplings, is used in Eq. 3 to calculate not only the limit value but also the initial rate (k). The k value obtained from Eq. 3 reflects a more "true" initial decomposition rate. We may point out that the k calculated with Eq. 3 is different from that calculated with the exponential function (Eq. 2) and is calculated for $t = 0$. Thus, this k value can be considered a maximum potential decomposition rate.

1. Different Indices Related to Initial Decomposition Rates

Different approaches have been undertaken to find and determine a chemical index for the initial decomposition rate. One option is simply to use the concentration of a given nutrient, such as N, P, or S, in the litter organic matter or the C-to-nutrient ratio. Another obvious possibility is the content of water-soluble substances (see preceding text). When we discuss this problem, we relate it to the major nutrients that are part of the three-phase model. Still, we should keep in mind that other nutrients or compounds may be as important, for example, Mn in Norway spruce needle litter (Section IV.E).

A discussion about which one of the main nutrients (N, P, S) is rate-regulating in the early stage is not always meaningful when considering that, of the total N, only part of the nutrient contained in the litter is readily bioavailable. Moreover, in general, the concentrations of these nutrients are normally highly correlated (Berg and Staaf, 1980a; Taylor *et al.*, 1991), which makes it difficult to select the one that is (most) determining for the decomposition rate. This comes from the fact that these nutrients appear together in defined ratios, for example, in proteins and nucleic acids, both in the decomposing microorganisms and in plant material, thus creating rather constant ratios in the decomposing litter as the decomposition proceeds. This is nicely demonstrated for a number of different litter species incubated in the same forest floor. The relationship between concentrations of N and P give a common regression line over Scots pine needles, green Scots pine needles, as well as brown and green leaves of silver birch (Fig. 9). The initial composition (circled values) deviated for green Scots pine needles and the birch litter, but after this initial deviation, the relationship became constant and similar to the other litters. Such relationships may be expected to vary among ecosystems, though, with different microfloras.

We may see (Table 3a) that for decomposing Scots pine needle litter, P and S give significant relationships to the first-year mass loss, relationships that are emphasized even more when data from more nutrient-rich green needles are included in the relationships. This was emphasized by the study of Taylor *et al.* (1989). The different values for the regression coefficients (r) resulting from regressions of first-year mass loss for Scots pine needles versus concentrations of N, P, and S (Table 3b) probably reflect differences in availability of nutrients to the degrading microorganisms. The lower r-value for the relationship to concentration of total N could reflect the fact that part of N is stored in forms that are unavailable to the microorganisms that first invade the litter. Nevertheless, the fact that the relationships to N are weaker does not mean that N is without effect.

In a Scots pine monocultural stand, a long-term experiment was performed using Scots pine needle litter with the annual variation among N,

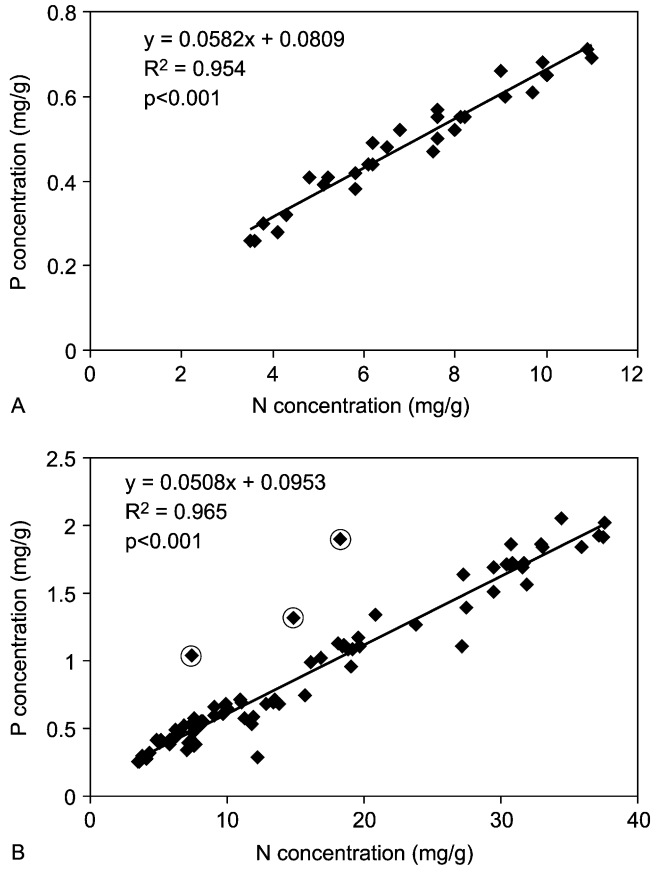

Figure 9 Linear relationships between increasing concentrations of N and P in decomposing litter. (A) Scots pine needle litter. (B) Decomposing needle litter of Scots pine and silver birch leaves as well as green needles and leaves of Scots pine and silver birch. We note that the balance between N and P is constant over different species with different concentration ranges of N and P. The three circled points show the initial concentrations in birch leaves and green pine needles. In the course of the decomposition process, the proportions of N and P became similar.

P, and S given in Table 10, Chapter 2. The decomposing microorganisms need at least the three major nutrients in a certain ideal proportion (see preceding text). A nutrient that is limiting would thus be the one with a proportionally lower concentration than the ideal one. With the variation in proportion between years seen in Table 10, Chapter 2, we may expect that, in the litter fall in one year, one nutrient may be limiting and, in another year, another one or—at least—considering the annual variation, we cannot exclude such a possibility. As an example, Cotrufo *et al.* (1998) found that

Table 3a Regression coefficients (r) and significance levels (p) for linear relationships between first-year mass loss and initial concentrations of some main nutrients, water-soluble substances, and lignin as well as the lignin-to-N ratio[a]

Litter species investigated	Regression coefficients and significance levels (p)										
	N	P	S	K	Ca	Mg	Mn	Water solubles	Lignin	Lignin/N	n
Scots pine needles[b]											
r	0.446	0.904	0.78	0.899	0.148	0.52	nd	0.217	−0.145	−0.65	11
p	ns	<0.001	<0.01	<0.001	ns	ns	–	ns	ns	<0.05	
Norway spruce[c]											
r	0.305	0.556	nd	0.511	−0.693	0.326	−0.226	0.888	−0.663	−0.593	9
p	ns	ns	–	ns	<0.05	ns	ns	<0.01	<0.1	ns	
Norway spruce[d]											
r	0.045	0.063	nd	0.126	0.032	0.195	0.57	0.265	0.122	0.055	14
p	ns	ns	–	ns	ns	ns	<0.05	ns	ns	ns	
Different litter spp[e]											
r	0.643	0.797	0.508	0.649	0.161	0.75	nd	0.792	−0.118	−0.773	18
p	<0.01	<0.001	<0.05	<0.01	ns	<0.001	–	<0.001	ns	<0.001	

*a*Scots pine needles from N-fertilized trees were used for a within-species comparison and a set of different litter species for a comparison over species; ns stands for not significant ($p > 0.05$).

*b*Experimental Scots pine needle litter with increased nutrient levels originating mainly from fertilized plots and incubated at the SWECON site Jädraås. Data from Berg and Staaf (1982).

*c*Experimental Norway spruce needle litter with increased nutrient levels originating from fertilized plots and incubated at a control plot in the same forest. Data from Berg and Tamm (1991).

*d*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 on the first-year mass loss. Data from Berg *et al.* (2000).

*e*Experimental Scots pine litter (above) as well as brown and green leaf litter from Scots pine, lodgepole pine, silver birch, and grey alder. Data from Berg and Ekbohm (1991).

Table 3b Correlation coefficient (r) and significance levels (p) for initial decomposition rates over several species related to litter nutrient concentrations[a]

	Correlation coefficients and significance levels (p)									
Study	N	C-to-N	P	C-to-P	Labile comp.	Cellulose	Lignin	Lignin-to-N	Lignin-to-P	n
Mass loss										
r (Taylor *et al.*, 1991)[b]	0.698	−0.728	0.709	−0.764	−0.854	–	−0.935	−0.92	−0.776	35
p	0.01	0.001	0.01	0.001	0.001		0.001	0.001	0.001	
Remaining mass										
r (Taylor *et al.*, 1989)[c]	−0.933	−0.946	−0.863	0.766	0.673	−0.711	0.811	0.896	0.811	40
p	0.001	0.001	0.001	0.001	0.01	0.01	0.001	0.001	0.001	
r (Melillo *et al.*, 1982)[d]	0.1	–	–	–	–	–	0.819	0.975	–	6
p	ns						ns	0.01		
McClaugherty *et al.* (1985)[d]	ns	ns	–	–	ns	–	ns	–	–	5 and 6

*a*ns stands for not significant ($p > 0.05$). Please note: in some cases, correlations were made between nutrient concentration and remaining mass, which changes the sign of the relationship compared to those where mass loss was used.
*b*Data for several litter types incubated in three different ecosystems, that is, pine, spruce, and fir forests. Ranges in nutrient concentrations were 0.19 to 1, 89%; P 0.01 to 0.26%, lignin 6.8 to 39.2%, and labile 9.9 to 62.8%.
*c*A microcosm study. Range in litter N concentrations was 0.52 to 1.31% and for lignin 3.4 to 20.5%.
*d*A temperate forest system. Mass loss range in the first 12 months was about 8 to 38%.

decomposition rates did not increase when only the initial N concentration in litter was unproportionally high and concentrations of P and S had more normal levels and their proportions to N were not balanced.

The fact that a nutrient, in our case N, is, in part, not directly bioavailable indicates that a relationship between its total concentration and initial decomposition rate is only a crude measure of its rate-regulating function. Part of the N in newly shed litter is tied to the lignin fraction (for Scots pine, initially about 1/3 of the total N; Flaig and Schobinger, 1959; Berg and Theander, 1984). This may simply reflect that part of the litter N has reacted with reactive groups in the lignin molecule and that the humification process has started. This N appears not to be readily available to the microorganisms that start the decomposition process. Thus, the total N concentration may be used only as an index for available N but it does not provide the actually available N. A consequence is that such an index cannot be expected to be reliable over species where N availability may vary. According to the literature, P and S appear not to be bound in similar ways but may be potentially more available (see, e.g., Stevenson 1994).

When the C-to-N ratio is used rather than N concentration alone, ash content is actually taken into account (Textbox 2). The ratio, which basically has the same meaning as N concentration related to organic matter, also gives a good relationship to mass loss for this early stage. This concept (C-to-N) is an index that originally was developed to be a rule-of-thumb for digestibility of fodder (e.g., fresh hay) but is today in use also for soils often in a relatively undefined way. Still, for newly shed litter of most species, a low C-to-N ratio often enough reflects an initially high decomposition rate.

A further index is the lignin-to-N-ratio (Melillo *et al.*, 1982) in which N represents the rate-stimulating and lignin the rate-retarding factor. This ratio was based on the hypothesis that N and lignin had different effects on the decomposition rate of whole litter throughout the decomposition process. For the late stage (Section IV.C), this basis has proven not to be correct since N, for the late stage, has a rate-retarding effect. It should be pointed out that although this quotient is useful to index the decomposition rate in the early stage, it is often used as a predictor and related to the accumulated mass loss over longer periods, although its value and predictability decrease the further the decomposition process develops. For Scots pine, it may serve as a better predictor than N, though not always as good as P or S (Table 3a).

In a comparative study, Taylor *et al.* (1989) evaluated different initial concentrations of nutrients, solubles, and lignin as well as the lignin-to-N ratio. For initial rates, they found N concentrations or C-to-N ratios to be superior indices, giving higher r values than, for example, the lignin-to-N ratio. In their study, the solubles component (“labile”) was negatively related to initial mass losses (up to 15.9– 47.8%, depending on litter type) (Table 3b).

The results of Taylor *et al.* (1989) (Table 3b) emphasize that it may be less meaningful to evaluate the relative roles of N, P, and S as limiting individual nutrients (see also the ratios among the nutrients in Table 10, Chapter 2). We speculate that it could be possible to determine a quotient with ratios of the three nutrients that would inform about which one is the limiting one. For N and P, this appears possible, considering the relationship seen in Fig. 9, where for litter incubated in one forest floor, the ratio between N and P in decomposing litter remains constant over species with a good range in initial N and P concentrations.

Water solubles in fresh litter, being rather easily decomposed (Section II.A) and called labile components by Taylor *et al.* (1991), may also be related to initial mass-loss rate (Berg and Ekbohm, 1991; Berg and Tamm, 1991; Taylor *et al.,* 1991). Since water solubles appear to be more easily decomposed than, say, ethanol solubles, their concentration may be a better index than total solubles.

The indices for early-stage decomposition rates previously mentioned or initial chemical composition as rate-regulating factor may vary among litter types (Table 3a). For Scots pine needle litter, correlations between first-year mass loss and concentrations of P and S were highly significant whereas for N, they were not. When combining several litter species, all of the nutrients N, P, S, and water-soluble substances, had significant relationships. Potassium and Mg are neglected here as rate-limiting components since their concentrations drop heavily immediately after the start of incubation and no causal relationships have been found for them to act as limiting nutrients in natural and unpolluted forest systems. We may note that, for Scots pine litter, the lignin-to-N ratio was significant, although neither N nor lignin concentrations taken alone were. For a combination of different litter species incubated at the same site, a relationship between N concentration and mass loss, but not that of lignin, was significant; still, the lignin-to-N quotient was highly significant and predicted the decomposition rate better than N concentration taken alone.

C. Decomposition in the Late Stage—A Phase Regulated by Lignin Decomposition

Berg and Staaf (1980a) distinguished a late phase (Fig. 1) in which the decomposition rate was regulated by lignin decomposition. They noted that when the effect of the main nutrients ceased, the rate was related negatively to th lignin level. For Scots pine needle litter, they 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 be at about 25% mass loss. Still, that is

for just one species. Using nine foliar litter species, Taylor *et al.* (1989) noticed that a shift occurred for different litter species at mass losses ranging from 15.9 to 47.8%, which supports the reasonable assumption that the length of the early stage should be different among species. They also found that for litter types initially richer in lignin, the effect of the lignin appeared relatively earlier. The basis for this was a comparison of pine needle litter (initial lignin level 26.2%) with eight litter species with lignin concentrations in the range from 3.4 to 20.5%.

If we use the definition that the late stage begins when the degradation of lignin starts, we may find that the onset in terms of lignin mass loss probably can be related to initial lignin concentration (Fig. 5). Actually, when using the data of Taylor *et al.* (1989) that have a good range in lignin concentrations (3.4 to 26.2%), we can see a negative linear relationship between initial litter lignin concentration and the suggested onset of the late phase. In conclusion, we may state that the lignin-regulated stage does start at clearly different mass loss values for litter, depending on litter species, and that the initial lignin concentration may be the main cause of these differences.

In decomposing litter, the concentration of lignin and its recombination products increases (Fig. 5). When the decomposition has reached a certain magnitude, the (foliar) litter contains only such material that is rich in lignin and recombination products (secondary products) in which the remaining cellulose and hemicelluloses are enclosed and protected by lignin and humins. 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 resistant to decomposition while the unshielded cellulose and the hemicelluloses in litter are decomposed considerably faster. Newer findings allow us to conclude that lignin appears resistant to degradation only under certain circumstances, however, and that its degradation is ruled, at least in part, by the litter N and Mn levels (Section III.C, Chapter 3) and the physiology of the lignin-degrading organisms present. Most studies on litter decomposition have been carried out on foliar litter and their levels of N have been high enough to influence the microbial lignin degradation, thus creating an image of lignin being more recalcitrant than other litter components (cf. Tables 7 and 8, Chapter 2).

Through the effect of N, the degradation of lignin regulates the decomposition of the whole litter (Berg and Ekbohm, 1991; Berg *et al.*, 1987). That the N level in litter increases with time as litter decomposes (Fig. 1) is a well-known and general phenomenon. As a result, the concentration of N is positively correlated to accumulated litter mass loss (Fig. 6). The rate at which the N concentration increases has also been observed to be in proportion to the initial concentration, namely, the higher the initial N level, the steeper the increase in N concentration versus accumulated mass loss (see Fig. 12, Chapter 5). Thus, with N exerting an effect on lignin degradation,

the rate-retarding effect could be expected to be emphasized as decomposition proceeds. Earlier, the rate-retarding effect of aging litter has been ascribed to increasing lignin levels in litter (Fig. 11). Actually, it may as well be ascribed to (i) the increasing total N concentration, (ii) N associated with lignin and lignin remains reflecting humification products, or (iii) to the more readily bioavailable N that may reflect a suppressing effect on the formation of lignin-degrading enzymes.

The suppressing effect of N on the degradation of lignin as well as on the decomposition of whole litter has been observed in studies on different resolution levels, and is based on both organic–chemical observations (Nömmik and Vahtras, 1982) and on a microbial–physiological analysis (Eriksson *et al.,* 1990; see also the following text). We may note that the influence of the lignin degradation rate or possibly that of a nitrogen–lignin complex (Textbox 3) on the litter decomposition rate in late stages for foliar litter is so strong that the effect of climate is not only suppressed but appears to disappear completely (Chapter 7).

1. Mass-Loss Rates of Sulfuric-Acid Lignin as Compared to Initial Litter N Levels

It has been possible to distinguish differences in lignin degradation rates and relate them to litter N concentrations. The mass-loss rates of lignin in that comparison were based on the measured values for sulfuric-acid lignin. Sulfuric-acid lignin in decomposing litter is degraded at very different rates in green, N-rich, as compared to brown, N-poor, needle litter (Berg *et al.*, 1982). This was also observed later by Berg and Ekbohm (1991), who fitted a model including the N concentrations of seven litter types and lignin degradation with time and found a clear relationship: the lignin mass-loss rate was lowest for the N-rich litters and highest for the N-poor ones (Fig. 10).

We have focused so far on the suppressing effect of N on lignin degradation rates. However, there are other nutrients, such as Mn and Ca (Chapter 3), that influence the lignin-degrading ability of the microflora.

2. The Biological Regulation and the Chemical Mechanisms

As has been discussed (Section III. C, Chapter 3), high N levels may suppress the degradation of lignin. The relative contributions of the two possible partial effects, biological and chemical, on lignin degradation in litter have not been determined so far. 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 simultaneously. In Table 7,

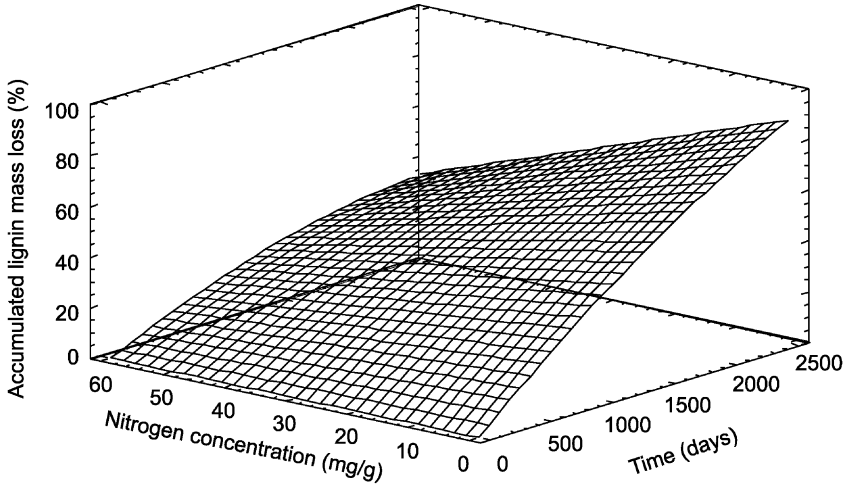

Figure 10 Accumulated lignin mass loss (ALML) with time (t) is related to litter nitrogen concentration (N), as shown on the graph. The 3-dimensional surface was plotted according to the equation given by Berg and Ekbohm (1991): $ALML = 45.4 \times 10^{-3}\ t - 0.0041 \times 10^{-3}\ t^2 - 0.35 \times 10^{-3}\ tN$.

Chapter 2, we have given N levels in needle and leaf litter at which lignin degradation was suppressed. In general, much higher N concentrations are found in foliar litter than those needed in pure fungal laboratory cultures to hamper lignin degradation. For example, in relatively N-poor brown Scots pine needle litter (initial N level about 4 mg g^{-1}), N concentrations were 40 to 100 times higher than those suppressing ligninase formation in pure fungal cultures. In litter species with higher initial concentrations of N, ranging up to approximately 30 mg g^{-1}, the relative N levels are up to 800 times as high as the concentrations having an effect on lignin degradation in pure cultures of white-rot fungi. Although not all N in litter is bioavailable, still the concentrations are so much higher than in laboratory cultures that we may assume an effect. A suppressing effect of N additions on respiration rate from humus has been observed within hours (review by Berg and Matzner, 1997) and we may expect that a repression on the fungal ligninase synthesis takes place also in litter, considering the relatively high levels of N present.

The chemical reaction between N in ammonium/ammonia and remains from partly degraded lignin is slow at the low pH values (around 4) in, for example, boreal needle litter. The reason is that the reacting form is NH_3 and its concentration decreases with decreasing pH. Still, in a laboratory experiment, the reaction proceeded at a rate of 14 to 19 mg N per kg litter daily (Axelsson and Berg, 1988). The reaction rate was limited by N avail-

ability and, using Scots pine needle litter as a substrate, the rate increased with increasing N additions. Thus, with the long-term decomposition taking place in nature we may speculate that on a more long-term basis, the reaction between N and lignin becomes prominent.

3. Comments to the Decomposition Patterns for Spruce Needle Litter

Two studies on decomposition of newly shed litter of Norway spruce indicate a different decomposition pattern as compared to those litter species and types fitting the described three-phase model. When Berg and Tamm (1991) compared the decomposition rates of newly shed spruce needles with different chemical composition, there was no statistically significant relationship between first-year mass-loss and concentrations of nutrients. In particular, there was no relationship to N concentration or to the lignin-to-N quotient and the negative relationship to lignin concentration was weak. However, the relationship between initial rates and concentration of water solubles was clearly significant (Fig. 12; Table 3a).

In another study on Norway spruce needles (Berg *et al.*, 2000), carried out in a climate transect, there was no relationship between first-year mass loss and climate factors or climate indices for the range of actual evapotranspiration (AET) values from 371 to 545 mm across Scandinavia. When the combined data were compared to substrate-quality factors, the main nutrients usually indexing substrate quality (N, P, S) did not give any significant relationship but the concentration of Mn correlated positively with the first-year mass loss ($R^2 = 0.325$; $p < 0.05$; Table 3a). The background to this relationship may be that also in this study, the early stage had passed and the litter had entered the late decomposition stage already before shedding. A reasonable conclusion of that study is that Mn concentration gave the positive relationship through its effect on lignin degradation rate (Section III.C., Chapter 3).

4. Different Lignin-Related Patterns among Litter Types

Using available data, it has been possible to distinguish three patterns for foliar litter decomposition, which appear to be characteristic and possible to follow through the early and late stages. We have given them the provisional names type 1, type 2, and type 3 and they are discussed in that order (Table 4). We emphasize that these three patterns should be considered as a first attempt to organize existing information that is based on a very limited number of litter species. Thus, we cannot exclude that, with an increasing number of studies on different litter species, the number of groups will increase.

Table 4 Overview to a provisional division of foliar litter types into groups of different properties, organized into the three-stage model*

Group	Stage of decomposition		
	Early stage	Late stage	Humus-near stages
Type 1, e.g., pine needles	1. Low initial leaching (<2%) 2. Decomposition of solubles within the litter structure 3. Initial decomposition rates may be related to initial concentrations of N, P, S 4. Initial decomposition rates may be related to climate	Slow continuous increase in lignin concentration. Relationship between lignin concentration and mass-loss rate	Limit values normally above 80%
Type 2, several deciduous litters	1. High initial leaching (>5%) 2. Fast initial mass loss 3. Initial decomposition rates may be related to initial concentrations of N, P, S 4. Initial decomposition rates may be related to climate	Maximum lignin level normally reached quickly. Relationship between lignin concentration and mass loss rate	Limit values normally below 80%
Type 3, e.g., spruce needles	1. Low initial leaching (<2%) 2. Relationship between mass loss rate and nutrients not clear 3. Climate influence on mass loss rate is probably low 4. Possibly a very early phase is missing	Slow continuous increase in lignin concentration. Relationship between lignin concentration and mass loss not clear	Limit values 70–90%

*The names of the groups are provisional but refer to those litter types characteristic for the properties.

Type 1 relates to a pattern so far seen mainly in pine needle litter. In this pattern, the higher the lignin level, the slower the decomposition and clear negative linear relationships between lignin concentration and litter mass-loss rate result (Fig. 11). This kind of relationship has been observed repeatedly in Scots pine ecosystems as well as in ecosystems of other pine species (Berg and Lundmark, 1987; McClaugherty and Berg, 1987). In the case of two pine species, Scots pine and lodgepole pine, with similar N levels and growing in systems of the same soil richness (Fig. 11), we may note that the relative lignin-mediated (NIT-LIG) effect is similar.

Type 2 relates to a pattern so far seen mainly in deciduous litter. Whereas the pine litter gave negative linear relationships for mass-loss versus lignin, such linear relationships are not seen for the studied deciduous litter types. Still, there is a clear effect of lignin, which may be illustrated by the initial

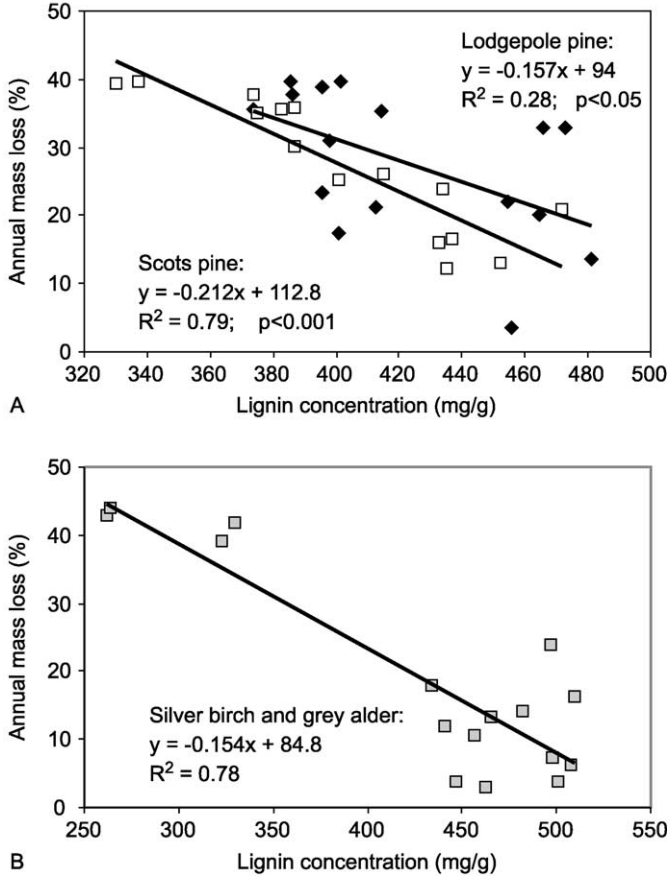

Figure 11 Normally, lignin in foliar litter is resistant to degradation (Section IV.C) and an increasing lignin concentration may be negatively related to the decomposition rate of the litter, at least in most foliar litter types. The relationship shown, namely, a decreasing rate for one type of litter incubated at its own forest stand, has been observed by several scientists. Still, it has been observed in few types of systems. One basic method to investigate for the 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 as a new substrate, for example, at the start of each year. The mass loss for an individual year is compared to data on litter chemical composition at the start of that year. In the present figure, the lignin concentration at the start of each one-year period is regressed against the mass loss over that one-year period to obtain a slope for each site describing the effect of lignin concentration on litter mass loss. (A) Scots pine needle litter (□), lodgepole pine litter (◆). (B) Leaf litter of silver birch and grey alder. With kind permission of Springer Science and Business Media.

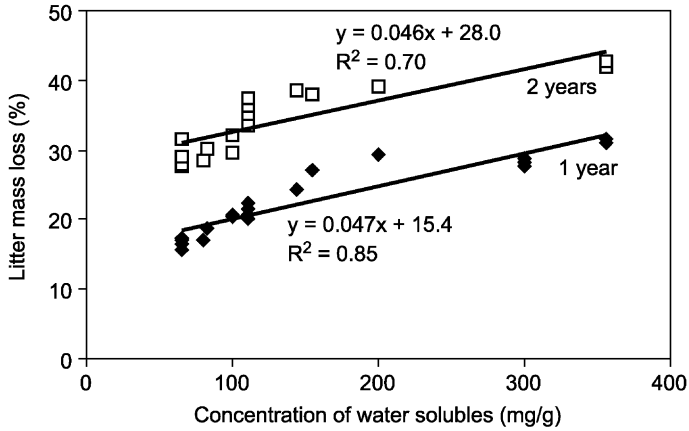

Figure 12 Litter mass loss of Norway spruce needle litter as dependent on the initial concentration of water-soluble substances. Accumulated mass loss after 1 year (◆) and after 2 years (□). From Berg and Tamm (1991). Adapted with permission from the Scandinavian Journal of Forest Research.

decomposition rate (often first-year mass loss) and the decomposition rates of the following years (Fig. 11B). After a rather quick initial decomposition, the lignin concentration reaches its highest value, which causes a decrease in decomposition rate, creating a graph with two clusters of points rather than showing a continuous change.

Type 3 illustrates a pattern so far observed only in spruce needle litter. Norway spruce needle litter appears to deviate from the two previously mentioned cases and two studies published deserve attention. The general rate-retarding effect ascribed to lignin has been noted to start at raised lignin concentrations (NIT-LIG effect) and when all unshielded holocellulose is degraded. It has often been recorded as decomposition in the 2nd, 3rd, and 4th years. In their study, Berg and Tamm (1991) compared the effect of lignin concentration on litter mass-loss rate for individual incubation years and found significant relationships only in the first year, and none in years 2, 3, and 4 (Table 5; Fig. 13). When comparing annual mass loss and lignin concentrations, they found that litter decomposition was related to the concentration of lignin until approximately 440 mg g^{-1}, basically during the first year of incubation. Using the relationship presented in Fig. 13, we see that an increase in lignin concentration from 350 to 440 mg g^{-1} caused a decrease in annual mass loss from 24 to 10%. Above a lignin concentration of ca. 450 mg g^{-1}, the deviation in annual mass-loss values increased considerably and no pattern was seen.

Table 5 Correlation coefficients (r) for the linear relationship between annual mass loss of Norway spruce needle litter and initial concentrations of lignin at the start of each one-year period*

Incubation year	r	n	p
1st	−0.894	10	<0.001
2nd	−0.482	11	n.s.
3rd	0.234	11	n.s.
4th	−0.376	8	n.s.

*Model based on incubation year. n.s. stands for "not significant" (see Fig. 13). From Berg & Tamm (1991).

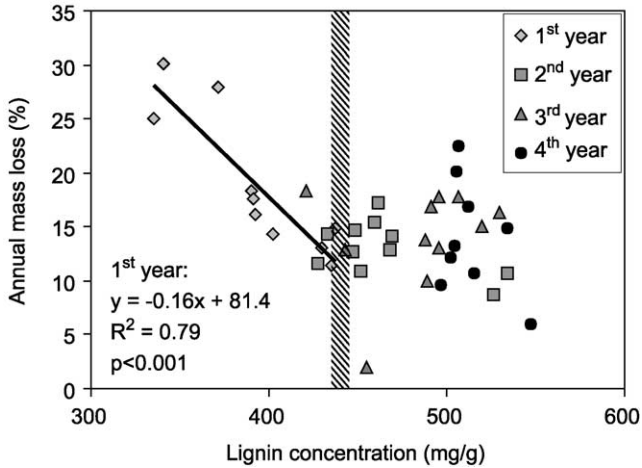

Figure 13 Annual mass loss of Norway spruce needle litter as compared to lignin concentration in litter at the start of each one-year period. From Berg and Tamm (1991). Adapted with permission from the Scandinavian Journal of Forest Research.

D. Link between the Retardation of Litter Decomposition, Lignin Degradation Rate, and N Concentration

The "effect of lignin" on decomposition rate usually is illustrated as a decreasing rate with increasing lignin concentrations. A higher concentration of lignin would thus reflect a higher percentage of a compound resistant to decomposition, the decay of which depends on the kind of microorganisms that have invaded the litter and litter concentration of N, Mn, and Ca (cf. Section III.C, Chapter 3). With the effect of N on the fungal population and thus on lignin

degradation, we may distinguish some possible cases which represent the extreme scenarios. We have focused the discussion on N, being aware that litter Mn concentration may be at least as important, although we still know much less about the effect of this nutrient in litter decomposition (Section IV.E).

If N-sensitive white-rot fungi have invaded the litter and dominate the microbial community, we should expect that the N concentrations, increasing with accumulated mass loss, are suppressing the degradation of lignin to an increasing extent and thus are retarding decomposition of the whole litter. At least some of the white-rot fungi have the ability to degrade lignin fast when N levels are low so the effect of increased N concentrations should be seen. As we can expect that N-sensitive fungi would dominate in nutrient-poor systems, we may expect that the retarding effect of N on decomposition should be seen particularly in such ecosystems.

An alternative is that the litter is invaded by white-rot fungi that are not sensitive to nitrogen. Such a population would not be hindered by high N concentrations to degrade lignin and lignin would thus not be a barrier to degradation of the litter. Ideally in such a case, there would be no relationship between lignin levels and decomposition rate. Such a microbial population may be expected to develop in a forest floor rich in N.

Brown rots cannot 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 nonsensitive species. Further, a domination of brown-rot fungi in the litter is likely to be a hindrance for white-rot fungi to grow into the litter substrate.

Consider that we regard the decomposition of foliar litter in natural systems where the most likely case is that litter is invaded by a mix of fungal species. Thus, both sensitive and nonsensitive white and brown rots participate in the degradation. We expect that such a mix of species would result in some suppression of lignin degradation already at the initially low N levels and increasing levels would have a stronger effect. We may expect that a difference between systems can be reflected in the slope of the relationship between lignin concentration and decomposition rate. We may also assume that, over a range of ecosystems, the late-stage decomposition rate of a litter richer in N would be more retarded than that of an N-poor one incubated under the same conditions. Further, we speculate that a system richer in N would have relatively more fungal mycelia of species not sensitive to N, or at least less sensitive ones, and that really nutrient-poor systems could have a relatively high frequency of N-sensitive fungi, thus allowing a stronger retardation of the decomposition in the latter type of system.

Judging from the cases reported in the literature, a suppression of lignin degradation rates by high N levels is commonly found for foliar litter. In fact, there may be just one case reported for which the lignin degradation

has not been hampered by high N concentration. In a paper on lignin decomposition in beech leaf litter, Rutigliano *et al.* (1996) reported that lignin concentrations decreased in the beginning of the study. Later, the concentrations started to increase slowly from a level much lower than the initial one. The system was very rich in nutrients and the humus held approximately 3.7% N as related to the organic matter, so a possible explanation would thus be that there was a dominance in this system of white-rot fungi that were either not sensitive to N or very little so to raised N levels.

E. Comments on Spruce Needle Litter Decomposition versus the Three-Phase Model

Spruce needle litter appears not to have a decomposition pattern similar to that of, say, pine needles or birch leaves (Tables 3a, 5). We have therefore included this section to summarize what has been found so far for spruce needles and to compare these findings to the three-phase model previously described.

The effects of lignin concentration on litter mass loss for spruce needles took place mainly in the first year and, above a lignin concentration of 440 mg g^{-1}, no effect was seen (Fig. 13). Although the concentration of lignin increases up to about 500 to 550 mg g^{-1}, no effect was seen in the interval above 440 mg g^{-1}. We speculate that in this late stage, the influence of some other component(s) may dominate the lignin degradation. Berg *et al.* (1987) noted a similar phenomenon for Scots pine needle litter although it was less pronounced and at a very late stage.

In a north–south transect study with locally collected Norway spruce needles, only part of the incubated litter showed a negative relationship between lignin concentrations and annual mass loss, thus following the pattern described for pine (Berg *et al.*, 2000). In this case, the lignin concentration at the start of each one-year period was regressed against the mass loss over that one-year period. The resulting linear relationships gave a slope for each site, describing the effect of lignin concentration on litter mass loss. Lignin concentrations correlated negatively with litter decay rates for seven of the 14 sites used in the transect. For the other seven, no such effect was seen. There was thus a difference among stands and they could be divided into two groups.

Within each of the two groups, the data was combined (Table 6). One group was thus formed by the stands with significant relationships between lignin concentration and annual litter mass loss (Group 1; Fig. 14A). Another group (Group 2) was formed from the data of the seven sites without significant relationships to lignin. The purpose was to use the larger data sets

Table 6 Linear regressions between litter mass loss rate and litter chemical components for combined data of decomposing Norway spruce needle litter*

	Significant relationships (Group 1)			Non-significant relationships (Group 2)		
	r	R^2	p	r	R^2	p
Lignin	−0.775	0.6	<0.001	–	–	n.s.
Water solubles	0.673	0.453	<0.001	–	–	n.s.
Nitrogen	−0.608	0.37	<0.001	–	–	n.s.
Phosphorus	−0.498	0.24	<0.01	–	–	n.s.
Potassium	0.33	0.109	<0.05	–	–	n.s.
Magnesium	0.554	0.307	<0.001	–	–	n.s.
Manganese	0.316	0.1	<0.1	0.526	0.277	<0.01
Calcium	0.281	0.079	<0.1	–	–	n.s.

*Data from seven sites at which a significant negative relationship was seen between increasing lignin concentration and litter mass-loss rate form Group 1 (n = 55). Group 2 (n = 33) is formed from data from seven sites at which no significant relationships to lignin concentration were seen. From Berg *et al.* (2000) (see Fig. 14).

to investigate whether the pattern observed in a single experiment would still hold when a larger set of data was used. This combination of data into these two groups was reasonable since no effect of climate on mass-loss rate was found among sites. Further, the ranges in lignin concentration in both groups were about equal (277 and 524 mg g^{-1} in Group 1 and 282 to 513 mg g^{-1} in Group 2). Thus, if the concentration of lignin and N (Nitrogen–Lignin effect; Textbox 3) had been rate-regulating, then there should be a negative relationship in both cases.

The litter of Group 1 (n = 55) gave a highly significant and negative relationship between annual mass loss and concentrations of lignin (Fig. 14A). For Group 2 (n = 33), only the relationship between annual mass loss and Mn concentration was significant ($R^2 = 0.277$; $p < 0.01$; Fig 14B). For Group 2, there was no significant relationship between annual mass loss and concentrations of lignin, water solubles, N, P, K, Mg, or Ca (Table 6). In Group 1, the Mn concentrations ranged from 0.31 to 3.0 and in Group 2, from 0.41 to 7.69 mg g^{-1}. Also, when combining all data for late stages (Groups 1+2) with the Mn concentration interval from 0.31 to 7.69 mg g^{-1}, a highly significant relationship between Mn concentration and mass loss was found.

We have already discussed (Chapter 3) the effect of N and Mn concentration in litter. It appears possible that the wider range of Mn concentrations in Group 2 caused different decomposition rates, and the more similar concentrations in Group 1 limited the decomposition of lignin and of

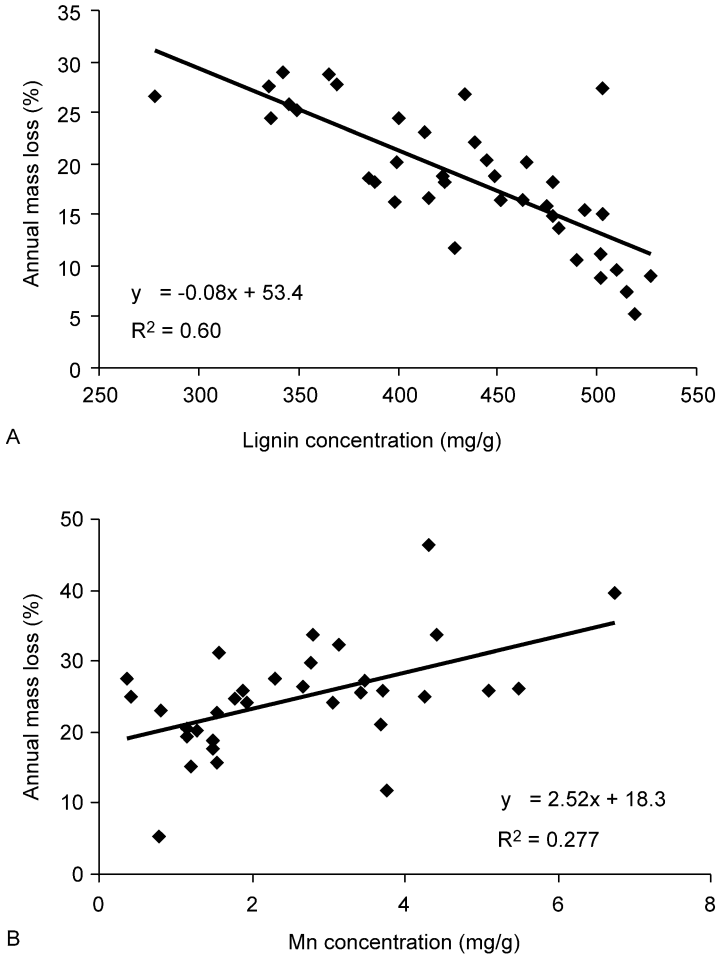

Figure 14 Annual mass loss versus substrate-quality factors at the start of each year for local Norway spruce needle litter in late decomposition stages incubated in Norway spruce forests in a climate transect across Sweden (cf. Table 6). At seven sites, significant negative relationships were found for annual mass loss as related to lignin concentration and, at seven sites, no significant relationships were seen. (A) Mass loss versus lignin concentration for decomposition at those sites where lignin gave significant relationships versus annual mass loss. (B) Mass loss versus Mn concentration for those sites for which no relationship to lignin was seen.

whole litter, and thus that an effect related to Mn could not be distinguished. A higher Mn concentration would therefore cause a faster degradation rate of lignin.

The litter Mn concentration could be dependent on site (soil) properties, for example, the availability of Mn in the parent rock material and its mobility influenced by soil pH. We can not exclude that tree species may play a role, too with some species simply allocating more Mn up to their leaves.

F. The Litter Close to the Limit Value and at a Humus-Near Stage

1. General Relationships

Models of litter decomposition indicate that most foliar litter types do not decay to 100% but to a certain level, a limit value for decomposition (Fig. 8) that differs among litter types (Howard and Howard, 1974; Berg and Ekbohm, 1991) and can be described with an asymptotic function (Eq. 3).

Limit values are related negatively to initial litter N concentrations and positively to initial Mn concentrations. Berg *et al.* (1996b) presented the hypothesis that the fraction of litter remaining at the limit value is regulated by lignin remains that had become recalcitrant by fixation of ammonium, a process enhanced by increased litter N levels.

The relationships between N and Mn concentrations and the limit value that we present are empirical. At present, we may state that the empirical relationships have been confirmed and the recalcitrance of the remaining litter has been validated by soil organic matter budgets (Berg *et al.*, 2001) but still there is no clear and comprehensive theory explaining the phenomenon. In a search for possible factors regulating the limit value, relationships have been found to litter concentrations of N, Mn, Ca, and lignin, all of which have potential causality. Inventories have been published with increasing numbers of litter species as well as increasing numbers of decomposition studies, resulting in limit values significantly different from 100% (Berg, 2000; Berg *et al.*, 1996b) and the main patterns observed have held. After an inventory of existing decomposition studies, Berg (2000) published in all 128 limit values, of which 106 originated from forest sites that were natural and not disturbed.

2. Repeatability of Limit Values

There is a homogeneity in limit values within groups of decomposing litter, for example, within Scots pine and lodgepole pine, and also a significant difference between the two species (Berg and Ekbohm, 1993). We have used two case studies to show a homogeneity in limit values using several sets of

local Scots pine needle litter decomposing at the same plot in a series of years. The limit values for Scots pine needle litter ranged between 76.0 and 92.2% in the same nutrient-poor Scots pine system, and the mean for the 11 limit values was 84.7%, with SE being 1.57 (Table 7b).

In another study, a comparison of limit values for needle litter of Scots pine and lodgepole pine, we see that these two groups had significantly different average limit values (Table 7a), with 85.5% for Scots pine and 97.1% for lodgepole pine. This comparison was made in three groups of paired stands.

Higher N levels in the litter result in lower limit values. The possible reasons for the negative relationship between limit values (litter recalcitrance) and N concentration have been discussed previously (Section IV.C). When the existing 106 limit values for foliar litter decomposing in natural systems were regressed against concentrations of nutrients and lignin, a highly significant and negative relationship was found to N concentration, meaning that the higher the initial concentration of N, the lower was the limit value and thus the smaller the part of litter decomposed ($R^2 = 0.323$; $n = 106$; $p < 0.001$) (Fig. 15, Table 8). Behind this observation, there may be a causal relationship, valid both for litter in the late decomposition stages and for humus, and the reasoning applied to litter in the late stage (Section IV.C) may be used in this case also. The fact that in this large data set the relationship to N concentration was significant indicates a general effect of N over no fewer than 20 tree species, including deciduous and coniferous ecosystems in boreal and temperate forests.

The low R^2 value (0.323, $p < 0.001$) when including all 106 limit values may result from the fact that, in this data set, several other factors potentially influencing the limit value increased the variation. Since the data were collected from different forest ecosystems with litter being incubated on soils with different properties and under different climates, this is not strange.

We can calculate the average limit values and average initial N concentrations for the eight best represented species. These average limit values have been related to the average N concentrations (Fig. 16), resulting in a relationship with an R^2 value of 0.761 and $p < 0.01$. In most cases, the species differed significantly in N level and some of the limit values also were significantly different.

In contrast to N, litter Mn and Ca concentrations are positively correlated to limit values (Table 8, Fig. 15). Also in these cases, limit values originated from very different systems, which may explain the relatively low R^2 values. We discussed possible effect of Mn on microorganisms in Chapter 3.

Higher lignin concentrations seem to result in lower limit values and a higher fraction of stable remains. Using all available 112 limit values, we see a general but weak negative relationship to lignin concentrations (Table 8). Such a relationship might be expected, considering that lignin appears to be

Table 7a Estimated values for initial mass-loss rates (k) and limit values (asymptotes) (m) for decomposing Scots pine and lodgepole pine needle litter in their respective forest stands*

	Scots pine					Lodgepole pine				
				max m.l.					max m.l.	
Set No.	n	k	m (%)	(%)	days	n	k	m (%)	(%)	days
1	10	0.142	85.4	75.5	1406	10	0.106	99.9	71.7	1406
2	10	0.147	79.9	72.9	1406	10	0.105	85.7	68.9	1406
3	11	0.137	80.6	73.2	1438	11	0.094	100	75.3	1438
4	7	0.108	100	68.7	1079	8	0.103	100	66.8	1079
5	11	0.123	86.4	73.9	1439	11	0.098	96.5	70.6	1439
6	8	0.156	74.6	66.3	1075	8	0.09	100	66.8	1075

*The adjusted R^2 value for the whole system was 95.8%. Number of measurement values and maximum measured mass loss (max. m.l.) are given as well as the number of days at which the maximum actually measured mass loss was reached. The average limit values, for Scots pine 84.5% (significantly different from 100%) and for lodgepole pine 97.1% (not different from 100% mass loss). From Berg and Ekbohm (1993).

Table 7b Limit values for litter decomposition and initial concentrations of N and Mn in local Scots pine needle litter incubated in its own system (SWECON Site Jädraås)*

Initial concentration of			
N (mg g^{-1})	Mn (mg g^{-1})	Limit value (% mass loss)	(SE) (% mass loss)
4.0	n.d.	93.2	11.7
3.8	1.0	86.6	3.02
4.0	1.13	92.2	8.51
4.4	n.d.	78.23	4.03
4.8	0.79	89.0	7.0
3.8	0.38	89.43	17.04
3.9	1.17	83.22	9.23
3.8	0.41	82.56	3.1
3.8	0.39	85.37	8.19
3.8	0.53	84.32	5.21
3.7	0.44	76.0	5.8
Average		84.66	
SD		5.21	

*n.d., not determined. From Berg *et al.* (1999, 1991).

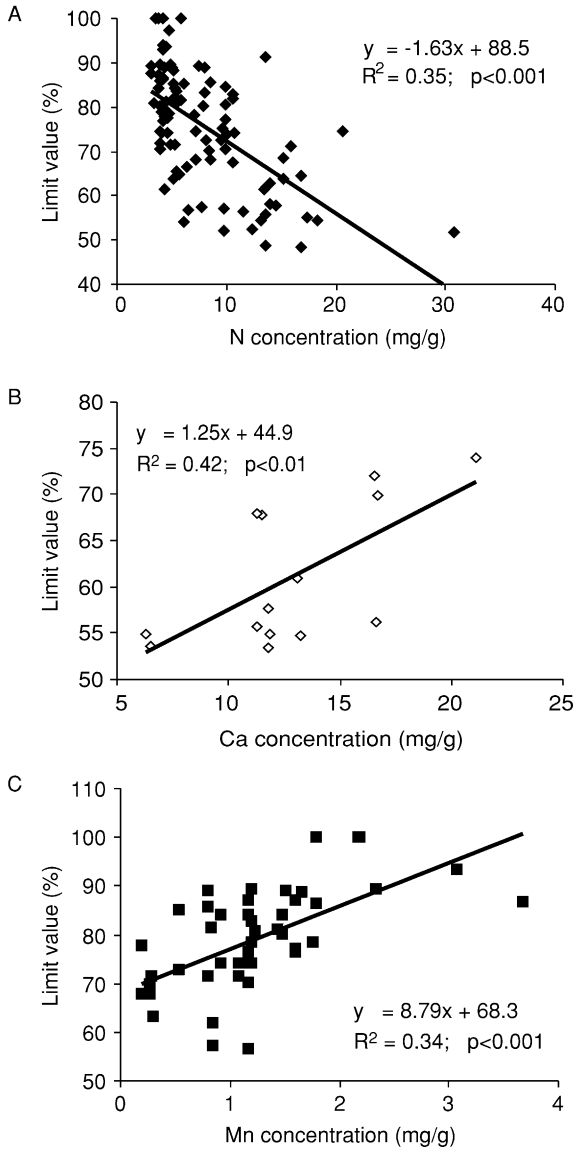

Figure 15 Linear relationship between limit values for decomposition and initial concentrations of N, Ca, and Mn in foliar litter (from Berg and Johansson, 1998). (A) All available data from natural forest systems versus litter N concentration. (B) Limit values from Norway spruce litter plotted versus litter Ca concentration. (C) Limit values plotted versus litter Mn concentration.

Table 8 Correlations between limit values and initial concentrations in litter of N, P, S, K, Mg, Mn, Ca, and lignin*

Nutrient	r	R^2	n	p<
All available data				
N	−0.569	0.324	128	0.001
Mn	0.511	0.261	98	0.001
Lignin	−0.21	0.044	112	0.05
N, Mn	0.651	0.424	98	0.001
N, Mn, lignin	0.66	0.436	98	0.001
Natural systems				
N	−0.568	0.323	106	0.001
Mn	0.519	0.269	83	0.001
All deciduous litter				
Mn	0.618	0.382	13	0.05
Ca	0.675	0.456	18	0.01
N	−0.438	0.192	30	0.05
All coniferous litter				
N	−0.66	0.436	86	0.001
Mn	0.513	0.263	74	0.001
Scots pine litter				
N	−0.683	0.466	42	0.001
Mn	0.485	0.235	35	0.01
Norway spruce needle litter				
Lignin	−0.742	0.551	11	0.01
Ca	0.636	0.404	11	0.05

*Data originate from several sites and all available data on nutrient analyses were used. From Berg *et al.* (1996).

the nucleus of the recalcitrant part. The rather low R^2 value may be ascribed either to a relatively small variation in the initial lignin concentrations or, alternatively, to the possibility that the recalcitrance of lignin itself varies among litter species.

Different types of litter have different empirical relationships. The observed relationships between N and Mn concentrations and limit values were also seen for selected groups of litter and allowed a first subdivision into coniferous and deciduous litter as well as groups of separate species. The coniferous litter types as a group produced a highly significant relationship between limit values and litter N concentrations ($R^2 = 0.436$, $n = 86$, $p < 0.001$) (Table 8) as they did to Mn concentrations ($R^2 = 0.263$, $n = 74$, $p < 0.001$). Berg and Meentemeyer (2002) found enough studies using Scots pine needle litter to allow a special investigation of the factors regulating the limit value for that specific litter species and found a highly significant and negative relationship

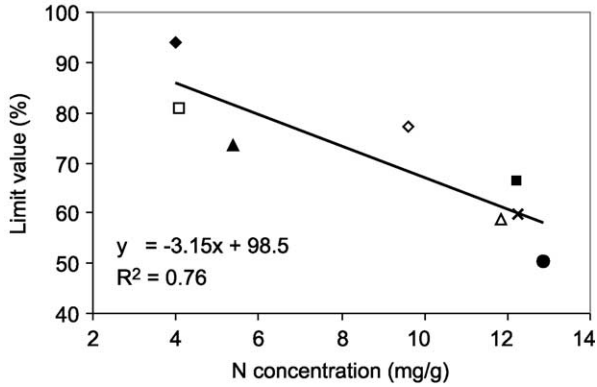

Figure 16 Linear relationship between initial litter N concentrations and limit values. Average values for eight litter species are given. From Berg (2000).

between N concentrations and limit values with $R^2 = 0.466$ ($n = 42$, $p < 0.001$). Also experimental litter, that is, needle litter from fertilized trees with raised levels of N and other nutrients, followed the same main pattern, with the best relationship being that to N. Manganese gave significant relationships too and, in this modified system with nutrient-manipulated litter, Ca and lignin also gave significant relationships. However, such subdivision into litter types disregards the effects of site quality (Table 8).

For the group of Norway spruce needles, a significant and negative relationship was found between limit values and the concentration of lignin ($R^2 = 0.551$, $n = 11$, $p < 0.01$; Table 8). A positive relationship was seen to Ca concentrations but there was no relationship to either N or Mn concentrations. When investigating spruce needle litter from N-fertilized plots with heavily manipulated concentrations of N (range 4.2–18.3 mg g^{-1}), Berg (2000) found relationships to initial litter concentrations of Ca and Mn. Also, for these nutrients, the concentration ranges had increased as a consequence of N fertilization.

For deciduous litter as a separate group, the limit values were best and positively related to litter concentrations of Mn ($R^2 = 0.382$, $n = 13$, $p < 0.05$) and Ca ($R^2 = 0.456$, $n = 18$, $p < 0.01$). Nitrogen gave a barely significant relationship (Table 8).

3. Heavy Metals

A few studies have been done in which heavy metals have been measured and related to limit values. There was no clear relationship as judged from these studies but negative relationships between limit values and litter

Cd and Zn concentrations have been found on the brink of significance with $p < 0.1$. The data originate from a nutrient-poor and unpolluted system. We may speculate that with the very pronounced increase in heavy metal concentrations (see Fig. 6) during the decomposition process, they may contribute to the stabilization of litter/SOM at the limit value.

4. The Concentrations of Nutrients and Heavy Metals are Empirical Indices

The fact that significant relationships exist between limit values and initial concentrations of, for example, N and Mn is good support for a regulating mechanism. However, it must be emphasized that the initial concentrations of these nutrients should be seen as empirical indices only as long as the causal relationships are not fully understood. Such indices may be regarded in different ways. For a nutrient such as N, the concentration increases linearly versus accumulated mass loss and generally in proportion to the initial concentration (see Fig. 6 and Chapter 5; Berg *et al.*, 1999a) and the use of initial concentrations should thus not cause any problem when used as an index. Similar reasoning may be applied for some heavy metals with an increase in concentration during decomposition. For nutrients and heavy metals such as Mn, the mobility of which is pH dependent, such an increase does normally not take place and it remains—still on an empirical level—to be determined how we should interpret the relationship between limit values and the concentrations of these nutrients. Specific effects as regards lignin degradation have been observed in pure cultures of fungi in laboratory studies but the step between laboratory studies and the effects on the soil-system level are far from clear. We may expect, for example, that the concentration of Mn can influence the ingrowing microbial population.

5. Site Properties May Influence the Limit Value

Forest SOM/humus systems have different levels of nutrients. For example, in a Scots pine stand, the humus N level was 11.8 mg g^{-1} as compared to that of a silver fir system with an N level of 38.2 mg g^{-1} in the organic matter and a generally higher level of other nutrients (Table 9). When comparing the N levels in the organic matter, we expect that the soil microorganisms have adapted to the different nutrient levels and that they may have different properties. A very N-rich system could thus be expected to have a higher percentage of lignin-degrading organisms that are not sensitive to N, which could mean that the limit values are ruled, to a less

Table 9 Initial chemical composition of humus layers at two different sites (Jädraås and Monte Taburno) (Berg *et al.*, 2003)[a]

		Concentrations of nutrients										
		(mg g^{-1})								(mg kg^{-1})		
Site (TC/AF)	C-to-N	N	P	S	K	Ca	Mg	Mn	Fe	Zn	Cd	Cu	Pb
Soil (humic surface horizon)													
Taburno (TC)	13	8.5 (38.2)[b]	2.84	–	17.7	20	4.76	0.76	6.5b	0.11	0.9	62.6	9.7
Taburno (AF)			0.01	–	0.2	7.73	0.23	0.12	0.3b	0.03	0.2	12.9	24.2
Jädraås (TC)	42.3	10.6 (12.8)[b]	0.47	–	10.9	3.2	0.98	0.37	9.4b	0.06	0.7	9.2	8.9
Jädraås (AF)			0.06	–	0.13	0.79	0.06	0.17	0.5b	0.02	0.1	1.02	1.1
Relative composition of nutrients Monte Taburno/Jädraås													
			6	–	1.6	6.2	4.9	2.1	2.8	1.9	1.3	6.8	1.1

*a*Total concentrations (TC) and available fraction (AF) of nutrients and heavy metals of the humic surface horizon, as well as the ratios between Monte Taburno and Jädraås TC values, are shown. Please note that the C concentrations of the two humus layers are very different. At Monte Taburno the C concentration in the upper humus is 11.05% and at Jädraås 44.8%. We therefore have indicated the N concentration both in the whole soil and in ash-free SOM.

*b*mgN g^{-1} ash-free SOM.

extent or not at all, by the concentration of N but other factors may limit the extent of litter decomposition. Thus, in a comparison of two such systems, Berg *et al.* (2003) found that the limit values in the richer system were not related to litter N concentrations, whereas they were in the nutrient-poor one.

G. Do Limit Values Indicate a Stop in the Litter Decomposition Process?

Although limit values for litter mass loss have been estimated for a variety of litter types by using asymptotic functions, we cannot conclude that such limit values indicate that the remaining organic matter is completely undegradable by biological agents (see following text). 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 change in that environment, say, by soil disturbance, can allow a decomposition to start and proceed. 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, for example, lignin concentration, nutrient status, or other environmental factors. Just the fact that allofanic humus exists shows that "eternal" storage is possible and although allofanic organic material may be regarded as an extreme case, the level of stabilizing components (e.g., aluminum and iron ions) necessary to stop the decomposition process is not known (Paul, 1984).

Couteaux *et al.* (1998) applied both a three-factorial model (see also Chapter 9) and a limit-value function using measured mass loss and respiration values of decomposing Scots pine needle litter as well as respiration values from the humus formed in the same stand. The decomposition rates of a stable fraction, that is measured close to the limit value, was in the range from approximately 0.0001 to 0.00001% per day. This corresponds to a rate of about 1% per 30 to 300 years. That study included an analysis of stable, meta-stable, and labile components (Table 10), of which the stable fraction encompassed approximately 90% of the material and may be considered as rate limiting (or decomposition of the whole litter).

V. LIGNIN DYNAMICS IN DECOMPOSING LITTER

A. Repeatability of Patterns in Lignin Concentration Changes

In general, in decomposing litter, the dynamics of lignin concentration resembles that of nitrogen: lignin concentration increases asymptotically when related to incubation time. When related to accumulated litter mass

Table 10 Decomposing Scots pine needle litter and humus formed from decomposing needle litter*

Labile comp (%)	K_L	Intermediate comp. (%)	K_{IN}	Recalcitrant comp. (%)	K_R
Pine needle litter incubated in the L layer for 16 months					
4.67 (0.61)	0.124	21.9 (1.54)	0.0087	78.5 (0.10)	< 0.0001
Particles from the H layer, < 2 mm diameter					
0.00 (–)	0.124	9.8 (1.32)	0.0087	91.2 (1.38)	< 0.0001

*In a study, the rates for decomposition and the sizes of the compartments with organic matter were examined. Incubations were made in a temperate Scots pine forest south of Paris. For the labile, the intermediate and the recalcitrant compartments the standard deviation is given within parentheses. After Couteaux *et al.* (1998). The compartments were used in the equation; K_L rate coefficient for the labile compartment, K_{IN} rate coefficient for the intermediate compartment, K_R rate coefficient for the recalcitrant compartment.

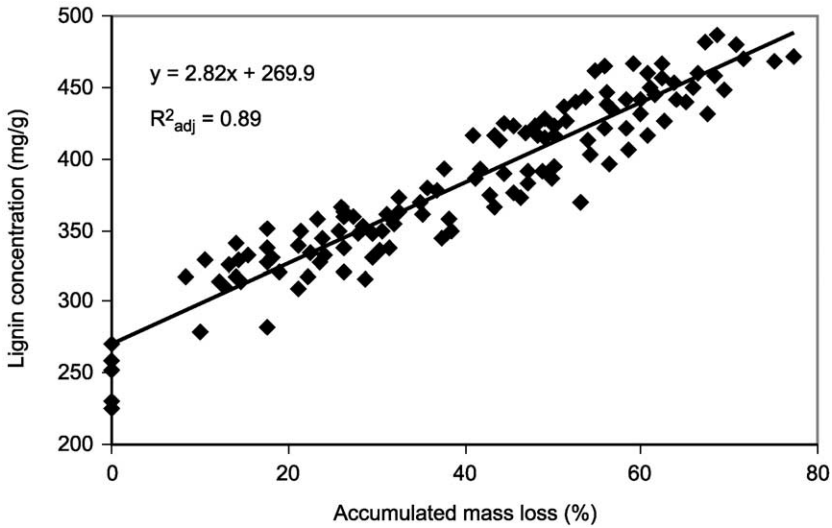

Figure 17 The relationship between the increase in lignin concentration and accumulated mass loss for 14 different incubations of local Scots pine needle litter at a site with Scots pine on nutrient-poor soil. All measurement points shown together with the common linear regression line. From Berg *et al.* (1997).

loss, a linear increase is observed (Fig. 17). Such a linear increase in lignin concentration has been found for decomposing needles of, for example, Scots pine, lodgepole pine, and Norway spruce. For Scots pine, the concentration increases to above 500 mg g^{-1} (Fig. 17) for the reasons discussed earlier (Section II.A) and in this interval (200 to 500 mg g^{-1}), the linear

relationship is highly significant. Deciduous litter like birch leaves also gives relationships that may be seen as linear, but much mass is lost initially, resulting in a rather quick increase, after which the concentration levels out (Berg *et al.*, 1984).

When lignin concentration is plotted versus litter mass loss, the slope of the straight line reflects a rate in concentration increase. This linear increase has been called LCIR (lignin concentration increase rate) (Berg *et al.*, 1997). The LCIR during decomposition appears to be repeatable with good accuracy within a given stand. We compared lignin concentration versus decomposition for native Scots pine needle litter incubated annually for 14 consecutive years in the same stand. The difference between years was the natural variation in initial lignin concentration (Berg *et al.*, 1993; Johansson *et al.*, 1995) and the annual variation in climate influencing decomposition. It appeared that although initial lignin concentrations differed among years, the LCIRs for different studies did not differ significantly. The slope when using all measurement points in one linear regression was 2.42 with an R^2_{adj} of 0.89 (Fig. 17; Table 11).

Table 11 A comparison between lignin concentration increase rates (LCIR) for local needle litter of three litter species incubated at their own stands[a]

	Constant (S.E.)	Coefficient (S.E.)	R^2_{adj}	r	n	p<
Scots pine						
All values combined (brown needles)	267.8 (26.6)	2.824 (0.099)	0.89	0.918	167	0.001
All values combined (brown needles, N fertilization experiment)	261.1 (24.2)	4.25 (0.22)	0.91	0.95	37	0.001
All values combined (green needles)	211.8 (8.6)	5.17 (0.12)	0.93	0.974	14	0.001
Lodgepole pine						
All values combined (brown needles)	370.6 (25.6)	1.24[b] (0.134)	0.62	0.785	55	0.001
Norway spruce						
All values combined (brown needles)	362.7 (18.7)	2.95 (0.174)	0.84	0.91	56	0.001
All values combined (green needles)	288.1 (40.2)	3.38 (0.61)	0.75	0.88	11	0.001

*a*Comparisons are made both by combining all values.
*b*In a measurement in pared stands, brown Scots pine litter gave the slope 2.55.

Two further boreal coniferous species investigated (Berg *et al.*, 1997), namely, lodgepole pine and Norway spruce, also showed good consistency in LCIR values. Thus, for lodgepole pine, five individual incubations at the same site showed a low variation among slopes and the slope when all the five data sets were combined became 1.24 ($R_{adj}^2 = 0.62$; n = 55). A similar comparison for native Norway spruce litter using data for incubated litter at one site gave straight lines for four combined data sets with the slope 2.95 ($R^2_{adj} = 0.84$; n = 56; Table 11).

B. Variation in the Increase in Lignin Concentration Relative to Different Initial Lignin Concentrations in the Litter

Different litter types have different behaviors as regards lignin disappearance. So, for example, for litters rich in lignin (for example lodgepole pine and Norway spruce needle litter), lignin disappearance begins at or soon after litter decomposition has started (Berg and Lundmark, 1987; Berg and Tamm, 1991) (Fig. 5). Still, the concentration of lignin increases as decomposition proceeds in spite of degradation taking place. There is, however, a variation among LCIR values for different litter species collected and incubated at their own ecosystem. At a site with monocultures of lodgepole pine and Scots pine in paired stands, the litter of lodgepole pine had a lignin concentration of about 350 mg g^{-1} and Scots pine about 290 mg g^{-1}. Both litter types had significant relationships between accumulated mass loss and lignin concentration with the slopes being 1.24 and 2.55, respectively. Lodgepole pine litter with initially higher lignin concentrations thus had significantly lower slope (Table 11).

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 LCIR and initial lignin concentrations, indicating that the higher the initial lignin concentration, the lower the increase rate. This may be explained by the molecular arrangements of lignin and polymer carbohydrates in the fiber (Fig. 7, Chapter 2). We may also refer to the highest lignin concentration reached in the litter, about 500 to 550 mg kg^{-1}, a level that seems to be common among litter species (Fig. 5).

C. Variation in Lignin Concentration Increase Rate as Compared to Different Concentrations of N in Litter

Some data for decomposing litter have indicated a higher LCIR value for nitrogen-rich litters species. Such an observation may be reasonable since N reacts with lignin remains to form new compounds (Nömmik and Vahtras,

1982), and N availability appears to be limiting for that process (Axelsson and Berg, 1988).

A comparison among Scots pine needle litter types at a fertile site with Scots pine on till resulted in a significant difference between groups. Local, natural brown needles with a low initial N level had an LCIR of 2.99, whereas brown litter from fertilized trees gave a slope of 4.25 and the N-rich green needles gave a slope of 5.17 (Table 11).

Needle litter of Norway spruce exhibited similar, though nonsignificant, trends with green, N-rich needles yielding higher LCIR values. Local natural brown needles had an LCIR value of 2.95 whereas green needles gave a slope of 3.39.

VI. DOES THE LITTER CHEMICAL COMPOSITION INFLUENCE LEACHING OF COMPOUNDS FROM DECOMPOSING LITTER?

Very high N loads, for example, in N deposition, have been suggested to give a disintegration of humus, probably as a consequence of heavily increased microbial activity. This theory was originally forwarded in a paper published by Fog in 1988. He expressed the hypothesis that a higher concentration of N in litter/humus resulted in an increased production of soluble organic matter (DOM or DOC). His ideas were based on the theory that lignin-degrading organisms of the kind called "soft-rot" (Chapter 3) need or at least tolerate high N-levels in their surroundings and that, in an environment more rich in N, these organisms, to a certain extent, can replace white-rot fungi. Their degradation of lignin gives 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 but resistant compounds, but decrease the amount of humus that is formed, for example, in a mor layer. Ulrich (1981) has described a similar process and called it a "disintegration of humus, and David *et al.* (1989) reported higher concentrations of soluble organic matter with increasing acidity.

In a later study, Guggenberg (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 increase 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

suggests that a generally higher microbial activity follows the increased formation of water soluble products.

In 1982, Nömmik and Vahtras (1982) published a review of ammonium fixation studies based mainly on laboratory studies and mentioned that following ammonium fixation a certain number of soluble compounds formed in the process can be extracted by dilute acid whereas an extraction with water would not cause a release but rather more N would remain fixed to the organic matter.

Thus, there are several indications that raised N levels in litter/humus may cause increased leaching. Still, a set of experiments at least describing the conditions for the process(es) involved remains to be done.

Nitrogen Dynamics in Decomposing Litter

I. INTRODUCTION

As the chemical composition of litter, together with climate and environmental factors, governs the decomposition process, it also rules the dynamics and release of nutrients from litter in different decomposition stages. Numerous studies have been carried out on the dynamics of nutrients in decomposing litter but mainly in the early stage of decomposition, and relatively few cover the late phases (see Chapter 4). A good general conceptual model of the processes of leaching, accumulation, and release of nutrients is still missing, probably because of the complexity of the processes. Although there have been attempts to distinguish subprocesses, such as leaching from and uptake to litter in the N dynamics during the course of the main decomposition process (Berg and Staaf, 1981), we still do not have a good description of the dynamics, much less a good explanation of several observed subprocesses. In this chapter, we focus on nitrogen, since there appears to be more knowledge generated on N dynamics in litter and humus than on other nutrients, making it possible to create a conceptual model for its dynamics. The details of the dynamics and the release mechanism are still not well explained, though, and are often related to litter species, giving the

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observations an empirical character. We therefore focus on a common pattern for foliar litter.

Nitrogen becomes available to the ecosystem basically through the N_2 fixation process and other sources of N, such as deposition of NO_x, which is part of the low "background" N deposition of approximately 2 kg ha^{-1} yr^{-1}. In natural, unpolluted forests, the input of litter N to forest floor is of considerable magnitude. A boreal coniferous forest may shed between 2 and 20 kg N in foliar litter per ha and year (B. Berg and V. Gauci, unpublished data), and a temperate deciduous forest 20 to 40 kg N per hectare in annual foliar litter fall (B. Berg and V. Gauci, unpublished data). In the newly shed litter, a main part of the N is in the form of proteins and nucleic acids. When N is in high excess in the litter, for example, in forests under extremely high N deposition, it can be present also in the form of arginine, an amino acid that normally is a storage form of N.

It appears that the N dynamics pattern may vary not only among ecosystems and environments but also with properties of different litter species. Examples of factors influencing its dynamics are litter pH, and the ratio of N to P and S, the nutrients that normally may be limiting for microbial growth. A further influencing factor is the availability of the energy source, normally indicated by the litter lignin concentration, influencing N dynamics in a way that still needs to be explained but probably, among other functions, acting as a sink for N, binding N in covalent bonds as part of the humus formation process. A further factor is the litters cation exchange capacity (CEC).

Often, N is limiting in ecosystems, both to the vegetation and to the microbial decomposers. Furthermore, N is available only from the atmosphere and could thus be expected to have entirely different properties for retention and availability as compared to nutrients such as K, which normally is not limiting, is available through weathering, is highly mobile, and has a solubility that is not pH dependent.

Often when element dynamics is studied in decomposing foliar litter, the total content of a given nutrient is measured, which includes not only the amount of the nutrient originally present but also that transported into the litter. This means that only the net changes are measured and not the actual movements of the nutrient. In addition, not only is the N in litter measured but also the amount of N in the microbial biomass and, unless accounted for, this part is also included in the dynamics. Even when isotopes are used as tools, it may be difficult to estimate the magnitude of this phenomenon, especially during a long-term experiment.

In this chapter, we attempt to create a system for describing N dynamics in decomposing litter. To do this, we have used several case studies which we consider to be representative, at least for litter in boreal and temperate ecosystems. We present a system for N dynamics in decomposing litter, describing different phases of the dynamics as well as a suggested release

mechanism. Finally, starting with newly shed litter, we calculate the N concentration in humus. Please note that part of the N dynamics, namely, its sequestration in humus and calculations of amounts released in the forest floor, is presented at the end of Chapter 6.

II. THE DYNAMICS OF NITROGEN—THREE PHASES IN DECOMPOSING LITTER

A. General Comments

As mentioned in Chapter 4, the concentration of N increases as litter decomposes and the increase may be at least threefold compared to the initial concentration. This increase in concentration is a general phenomenon, also described as a decrease in the C-to-N ratio. The increase is normally linearly related to accumulated litter mass loss, usually with a high R^2 value (Berg *et al.*, 1995), irrespective of the initial N concentration and of how the absolute amount of N changes during decomposition (Fig. 1; see also Section III).

There are some rules of thumb presented in the literature regarding N dynamics in ecosystems. Such simplified rules are normally intended and useful for practical purposes and give general relationships, which may be applied in agriculture and forestry. Still, they have very little to do with ecosystem research and, from a scientific point of view, they are sometimes directly wrong. For example, a general and fixed initial C-to-N ratio in litter as a limit for net release or net accumulation in decomposing litter has been proposed (see, for example, Lutz and Chandler, 1947; Mulder *et al.*, 1969) given as a C-to-N ratio of 25, which means an N concentration of about 20 mg g^{-1} in the litter organic matter. There appear to be either no or very few experimental data to support the generality of such a statement, and when applied to a nutrient-poor Scots pine ecosystem, we see that it is wrong: a net release from decomposing needle litter could take place initially at C-to-N ratios of about 125 (N concentration of about 4 mg g^{-1}) (Berg and Ekbohm, 1983). We see from Fig. 2 that for four Scots pine litter types, incubated simultaneously in the same forest stand, a net release was dependent on N concentrations and started at an initial C-to-N ratio of ca 80.

In this section on N dynamics, we present and discuss different cases of net uptake and net release as well as three phases for N dynamics and their importance in the N budget of decomposing foliar litter. Nitrogen in decomposing litter is not just released but, since it is often limiting to the decomposing microorganisms, it may be taken up actively to the litter, and thus its absolute amount in litter increases (Fig. 1). Such an uptake may take place through ingrowing fungal mycelium, which also may transport N bound in

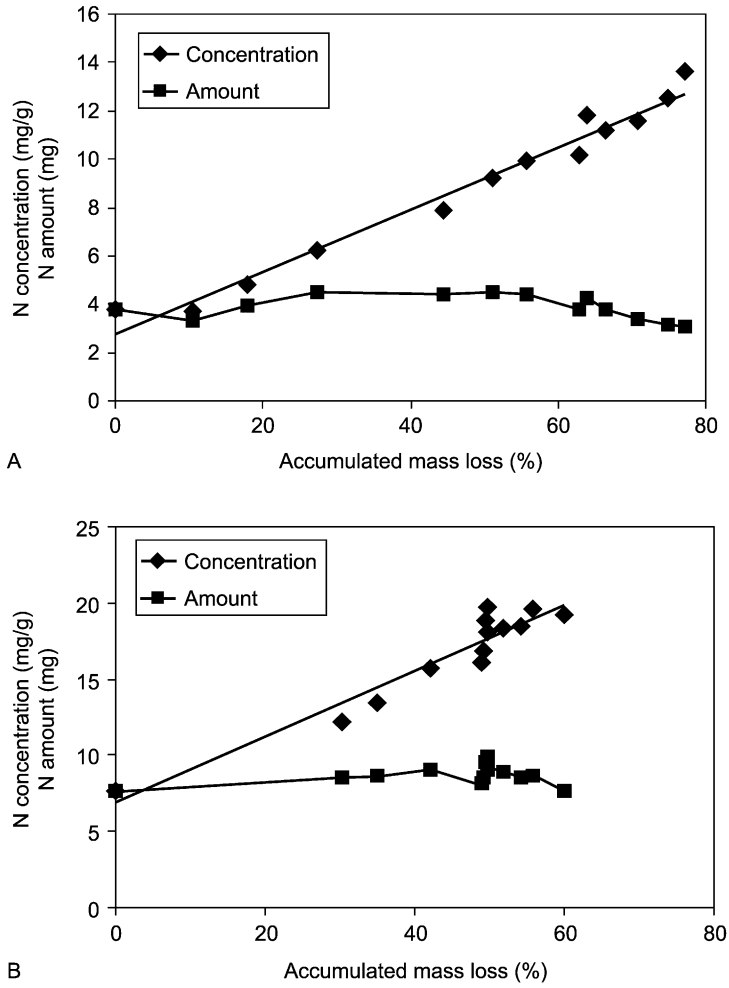

Figure 1 Concentrations and amounts of N in decomposing litter plotted versus litter mass loss. (A) Scots pine needle litter. (B) Silver birch leaf litter.

different compounds into the litter. The distance over which the transportation of N takes place from the surroundings into the litter probably is mostly in the order of millimeters or centimeters but may take place over distances of more than one meter.

It has been possible to construct a conceptual model for the dynamics of N in decomposing litter and a similar approach may be applied also to P and S, since these nutrients appear together in defined ratios, for example, in proteins and nucleic acids in the decomposing microorganisms, thus creating

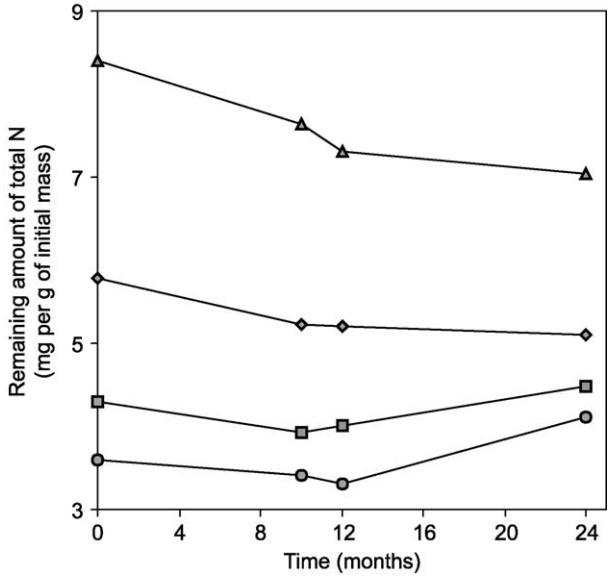

Figure 2 Four types of Scots pine needle litter originating from a nitrogen fertilization experiment were incubated simultaneously in a nutrient-poor Scots pine forest. The initial N concentration is of importance for whether an N release takes place or not.

rather constant ratios in the decomposing litter as decomposition proceeds (Section IV and Fig. 9, Chapter 4). During litter decomposition, the dynamics of the amounts of N may be divided into three different steps or phases. We may also see three cases of possible N dynamics (Fig. 3). In the first case, there is a short leaching of N followed by a net uptake and a net release (Fig. 3A). In another case, there may be a net uptake followed by a net release (Fig. 3B), and in a third case, only a net release is observed (Fig. 3C). Thus, all three phases are not always present and not always clearly distinguished. These will be presented more in detail.

B. The Leaching Phase

Newly fallen litter becomes invaded by microorganisms—a process which can take considerable time. Berg and Söderström (1979) found that the ingrown total (live plus dead) fungal mycelium in Scots pine needle litter reached a maximum first after approximately one year. Even in the early stages of this microbial invasion, the decomposition process starts. There is a very early period after litter fall, however, when litter mass loss and

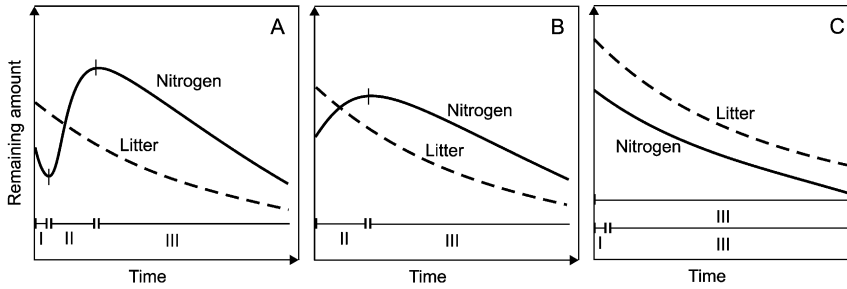

Figure 3 Three separate phases may be distinguished for the change in amount of litter N over time. Not all of them are always seen in practical experiments, though. For example, the accumulation phase could be missing, especially in litter with high N concentrations. (A) A leaching phase (I) is followed by an accumulation (II) and a release phase (III). (B) An accumulation (phase II) is followed by a release (phase III). (C) Only a release is seen (phase III or phase I + phase III).

nutrient release are not caused by microbial decomposition. This was first demonstrated as a short-term leaching using distilled water. Nykvist (1959) demonstrated the leaching of N from whole leaves of common ash and found that about 15% of their N could be physically leached (Table 1).

A rapid release of initially leachable N in litter constitutes this first phase of N dynamics (Fig. 3). Leachable, in this case, means extractable by water from whole litter. In its simplest form, studies on leachable N mean that, for example, a weighed amount of leaf litter may be allowed to soak in water for a certain time, maybe 1 to 24 h, and afterwards the water is analyzed for total N. A sequence of such short leaching events, sometimes studied in the presence of an inhibitor for microbial growth, will leach out what is possible to extract from a whole needle or a leaf. When litter decomposes on the ground, this leaching phase is rather short (Fig. 3A). In the case shown in Fig. 3C, leaching may take place but is not distinguished from the general release.

There are relatively few studies on leaching of substances from litter. Some results for N are compiled in Table 1. For nitrogen, leaching has been determined in laboratory studies on whole litter or milled samples and for whole litter in the field. Nykvist (1963) compared such leaching of soluble components from whole litter to that from milled samples and found the latter to be higher to a varying degree, which also may be valid for N (Table 1). We thus have two values—one for the actual leaching from whole litter and one for a maximum leaching, where the latter stands for potentially leachable substance, which is the same as the concept water-soluble substance (see Chapter 4). From the leaching data so far presented, it appears possible that the short-term leaching of whole litter in the laboratory could

Table 1 Leaching of nitrogen from some leaf and needle litter species (laboratory measurements)

Litter type	Total N (%)	Leached N (% of total litter N)	Reference
Black alder	2.1	13	(1)
Common ash	1.1	15	(2)
Common ash	0.86	18	(1)
Willow sp.	0.94	25	(1)
Downy birch	0.91	13	(1)
Trembling aspen	0.82	34	(1)
Mountain ash	0.71	42	(1)
European maple	0.51	40	(1)
Scots pine	0.38	3–4	(3)
Scots pine	0.36	15	(1)
Scots pine	0.49	9	(1)
Scots pine	0.73	2	(3)
Scots pine (green)	1.3	ca 6	(3)
Scots pine (green)	1.8	< 1	(3)

References: (1) Bogatyrev *et al.* (1983), (2) Nykvist (1959), (3) B. Berg, unpublished.

give lower values than those found in nature. Berg and Staaf (1981) found in field experiments that there was an initial release (leaching) of 10% of the N content of Scots pine needles versus about 2 to 4% for the same needle litter in the laboratory.

Some factors of importance for N leaching can be distinguished. Litter structure (seen as litter species) thus appears important, although only recognized as a difference among litter species rather than by specific physical properties. So far, we lack a systematic explanation regarding the litter properties versus leaching but leaching of both organic substances and N appears higher for deciduous leaves than for needle litter (Table 1). It may also be seen that leaching of N from one species, in our case, Scots pine needles, in laboratory measurements was not in proportion to the initial N levels in spite of the wide range from 3.6 to 18 mg g^{-1}.

A possible factor which determines the amount leached in the field would be rainfall and the movement of water, more intensive water movements promoting high leaching. Another factor may be freeze–thaw cycles, in which the freezing followed by thawing breaks tissue and cell structures and causes a release of N and other nutrients. Bogatyrev *et al.* (1983) showed that after all leachable substances had been extracted from intact leaves and needles by repeated leaching, a single freezing of the litter followed by a thawing again released high amounts of N.

It deserves to be emphasized that, in field experiments, the leaching phase relates to a net loss of N. At the same time as N is being released, the ingrowing fungal biomass transports N into the litter, both as an active

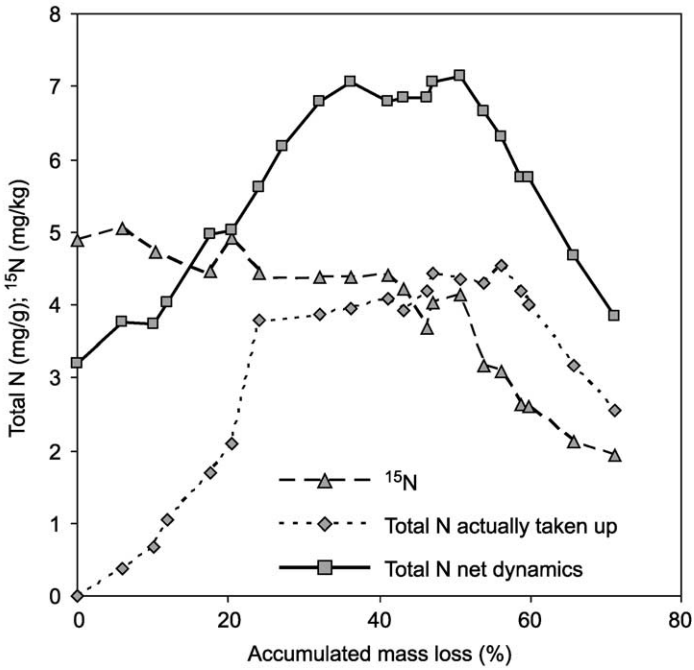

Figure 4 Laboratory experiment using decomposing Scots pine needle litter. Changes in absolute amounts of total N and ^{15}N as related to litter mass loss. The gross amount of N actually imported to the litter is also shown. The values refer to 1 gram (total N) or 1 kg (^{15}N) of initial litter. We see that part of the originally present ^{15}N is released from the litter at the same time as N is transported into it. From Berg (1988).

transport of N and other nutrients and as mycelial N in only ingrown mycelium. This means that we have two counteracting processes, which may be seen in Fig. 4, showing an experiment in which ^{15}N is leached from decomposing litter during a short initial period after the incubation, with a simultaneous transport of N into the litter structure.

C. Nitrogen Accumulation Phase—A Phase with a Net Uptake and a Retention of N

In this phase, a net transport of N takes place into the litter; thus, the absolute amount of N in litter increases compared to the initial amount. The phase ends when a maximum in the absolute amount of N is reached (Fig. 3A,B). For this accumulation, we could have used the already existing

term "immobilization." However, this term is often used in a general sense and thus is not unequivocal and, to avoid possible confusion, we prefer to call the absolute increase as defined here "accumulation." The accumulated amount is the increase in absolute net amount of N as related to the amount in the newly shed or incubated litter. Such an accumulation phase has been established for a number of litter species and ecosystems (Table 2). That an absolute increase in the amount of N may take place in decomposing litter was reported already by Bocock (1963) and by Gosz *et al.* (1973). The accumulation phase—when clearly visible—appears to start early in the decomposition process, sometimes directly after an initial leaching, and sometimes without a preceding leaching phase (Fig. 3A,B).

In the studies by Howard and Howard (1974) on different deciduous foliar litter, the accumulation phase lasted up to about 35% mass loss. Also, for Scots pine needle litter in a boreal forest, the accumulation ended at about 35% mass loss, after 1½ years of decomposition (Staaf and Berg, 1977). A mechanism for N release is discussed in Section II.D.

We will use a case study on Scots pine needle litter for a closer description of the accumulation concept. A laboratory study was performed using ^{15}N-labeled Scots pine needle litter. To obtain an experimental system for studying the microbial decomposition process, an acid forest soil was used, in which the effect of soil animals on litter decomposition was insignificant (Persson *et al.*, 1980). The incubated ^{15}N-labeled Scots pine needle litter had an initial N concentration similar to that of the local needle litter in the system where the incubations were made. In the laboratory experiment (Fig. 4), an incubation was made using undisturbed 0.5 × 0.5 m sections of the forest floor from a clear cut with very ammonium-rich humus below the litter layer (about 1000 mg kg^{-1} as related to the organic matter). Two field experiments confirmed that the observations from a laboratory experiment were valid in the two different field situations.

A field experiment using a nitrogen-poor humus layer in a mature forest and a nitrogen-rich in a clear cut was also made with an ammonium concentration of less than 50 mg kg^{-1} per organic matter and about 1000 mg kg^{-1}, respectively. In both incubations (low and high ammonium), the dynamics of N and ^{15}N were measured in whole litter (Fig. 4). The decomposition rate at the nutrient-poor Scots pine site was relatively low, and in the first year, only about 26% of the litter was decomposed. In both field experiments, the concentrations of total N increased significantly ($p < 0.001$) in proportion to litter mass loss. As in the laboratory experiment, the excess of ^{15}N decreased as decomposition proceeded. This dilution of ^{15}N was due to the uptake of unlabeled N from the litter surroundings and proportional to accumulated mass loss with $p < 0.001$. With a net uptake of N to the litter, the absolute amount of N increased, even though there was a simultaneous release of ^{15}N (Figs. 4 and 5).

Table 2 Net accumulation or net release of nitrogen in some needle and leaf litter species as compared to the initial nitrogen level

Species	Initial N concentration (mg g^{-1})	Release	No change	Accumulation	Observed maximum accumulation (% of initial amount)	Reference
Litter incubated in coniferous forest, no understory						
Grand fir	6			+	300	(1)
”	15		+			(1)
”	24	+				(1)
Sitka spruce	4			+	130	(1)
”	10		+			(1)
”	20	+				(1)
Scots pine	10		+			(1)
	28	+				(1)
Litter incubated in a chestnut forest						
Common beech	6			+	170	(2)
Chestnut	8		+		_	(2)
Chestnut	8		+		_	(2)
Litter incubated in a Scots pine forest (nutrient poor)						
Scots pine	3.8			+	130	(3)
	3.8		+		_	(4)
	4.2		+			(4)
	5.8		+		_	(4)
	8.5		+		_	(4)
	15		+		_	(5)
Litter incubated in a mixed deciduous/coniferous forest						
Sugar maple	6			+	170	(6)
American beech	8			+	150	(6)
Yellow birch	9			+	120	(6)
Litter incubated in a mixed forest, moder site						
Durmast oak	7.5			+	260	(7)
Ash	15	+			_	(7)

References: (1) Hayes (1965) (2) Anderson (1973), (3) Staaf and Berg (1977), (4) Berg and Staaf (1980b), (5) Berg and Cortina (1995), (6) Gosz *et al.* (1973), (7) Gilbert and Bocock (1960).

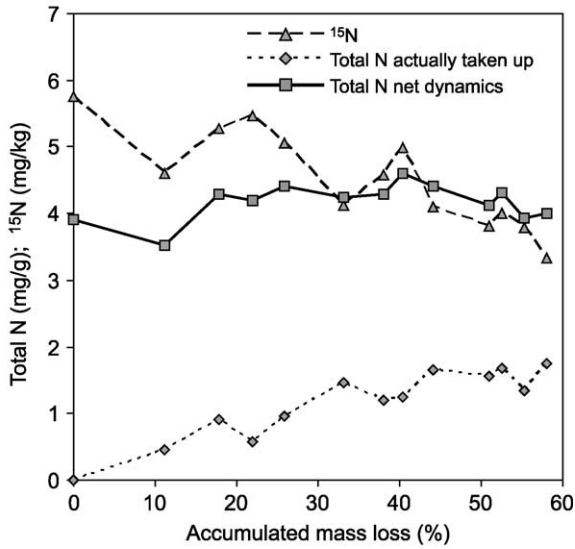

Figure 5 Field experiment using decomposing Scots pine needle litter. Changes in absolute amounts of total N and ^{15}N as related to litter mass loss. The gross amount of N actually imported to the litter is also shown. The values (mg) refer to 1 gram (total N) or 1 kg (^{15}N) of initial litter. From Berg (1988).

1. Sources of the N Taken Up

A net N accumulation in litter means an uptake of N to the litter from its immediate environment. The uptake could be, in part, due to N_2 fixation by microorganisms present in the litter, but in investigated cases in temperate and boreal forests, this process appears to be too slow to account for the observed net increases in amounts of N in needle and leaf litter. Such a net increase is almost exclusively due to uptake by fungal hyphae from the surroundings of the litter. Other sources were suggested by, for example, Bocock (1963), who showed that the amount of N taken up into decomposing sessile oak leaf litter mainly corresponded to the atmospheric deposition and to insect frass falling from the tree canopies. The quantity may be correct but the deposited N still needs to be transported into the litter and such a transport would be microbial. In a boreal pine ecosystem with only background N deposition, Staaf and Berg (1977) showed that the amount of N in deposition could not supply the amounts accumulated in the Scots pine needle litter of their nutrient-poor forest. Using ^{15}N, Berg (1988) demonstrated that, in the very same pine system, N was actively taken up to the litter from the soil and the surrounding litter (Fig. 4).

2. Influence of Litter N Level on the Uptake

The initial concentration of N in litter definitely has an influence on whether there will be a net accumulation of nitrogen or not. If N is the limiting nutrient for microbial growth, and thus for decomposition, an uptake would be expected. On the other hand, in litter with an N concentration above the level that is limiting, N would not be limiting and we can expect a lower net uptake or none. There thus should be an N concentration that would not make N the limiting nutrient. Such a concentration would mean an upper value of litter N concentration for an accumulation phase to be seen. Such a limit could be in common for several temperate and boreal forest ecosystems. In fact, for field experiments, we did not find any reports of an accumulation phase at initial N concentrations above 14 mg g^{-1} (Dowding, 1974). The suggestions about a fixed C-to-N ratio in litter (Mulder *et al.*, 1969; C-to-N = 25, N = 20 mg g^{-1}) as a limit for net accumulation or net release of N may be valid for a few systems only. Whether there will be a net accumulation or not may also be related to differences between systems, for example, nutrient-rich and nutrient-poor ones. Berg and Ekbohm (1983) incubated several sets of needle litter of different initial N concentrations in an N-poor and an N-rich forest system. They followed the decomposing litter, including its N dynamics, over a period of two years. As N-rich litter released N and N-poor accumulated, they calculated an "equilibrium" concentration for each system. In the nutrient-poor forest, the equilibrium level with no net release and no net uptake was 4.6 mg g^{-1} N and in the more N-rich system, the equilibrium level was 7.2 mg g^{-1}.

There are further observations on net accumulation of N in decomposing litter, mainly foliar litter, and we can distinguish a general pattern (Table 2). When foliar litter species with different initial N concentrations were incubated in the same forest floor, the more nutrient-poor ones clearly accumulated N. Such a very clear pattern is seen also in a comparison among the three species: Grand fir, Sitka spruce, and Scots pine within the same forest system. The most N-rich litter, with 20 mg g^{-1} N or higher, releases N; those samples with initially about 10 to 15 mg g^{-1} have neither release nor accumulation, and the N-poor litter types have a very clear accumulation. In that study (Hayes, 1973), a very clear general pattern is seen due to a large range in initial N concentrations. For other studies using deciduous litter, similar tendencies were seen. For example, in leaf litter of European ash and durmast oak, a high initial N concentration of 15 mg g^{-1} N resulted in a net release, while in durmast oak litter with 7.5 mg g^{-1} N, a clear uptake took place. In a comparison of leaf litter of common beech with that of chestnut, a similar trend was seen, with an accumulation for the low-N beech leaves and no change for those of chestnut (Table 2). In contrast, for softwood species, we have observed so far the same behavior over a good range

of N concentrations. Thus, for Scots pine needle litter decomposing in a nutrient-poor pine forest, no change in amount was seen over a range of litters with initial N concentrations from 4.2 to 15 mg g^{-1}.

We may interpret these results so that they indicate a general trend for N-poor litter to accumulate N and for N-rich litter to release N. Still, we may expect that although such a trend emerges, the results from Scots pine needles suggest that the trend is not general. We may also expect that the availability of N in the system where the litter is incubated may be of importance, although data in Table 2 do not help us with that conclusion. This discussion is based on the initial concentrations of total N, which does not necessarily mean that we can compare litter species from the point of view of N readily available to microorganisms.

3. The Effect of Lignin and Lignin-Like Compounds on the Accumulation of N

The analytical fraction consisting of lignin, modified lignin, and humification products, for example, "sulfuric-acid lignin," appears to decompose rather slowly (Fig. 2, Chapter 4) and increases its absolute content of N during litter decomposition (Fig 6). In a review, Nömmik and Vahtras (1982) thoroughly discussed the uptake of NH_3 by lignin remains, the formation of new, N-containing compounds as well as humification products. It is possible that,

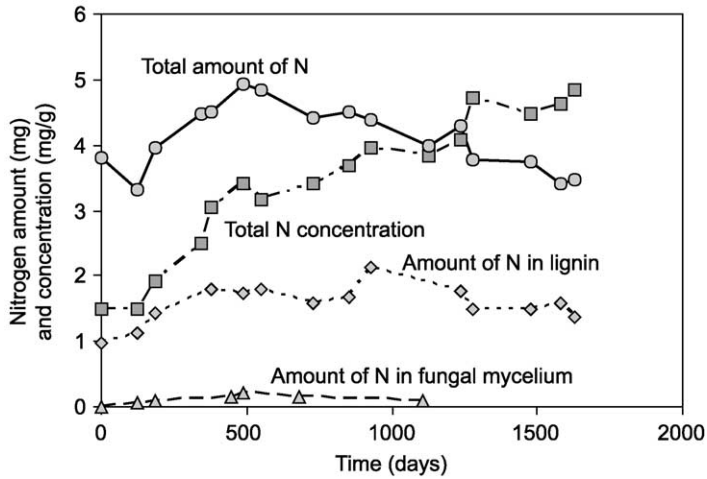

Figure 6 Changes over time in amounts of N in two fractions of decomposing Scots pine needle litter. Changes in N in fungal mycelium are also shown as well as total N concentrations versus time. From Berg and Theander (1984).

during the accumulation phase, the N mineralized in litter will be bound to the fraction of native and modified lignin. In water, the equilibrium

$$H^+ + NH_3 \rightleftarrows NH_4^+$$

is dependent on the concentration of H^+. The reaction in which N is bound to, for example, lignin remains is pH dependent and with NH_3 being the reacting form, a higher pH increases the reaction rate between NH_3 and reactive groups in lignin remains. In a decomposition experiment, a linear relationship was found ($R^2 = 0.806$, $p < 0.001$) between the total accumulation of N in litter and the increase of N in the sulfuric-acid lignin fraction during the accumulation phase. The amount of N found in the lignin fraction corresponded approximately to the total amount of N accumulating into the litter during the decomposition process. A number of studies give support for the combined effect of N and lignin concentrations as factors determining the accumulation of N during decomposition. It also appears that the N accumulation can be related to initial concentrations of N and lignin in the newly shed litter (e.g., Aber and Melillo, 1982).

There are further, older literature data which suggest that lignin/humification products serve as an internal sink for accumulated N in the litter. By 1950, Coldwell and Delong (1950) found a positive linear relationship between initial lignin concentration and the amount of N accumulated in the litter also when the initial N levels were similar. Likewise Töth *et al.* (1974) found net losses of N from litter species with a low lignin level and an accumulation in those with a high level. In the following section, we discuss a release mechanism for N based on an empirical relationship between lignin mass loss and N release.

D. A Release Mechanism

As has been discussed, the point at which N release from litter begins has often been related to a particular or "critical" C-to-N ratio of the litter (Mulder *et al.*, 1969). There does not seem though to be any proof that the concentration of a given nutrient (such as N, P, or S) is the sole determinant of its uptake or release in decomposing litter. Furthermore, such critical C-to-N ratios appear to vary with the ecosystem (Berg and Ekbohm, 1983). These suggested C-to-N ratios refer to a release that starts initially at litter fall but a release may also be initiated later and such a release may be initiated by factors other than the initial N concentration. Today, we can distinguish when a net release starts during the decomposition process.

We intend to describe a suggested empirical mechanism for N release from decomposing litter and refer to the release that takes place when there has been a net accumulation of the amount of N in the litter (Fig. 3A,B). It has been found that a net release of N starts after decomposition of the lignin

fraction has started (Berg and McClaugherty, 1987). To describe this, we first discuss the dynamics of N and lignin and how concentrations of lignin and N increase in decomposing litter and the fact that a net disappearance of lignin takes place before a net release of N starts. Then, we use a case study based on 11 boreal and temperate litter species and 34 decomposition studies. The mechanism is, in part, empirical in the sense that it consists of a set of statistically significant relationships that have not yet been explained satisfactorily from the point of view of causality.

Lignin and humic compounds in foliar litter, the latter formed during decomposition, normally decompose slowly and their concentrations in a foliar litter can, at least in part indicate the decomposability of the litter. N is incorporated into humic substances during decay (Nömmik and Vahtras, 1982; Stevenson, 1994). The combination of declining substrate quality and the incorporation of N into slowly decomposing compounds may allow us to hypothesize that N dynamics in decomposing litter would be closely related to the dynamics of the lignin-humus fraction of the litter. In fact, Berg and McClaugherty (1987, 1989) presented evidence that a net N release does not begin until the amount of lignin begins decreasing.

Net lignin disappearance begins before a net N release starts. There appears to be a generality of this phenomenon, namely, that there is a net loss of the lignin fraction, for example, sulfuric-acid lignin, before a net release of N starts. Although this relationship may not be valid for litter with exceptionally low initial lignin concentrations or high initial N concentrations, it has been shown to be valid for no fewer than 11 boreal and temperate litter species (Table 3). The litter for which the relationship was demonstrated had initial lignin concentrations in the range from 121 to 390 mg g^{-1} (Table 3). For flowering dogwood leaf litter, a possible exception has been observed (J. Melillo, personal communication), namely, that N release begins slightly before a net lignin disappearance. Initially, these flowering dogwood leaves contained 40 mg g^{-1} lignin and 14 mg g^{-1} N.

Concentrations of lignin and N increase linearly with accumulated litter mass loss and this applies to all foliar litter types and species so far studied. These relationships were previously described for N by Aber and Melillo (1982), and for lignin by Berg and McClaugherty (1987). For the case study presented here, all of the linear relationships for concentration increase in N and lignin were highly significant ($p < 0.001$). Examples of such linear relationships for N are shown in Fig. 1 and for lignin in Fig. 17, Chapter 4. We will use these linear relationships for calculating what we call "critical concentrations" of N and lignin and we use these critical concentrations as help parameters and call them "critical" in this context since they are determining for the onset of a net release of N.

The linear increase of lignin concentration with accumulated litter mass loss makes it useful as an index of changing litter quality during decay. It

Table 3 List of foliar litter species shown to follow the release mechanism for N suggested in Section II.D in which N is released after a net lignin mass loss has started[a]

Species	Initial lignin (mg g^{-1})	Initial nitrogen (mg g^{-1})
Scots pine	208–300	3.6–15.1
Lodgepole pine	357–391	3.4–4.0
White pine	225	4.4
Norway spruce	208–340	4.2–8.5
Eastern hemlock	206	8.3
Grey alder	264	30.7
Silver birch	322–363	7.6–17.4
Trembling aspen	214	8.3
White oak	202	8.4
Red oak	248	8.2
Sugar maple	121	8.3

[a]Ranges of initial concentrations of lignin and N are given. Data from Berg and McClaugherty (1989).

also leads to the hypothesis that the continuously decreasing "substrate quality" or decomposability will reach a point at which this microecosystem cannot bind any more nitrogen. The reasons for this are unknown and we suggest a possible explanation. When a net lignin degradation starts, this may mean that the available part of the more easily degradable carbohydrates are used up. In its turn, this may cause such a decrease in substrate quality that the microbial biomass decreases, releasing N. Further, part of the remains of "N bound to the lignin" may be released as a result of lignin decomposition. Thus, what has been measured in the studies we refer to was the release of total N, which does not mean that N had been mineralized.

So, we compare the concentration of lignin at the maximum amount of N, that is, just before a net release starts, with the concentration of lignin at the maximum amount of lignin. If a net N release begins after the onset of a net lignin mass loss, the Lignin Concentration at Maximum Amounts of N (LCMAN) should be higher than Lignin Concentration at Maximum Amount of Lignin (LCMAL) (Fig. 7). We calculated LCMAL and LCMAN for 34 decomposition experiments and compared them against the 1:1 line (Fig. 8). We see that LCMAN generally is higher than LCMAL, indicating that a net lignin disappearance starts before a net N release.

1. Calculation of Maximum Amounts of N and Lignin as well as the Concentrations of Lignin at Maximum Amounts of N and Lignin

The basic relationships necessary for this calculation are easily studied, simply by following the changes in lignin and N concentrations during decomposition (Fig. 7A). The maximum absolute amount of lignin and N

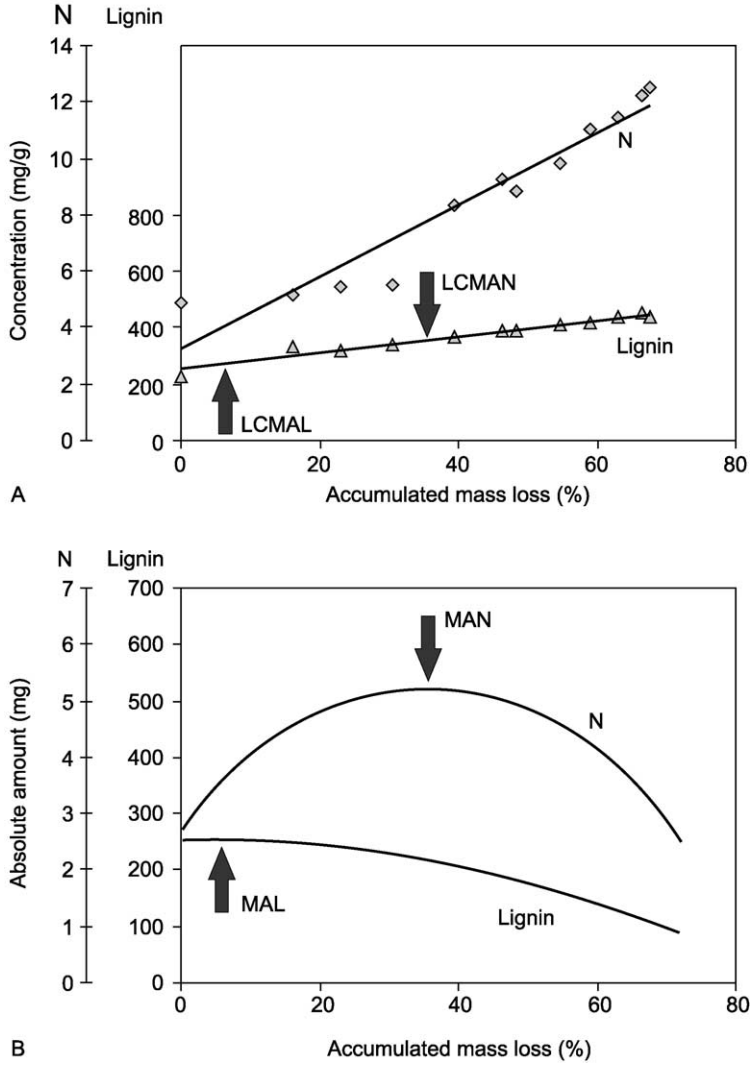

Figure 7 Relationships between accumulated litter mass loss and concentrations of total N and sulfuric-acid lignin (A) and absolute amounts of N and lignin (B). Arrows indicate (B) the maximum amount of nitrogen (MAN) and the maximum amount of lignin (MAL) and (A) the lignin concentration at the maximum amount of nitrogen (LCMAN) and lignin concentration at the maximum amount of lignin (LCMAL).

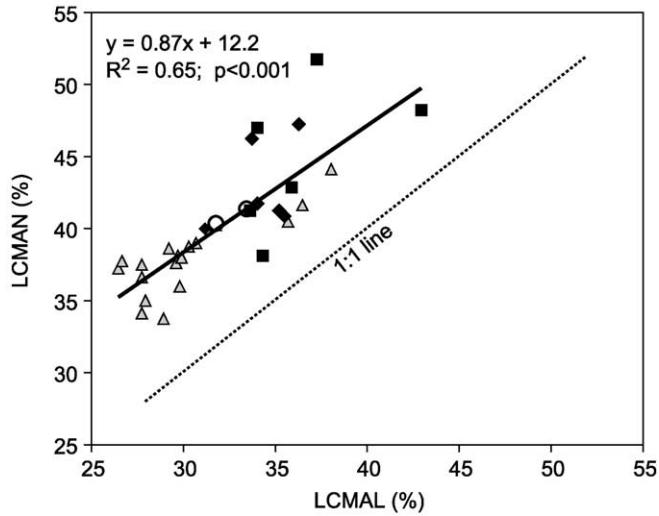

Figure 8 Lignin concentration at onset of a net nitrogen release (LCMAN) as compared to lignin concentration at the start of a net disappearance of lignin (LCMAL). (▲) Pine needles in field incubations; (○) pine needles in laboratory incubations; (■) Norway spruce and Easter hemlock needles in field incubations; (◆) deciduous leaves in field incubations. Broken line gives the position of line with the slope 1:1 and intercept zero.

in the substrate can then be estimated by interpolation from the measured data, that is, graphically from plotted amounts. However, such estimates may have a relatively high degree of error because interpolation is uncertain due to the nonlinear nature of the relationships of amounts versus time. We may avoid this problem by using the linear relationships between accumulated mass loss (or litter mass remaining, as was done in the original work; Aber and Melillo, 1982) and concentrations of N, on the one hand, and of lignin on the other. Therefore, we can estimate the maximum amounts of lignin and N using the linear relationships between their concentrations (in percent) and percentage accumulated mass loss. Both the maximum amount and concentration at maximum amount (critical concentration) of a substance (Fig. 7) can be calculated algebraically by using the set of equations provided by Aber and Melillo (1982). An alternative way of calculating this is provided by Berg and McClaugherty (1987), who used the positive linear relationship between litter N and lignin concentrations and accumulated mass loss.

In the next step, the maximum amounts of N and lignin are calculated (Fig. 7B) and, in a further step, the concentration of lignin at the maximum

amounts of both N and lignin (Fig. 7A). For example, the Lignin Concentration at Maximum Amount of Nitrogen (LCMAN) can be estimated and compared to Lignin Concentration at the Maximum Amount of Lignin (LCMAL). This procedure allows us to compare the Lignin Concentration at Maximum Amounts of Lignin (LCMAL) with the Lignin Concentration at Maximum Amount of N (LCMAN) (Fig. 7).

2. Comparisons of the Onset of a Net Disappearance of Lignin and Ligninlike Substances and of N

Once the critical concentrations of N and lignin (LCMAN and LCMAL) are calculated, they may be compared using linear regression (Fig. 8). In their study, Berg and McClaugherty (1987) found that the average difference between LCMAL and LCMAN was about 8.0 percentage units (in lignin concentration) when using all data, with the LCMAN being the higher value. A net release of N therefore starts after the onset of a net disappearance of lignin and continues later during the decay process.

The delay between time of maximum amount of lignin (MAL) and that of N (MAN) indicates that the potential for N incorporation remains even after a net loss of lignin has begun. Studies of the N content of the lignin fraction in decomposing litter support this view (Aber *et al.*, 1984; Berg and Theander, 1984). The linkage between the dynamics of lignin and that of N may be explained partly by the process of humification, in which N is incorporated into the lignin fraction of the litter (Stevenson, 1994).

For comparison to a traditional determinant of N mineralization, Berg and McClaugherty (1987) calculated the C-to-N ratio at the point where a net release of N begins (a "critical C-to-N ratio"), using the same data sets as shown in Fig. 8. Assuming that the fraction of C in litter is 50%, they noted that the observed C-to-N ratios at onset of the net N release ranged from 23 to 98, and the estimated ones from 39 to 80. Clearly, the C-to-N ratio is not a good predictor for the onset of net N release from decomposing litter. This probably is due to the fact that the C-to-N ratio does not consider the quality of either the C or N constituents in the litter. The question remains as to how the lignin concentration at onset of a net release for N is related to the lignin concentration at onset for lignin decomposition. Although the lignin concentrations at the onset of N release were consistently higher than those at onset of a net disappearance of lignin, we do not know whether the difference between LCMAL and LCMAN is related to the magnitude of the LCMAL. We hypothesize that the differences would decrease with increasing values of LCMAL since there may be less potential for the

incorporation of N when a net disappearance of lignin begins relatively late and at very high lignin concentrations. To test this hypothesis, Berg and McClaugherty (1987) calculated linear regressions for their entire data set and for selected subsets. The result for LCMAL indicates that the differences between LCMAN and LCMAL are similar regardless of the size of LCMAL. This is indicated by the slope of the regression line is being close to 1 (Fig. 8).

E. The Final Release Phase

This phase starts with a net release after a maximum amount of N has been accumulated in litter, and continues as far as the amount decreases (Fig. 3A–C). The release during this phase is often slower than in the leaching phase. If the accumulation phase is missing, the release can be preceded by a not always distinguishable leaching phase (Fig. 3C). Once a phase III release of N has started, it appears to be related to litter mass loss and we see that release from Scots pine needles appeared to be in a linear relationship to the accumulated mass loss ($R^2 = 0.85$; Fig. 9). A continued increase in N concentration (Fig. 1) is typical, however, for most litter types, indicating that, relative to carbon, nitrogen is retained, to a certain extent, in decomposing litter even when a net release takes place.

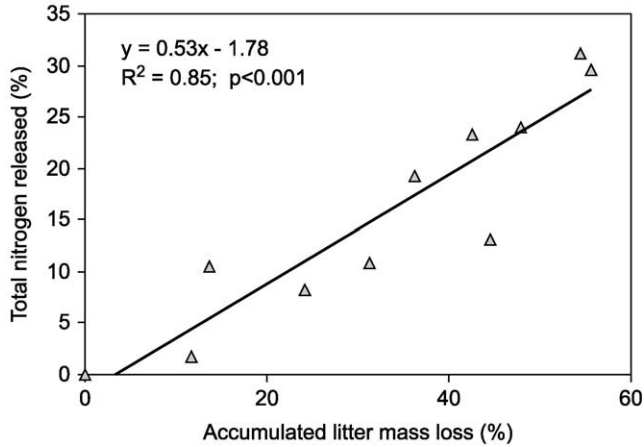

Figure 9 Linear relationship between N released from decomposing Scots pine needle litter and litter mass loss. In this case, the accumulated mass loss from the start of N release has been plotted on the X axis.

III. NITROGEN CONCENTRATION VERSUS ACCUMULATED LITTER MASS LOSS

The increase in N concentration in decomposing litter may be related to time since incubation, the result being a curve of an asymptotic appearance. When the N concentration is related to accumulated litter mass loss, for several litter types, this results in a linear increase, possibly until the limit value is reached (Berg *et al.*, 1999d; Fig. 10). Such a linear increase has been found, for example, for foliar litter of Scots pine and Norway spruce. For Scots pine litter, this increase goes from an initial N concentration of approximately 4 mg g^{-1} in fresh litter up to almost 13 mg g^{-1} at approximately 75% mass loss (Fig. 1). Deciduous litter, such as silver birch leaves, also tends to give linear relationships, but because much mass is lost initially, the increase in N concentration in proportion to mass loss is particularly fast and often the main increase in concentration is seen in the first sampling (Fig. 1). This linear relationship is an empirical finding and, at least for coniferous foliar litter, the relationship normally appears to be highly significant (Fig. 1). The reasons for the straight-line relationship are far from clear, considering simultaneous in- and outflows of N during the decomposition process (Fig. 3).

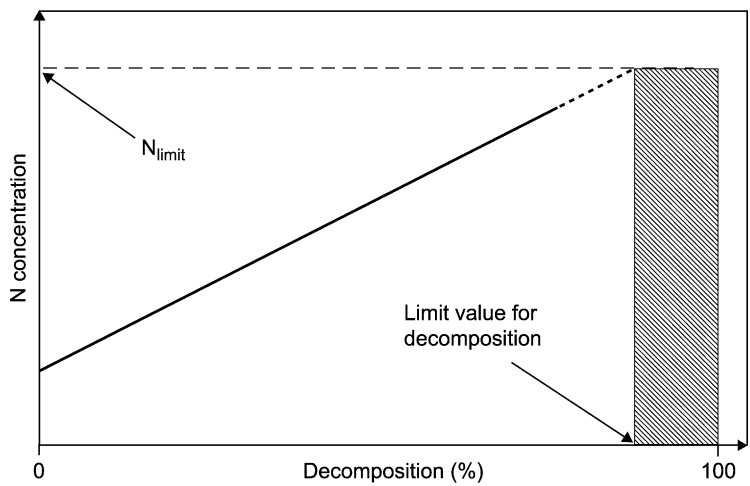

Figure 10 Nitrogen concentration at the limit value. Nitrogen concentration increases linearly in decomposing litter and the N concentration at the limit value is estimated by a short extrapolation (dotted line). The shaded area represents the recalcitrant mass.

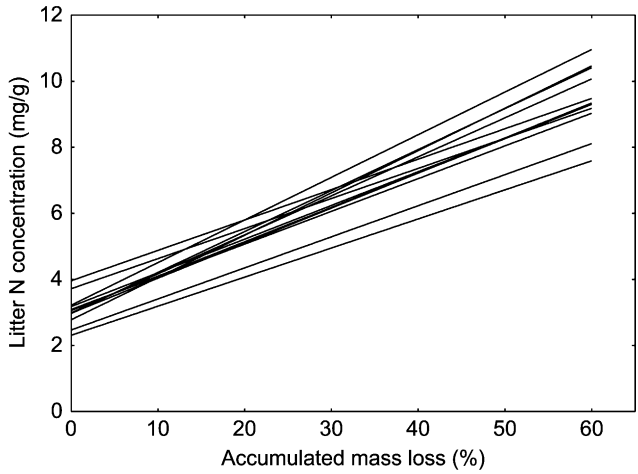

Figure 11 Repeatability for the relationships between mass loss and N concentration in decomposing Scots pine litter. Local needle litter was incubated in the same stand over nine consecutive years, the accumulated mass loss was followed until more then 60%, and the slope between litter N concentration and litter mass loss was determined (NCIR) (Table 4).

There appears to be good repeatability among sets of needle litter and over years as regards the linear increase in N concentration. This linear relationship for N concentration versus accumulated mass loss was compared for several sets of decomposing Scots pine needle litter in one ecosystem (Berg *et al.*, 1996b) (Fig. 11, Table 4). For the purpose of this comparison, they used the Nitrogen Concentration Increase Rate (NCIR), that is, the slope of the linear relationship to litter mass loss. In that investigation, the litter was native of the same Scots pine monocultural stands and the variation in initial N concentration was the natural annual variation. The relative increase rates in concentration showed significant relationships for individual data sets as well as for 9 combined sets of the litter (Table 4). The NCIR values in this comparison had an average of 0.12 and the slopes ranged between 0.092 and 0.129 (standard error = 0.0041), indicating that for a given litter type and system, the variation in NCIR was not large.

In a similar comparison of NCIR values for lodgepole pine needle litter, the slopes of five different decomposition studies gave an average slope of 0.1151 with a standard error of the same magnitude as that for Scots pine (Table 5). For needle litter of Norway spruce, the average slope was similar to that of the lodgepole pine litter (0.1171) and also reasonably consistent among four sets of litter. The natural needle litter of lodgepole pine, Scots

Table 4 Linear regressions of N concentration in decomposing litter versus accumulated litter mass loss[a]

Intercept	Slope	n	R^2
3.215	0.129	12	0.923
2.984	0.106	10	0.931
2.79	0.1286	13	0.973
3.275	0.1115	10	0.914
3.18	0.1021	9	0.933
3.27	0.1037	13	0.972
2.969	0.1236	8	0.952
3.958	0.0916	7	0.965
2.47	0.0936	13	0.885

[a]Data from Berg *et al.* (1997a). All data originate from local incubations of Scots pine needle litter in a mature Scots pine forest at the former research site of the Swedish Coniferous Forest Project (Jädraås). All regressions were significant at $p < 0.001$.

Table 5 Linear regressions of N concentration in decomposing litter versus accumulated litter mass loss for Scots pine, lodgepole pine, and Norway spruce[a]

Tree species	Intercept (SE)	Slope (SE)	R^2	n
Scots pine	2.941 (0.988)	0.1107 (0.0042)	0.846	131
Lodgepole pine	2.762 (1.128)	0.1171 (0.0065)	0.743	54
Norway spruce	4.769 (1.124)	0.1019 (0.0105)	0.638	56

[a]All data originate from natural, unpolluted stands in which local needle litter was incubated. Values from different decomposition studies were combined to common regressions. There were 14 studies for Scots pine, five for lodgepole pine, and four for Norway spruce. From Berg *et al.* (1997). SE stands for standard error of the mean.

pine, and Norway spruce had similar initial N concentrations and all of them also had rather similar average NCIR values.

Green needles of Scots pine with a higher initial N concentration had a much larger NCIR than did brown needles, meaning that the relative increase was larger than for the brown needle litter. A similar trend was observed for decomposing green and brown Norway spruce needles. Both green needles and N-enriched needles collected from N-fertilized plots had higher NCIR values than regular brown, N-poor needle litter (Berg *et al.*, 1997). That N concentrations increase relatively faster with accumulated mass loss when the initial N concentration is higher was also observed by

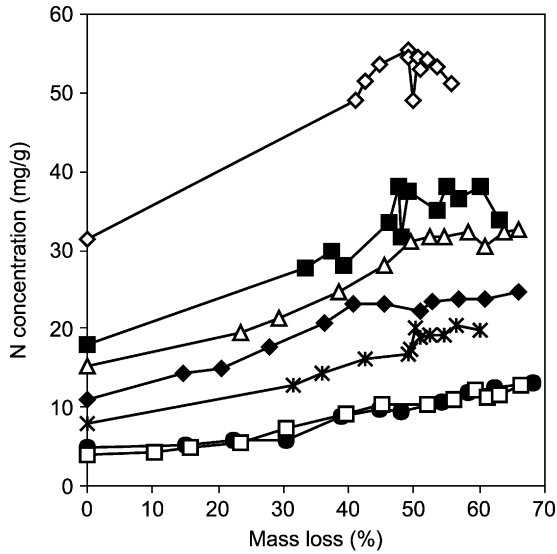

Figure 12 Changes in N concentration as related to accumulated litter mass loss for seven litter types incubated in a 130-year-old Scots pine forest. Brown Scots pine needle litter (●), green Scots pine needles (△), brown needles of lodgepole pine (□), green needles of lodgepole pine (◆), brown leaf litter of silver birch (*), green leaves of silver birch (■), and green leaves of grey alder (◇). From Berg and Cortina (1995). Adapted with permission from the Scandinavian Journal of Forest Research.

Berg and Cortina (1995) when comparing NCIR for seven very different litter types incubated in one system (Fig. 12).

That the increase in N concentration relative to accumulated mass loss appeared to increase with higher initial N concentrations (Fig. 12) was possible to systemize for a large set of data, and the Nitrogen Concentration Increase Rate (NCIR) was seen to be higher relative to mass loss the higher the initial N concentration in litter. The linear increase may continue until the decomposition reaches a stage at which it is extremely slow (Couteaux *et al.*, 1998) or appears to cease completely, for example at the limit value (Fig. 10). At a rather high N concentration of about 50 mg g^{-1}, a heavy release may start leading to a concentration decrease (Fig. 12) and this may be a limitation of the relationship.

Although the relationship between N concentration and accumulated mass loss is still purely empirical, the generality of this phenomenon and the consistency of regression slopes suggests the presence of a more precise regulation of biological and/or chemical origin. We have used this relationship for calculation of N concentration in humus and later for N sequestration (Section IX, Chapter 6).

IV. NITROGEN CONCENTRATION IN LITTER DECOMPOSING TO THE LIMIT VALUE AND IN HUMUS

A. Background and Some Relationships

In this section, we present calculations on the concentration of N in the soil organic matter. For this purpose, we make a stepwise presentation of a model. In the first step, we give the calculation of N concentration in litter decomposed to the limit value, which should be the same as that in the organic matter of the humus layer. The second step gives a validation of these estimates, presented as a case study.

As already discussed, the dynamics of N in decomposing litter may vary with plant species, initial N concentration (Fig. 12; Table 2), and stage of decomposition (Fig. 3). We have already commented on the linear increase in N concentration with litter mass loss (Section III). Using this linear relationship, we can develop the conceptual model on N dynamics. To do this, we first combine the linear relationship between N concentration and accumulated litter mass loss with the limit value concept and calculate the N concentration at the limit value, which is the same as the N concentration in the stable organic matter in the SOM (an F- or H- layer). In Chapter 6, we describe how we can calculate the amount of N stored.

We introduced the equation for limit values in the preceding chapter (Eq. 3). In this section, we use it to calculate N concentration in the SOM layer and start by calculating the limit value (Eq. 3, Chapter 4; see also Fig. 15 in that Chapter). In a next step, we use the linear relationship between the N concentration and litter mass loss to estimate the N concentration at the limit value (Fig. 10):

$$N = N_{init} + NCIR \times AML \quad (1)$$

where NCIR is the slope of N concentration increase (see Section III), AML accumulated litter mass loss, and N_{init} the initial litter N concentration (equivalent to the intercept of the regression line). The coefficient NCIR is empirical and may be related to species. This linear relationship normally has R^2 values well above 0.9 (Berg *et al.*, 1999d) and it is thus possible to make extrapolations with good precision. By extrapolating the relationship to the limit value (m) estimated with Eq. 3, Chapter 4, the value for N_{limit} can be calculated (Fig. 10) as:

$$N_{limit} = N_{init} + NCIR \times m \quad (2)$$

B. A Model and a Case Study for Calculating N Concentrations in Humus

We offer a case study with calculations of N concentration in the humus in the organic soil layers. Forty-eight decomposition studies of local litter and N dynamics originating from different boreal and temperate forest stands were used. Of these, 27 stands were monocultures with Scots pine, four with lodgepole pine, four with silver birch, and 15 with Norway spruce. Further, there was one site of each with common oak, black alder, silver fir, and common beech.

A calculation of N concentrations in a set of humus layers has been made following the procedure described previously. The limit value (m) for decomposing litter has been estimated using Eq. 3 (Chapter 4) and linear relationships have been calculated between accumulated litter mass loss and the N concentration in the decomposing litter for each data set separately. These have been extrapolated up to the decomposition limit value (Fig. 10). At the limit value, the increase in N concentration stops as the decomposition comes to a halt. We may thus assume that the N concentration becomes the same as that in the humus layer (SOM). A basic condition is that the humus, in the F- and H-layers, has been formed from the very same foliar litter as the decomposing layer (Berg *et al.*, 1999d). It should be emphasized again that the stands used in this case study were monocultures, with just one species of foliar litter, and that the stands were mature, and thus able to have formed a substantial humus layer.

At all the stands for which the these calculations were made, humus was sampled and analyzed for N concentration. When possible, the mor humus samples were sorted into F (A_{01}) and H (A_{02}) layers. When this was not possible, a combined F and H layer (A_0) was sampled. For humus of the moder type, part of the A_0 layers was sampled. Carbon and N analyses allowed a calculation of the N concentration in the organic matter. Care was taken not to use the N concentration in the total humus layer but only that in the organic matter. Humus layers always include mineral particles, and they may be found even in mor humus. The measured values for N_{humus} varied considerably among the samples from the different forests, from 9.9 mg g^{-1} in humus of a nutrient-poor northern Scots pine forest at the Arctic Circle to 39.9 mg g^{-1} in the humus of a more nutrient-rich silver fir humus in southern Italy. Within a stand, there were no differences between A_{01} and A_{02} layers as regards N concentrations in the organic material, neither in pine nor in spruce forests.

For foliar litter at the stands used in this case study, there were clear differences in initial N concentrations, not only among tree species but also within species. For Scots pine needles, the concentration ranged from 2.9 to 8.6 mg g^{-1}, for needle litter of Norway spruce from 4.0 to 10.0 mg g^{-1}, for

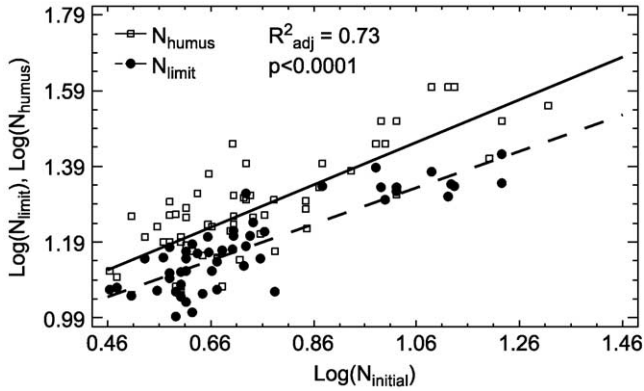

Figure 13 Comparison of the relationships between initial and estimated N concentrations at the limit value and between initial N concentration and N concentration in humus; R^2_{adj} for the common regression is 0.73 ($p < 0.0001$). Slopes do not differ from each other ($p = 0.21$), whereas the significant difference in intercepts is 6.8% ($p < 0.0001$).

that of lodgepole pine from 3.4 to 5.0 mg g^{-1}, and for that of silver fir from 12.3 to 13.6 mg g^{-1}. For the deciduous litter, the concentration for silver birch litter ranged from 7.5 to 13.4 mg g^{-1}, for common beech from 9.8 to 16.8 mg g^{-1}, and for common oak and black alder, the values were 15.9 and 20.7 mg g^{-1}, respectively.

In our case study, the calculations described gave a set of predicted N_{limit} values, which were compared to the measured values for N concentration in humus (N_{humus}). There was a highly significant positive correlation between N_{humus} and N_{limit} with $R^2 = 0.632$. The highly significant relationship between N_{limit} and N_{humus} suggests a general relationship between the estimated N_{limit} concentrations in humus and those measured. As may be expected, litter with high N_{init} produced an N-rich humus (Berg *et al.*, 1997a, 1999d).

An alternative approach to compare estimated and measured N levels in humus is to relate both of them to N_{init}. A comparison of the regression lines for N_{limit} versus N_{init} and N_{humus} versus N_{init} (Fig. 13) revealed no difference in slopes, but a highly significant difference in the intercepts ($p < 0.0001$). This means that the trends in relationships were actually the same. However, the measured N_{humus} values were significantly higher (by about 6.8%) than the estimated N_{limit} values. These results indicate that even if decomposition appears to stop at the limit value, the concentration of N increases further during later humification, possibly because reactive lignin remains adsorb and bind, for example, NH_3 or NO_3 in a sequence of condensation reactions (Nömmik and Vahtras, 1982; Axelsson and Berg, 1988).

Origin and Structure of Secondary Organic Matter and Sequestration of C and N

I. INTRODUCTORY COMMENTS

In this chapter, we use the terminology and definitions for humus and soil organic matter suggested by Waksman *et al.* (1928) and adopted by Stevenson (1994; Textbox 1). There are numerous definitions of the concept

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Textbox 1 Some definitions

Fulvic acids:	Colored material which remains in water solution after removal of humic acid by acidification to pH <2.
Humic acids:	The dark-colored organic material which can be extracted from soil by various reagents and which is insoluble in dilute acid (pH <2).
Humic substances:	A series of relatively high-molecular-weight, brown- to black-colored 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, that is, insoluble in water at any pH. 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.
Humus:	Total of the organic compounds in soil exclusive of undecayed animal and plant tissues, partial decomposition products, and the soil biomass.
Litter:	The same as litter remains (see newly shed litter).
Litter remains:	The part of decomposing litter that still has recognizable parts of original structures, such as needles, leaves, cones, and bark.
Newly shed litter:	Plant litter that has been shed so recently that the decomposition processes have not yet started.
Non-humic compounds:	Compounds belonging to known classes, such as amino acids, carbohydrates, fats, waxes, resins, organic acids, that are the product of living organisms and may frequently be found in soil.
Soil organic matter (SOM):	The same definition as humus.

"humus" and the one adopted by us is not uncontroversial. Still, this definition is widely accepted and appears to fit well with the concepts of litter decomposition and humus formation as we see it.

The term "decomposition" means degradation of complex organic molecules to simpler ones and to mineral nutrients. Sometimes, it is also used, not

fully correctly, in its broadest sense, to describe all microbial processes that dead organic matter undergoes in soil, not necessarily leading to actual decay (see the definition in Textbox 1). The majority of these processes lead to smaller molecules and, eventually, to mineralization of the organic matter. However, as described already in Chapter 4, during a foreseeable future, not all dead organic matter ends up in mineralized form. As we discussed in Chapter 4, it is commonly observed, in both boreal and temperate ecosystems, that litter does not ultimately decompose to 100%, as often is assumed, but the decomposition rather follows an asymptotic function (Section IV.F, Chapter 4) which normally gives a limit value for decomposition between 50 and 100% mass loss, indicating that between 50 and 0% of the litter should remain as a recalcitrant part. The remaining, ''nondecomposable'' organic fraction may remain in soil for at least centuries and probably millennia without significant further degradation. Thus, Berg *et al.* (2001) could reconstruct the accumulation of humus over a 3000-year period, using the hypothesis of such a recalcitrant fraction, thereby also confirming it.

To determine the age of an organic matter, usually concentrations of ^{14}C in specific isolated organic matter fractions are analyzed. Also, the average age of organic matter in soil can be sufficient and useful for certain conclusions. The average age of some soil organic matter fractions has been estimated to be thousands of years (Livett, 1988). Wang and Chang (2001) studied a number of Taiwanese soils and calculated that the mean residence time of stable organic substances ranged from approximately 140 to 2200 years. The lowest average residence time (143 to 1749 years) was recorded for fulvic acids, while the mean residence times of humic acids and humins were slightly higher and similar to each other with a range from 253 to 2200 and from 293 to 2173 years, respectively.

The limit value for decomposition appears to be a useful tool to calculate the stable fraction (Section IV.F, Chapter 4). What actually constitutes the limit value is not yet fully understood. Part of the original organic matter becomes so resistant to microbial degradation that its decomposition rate is close to zero and, in combination with the environment for the microorganisms, this may result in biologically stable compounds (see Berg and McClaugherty, 2003). The stable organic matter and the stability concept as such can be related to newly formed secondary substances that simply prevent further decomposition. Part of the original dead organic matter undergoes structural and chemical changes to form ''new'' organic matter— the secondary organic products of litter decomposition. These secondary products may be very resistant to decomposition (Spaccini *et al.*, 2002). As a consequence, they may make up a significant amount of the organic matter when the limit value is reached. These secondary products are probably formed during decomposition of all litter types, although we expect that

there are differences among litter species and between nutrient-rich foliar litter and, for example, nutrient-poor woody litter. These secondary products create a most important pool of soil organic carbon and are part of what are collectively called humic substances. We can thus divide the SOM into two main forms, one being humic substances and the other nonhumic substances.

Despite major research efforts for the last 40 years and substantial progress in humus chemistry, the molecular structure of the humic substances is not yet fully understood, not even for the humic substances originating from one plant species. It seems that humic substances (Textbox 1) originate mostly from modified plant macromolecules, rearranged in complicated decomposition–synthesis cycles, where mainly microbial processes and physicochemical environmental factors determine the structure of the products. Among the soil microorganisms, fungi and actinomycetes probably play a major role in creating secondary organic matter due to their ability to degrade lignin and lignin-like molecules. The degradation process includes the formation of numerous smaller molecules that may be chemically reactive. Because of their complex origin, the group of humic substances, even when formed from just one litter species, are considerably more variable than the original plant molecules, which are synthesized by strict and enzymatic processes and thus strictly regulated.

Due to the high molecular diversity, and our lack of knowledge about specific structures, humic substances are usually defined simply as "high-molecular-weight, dark-colored, organic soil substances formed by secondary synthesis." On the other hand, newer findings indicate that humic substances are loose associations of relatively small molecules, stabilized by weak hydrophobic forces, rather than macromolecular polymers (Conte and Piccolo, 1999). The more specific structures still remain to be discovered, though. For the time being, we may consider the humic substances to collectively form a large stabilized part of the SOM.

The rest of soil organic matter that can be identified as amino acids, fats, carbohydrates, waxes, etc., we may call the *nonhumic substances*. The definition of "nonhumic" refers to the tissue of the original organic matter. There is also a fraction of water-soluble substances the origin of which is less easy to specify. Thus, not all soil organic matter consists of humic substances and not all of it is resistant to decomposition. In fact, SOM may contain very different compounds and groups of compounds. In some humus forms, with mor humus as a very clear example, part of the SOM or humus consists of remains of far-fragmented litter in a very late decomposition stage or at the limit-value stage. Such remains contain original molecules such as hemicelluloses, cellulose, and lignin from the original plant structures that probably have been shielded by the recalcitrant secondary compounds.

The stabilized part of the soil organic matter, or stabilized humus as we use the term, is organic matter that has lost not only the original fiber and tissue structure but also has a modified chemical structure, is relatively resistant to decomposition, and is present either in an organic layer on top of the mineral soil or mixed with mineral soil. In this chapter, we describe and discuss SOM using the previously stated definitions. First (Section II), we present a traditional separation of SOM into the subgroups fulvic acids, humic acids, and humins. Further, we discuss secondary organic matter, and later humus buildup, quantified as sequestration of SOM (C), and finally, we comment on the stability and decomposition of humus. We describe and discuss SOM using the already stated definition.

II. TERMINOLOGY ACCORDING TO TRADITIONAL HUMUS CLASSIFICATION AND CHEMICAL COMPOSITION OF SECONDARY ORGANIC MATTER

Samples of humus layers or organic matter layers contain, in part, matter that is so modified that to the eye it is lacking structure. It also contains far-fragmented remains of litter, roots, original soluble and nonsoluble molecules of plant origin (nonhumic substance) as well as modified molecules, normally falling within the concept "secondary organic matter" (humic substances). Samples of organic layers, for example, of F and H layers, thus contain not only stable compounds but an array of compounds of very differing degradability. We intend to separate and describe these concepts as far as possible using today's knowledge.

Humic substances are traditionally classified by a sequential extraction procedure of humus layer samples rather than due to their mostly unknown and variable molecular structure. The most easily soluble fraction, which can be extracted with water under all pH conditions, has been called "fulvic acids" (FA) (Textbox 1). Among the distinguished fractions, they are the lightest in color, namely, yellowish to yellow-brown. A dark-brown to black fraction, insoluble in water at pH <2 but soluble at higher pH, is formed from humic acids (HA) (Fig. 1). This fraction normally makes up the largest part of the extractable humic substances. The remaining part, which is insoluble in water at any pH and even in strong alkali, is known as the "humins" fraction (H). The humins form the darkest fraction of soil organic matter, typically black. These three fractions (FA, HA, and H) can be roughly ordered from fulvic acids through humic acids to humins in terms of their solubility properties and color intensity, which increases in this order, as does the degree of polymerization.

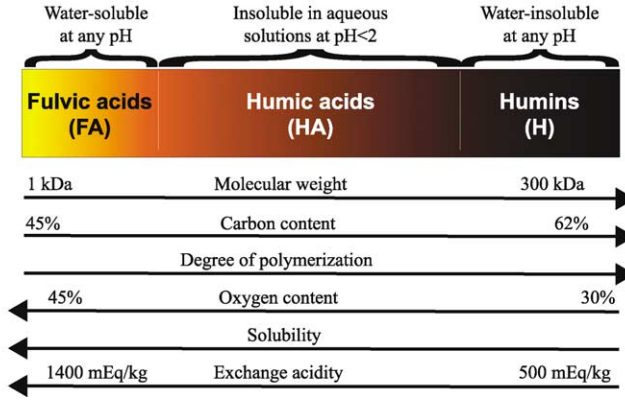

Figure 1 Some general properties of the three main groups of separation products of humus. The groups are distinguished mainly on solubility criteria and may thus contain rich spectra of compounds. As general properties, we see that the molecular weight increases from fulvic acids to humic acids to humins, as does the degree of polymerization and carbon concentration. In contrast, the concentration of oxygen and exchange acidity (see Textbox 2) decrease from humins to fulvic acids. One Da (dalton) corresponds to the mass of 1/12 of the ^{12}C atom. After Stevenson (1994), modified.

This classification is a traditional one and the classification method used, namely, a sequence of extractions, is not very specific and means that a broad spectrum of compounds is included in each group. A comparison to the subdivision of litter samples is possible only to a limited extent. We may thus compare the concept ''water solubles'' in samples of decomposing litter and fulvic acids when these are determined for, say, far decomposed plant litter or litter remains that we may find in, for example, mor humus.

The concept ''water solubles,'' normally used for decomposing litter, when applied to samples from a humus layer, may mean the same as fulvic acids or dissolved organic matter (DOM). This fraction may contain any compound that is water soluble, which means that both an original plant compound and a decomposition product of remaining plant structures belong here. The latter compounds can be, for example, aromatic compounds split off from decomposing lignin, simple sugars from decomposing polymer carbohydrates, amino acids from proteins and, of course, recombination products. A difference in the way the concepts are used is that the term ''fulvic acid'' normally is applied to samples from F- and H-layers and not to litter samples. The concept ''water solubles,'' as applied to newly shed litter, means extracts of original plant compounds (nonhumic substances) and, when applied to decomposing litter, we may expect that the fraction,

irrespective of whether we call it "water solubles" or "fulvic acid," will contain a decreasing fraction of original plant compounds and an increasing fraction of secondary products.

As a generalization, we may describe fulvic acids and thus water solubles in the following way when extracted from organic-layer samples. They are the simplest molecules in the concept "humic substances" and contain aromatic and aliphatic structures extensively substituted with oxygen-containing functional groups, such as carboxyl–COOH and phenolic–OH groups (Fig. 2). They may, in part, be decomposable. We may make a distinction, though. An extraction of water solubles from newly shed litter will, of course, contain only original plant material and can be expected to be decomposable to a very high level (see Section II.A and Tables 1–3,

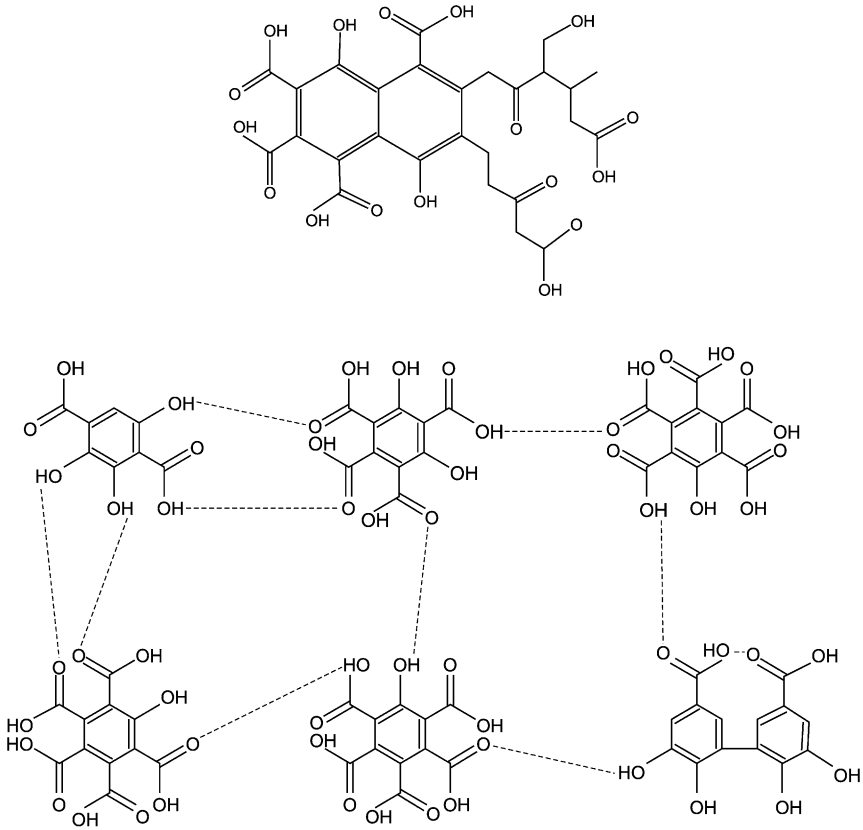

Figure 2 Examples of components within the concept of fulvic acids; dashed lines indicate hydrogen bonds between single molecules of fulvic acids (various sources).

Chapter 4), whereas water-extracted material from humus would be expected to decompose more slowly.

Also, humic acids are water soluble and may be compared to the analytical concept "water solubles." When a scientist analyzes a sample from a humus layer for water solubles or dissolved organic matter (DOM), pH is normally not adjusted, and if well above 2, the water solubles encompass also the concept humic acids. As a general rule, the compounds in the fraction humic acids are, in part, more complex macromolecules and larger than in the fulvic acid fraction, with large numbers of condensed aromatic and heteroaromatic structures linked by aliphatic compounds and nitrogen-containing rings.

The chemical composition of the main group of humic substances is variable as regards the basic elements. On the average, humic acids contain about 46 to 61% carbon, 2.8 to 6.6% hydrogen, 31 to 40% oxygen, and 2 to 6% nitrogen. As much as 30 to 50% of these (C, H, O, N) are contained in aromatic and heteroaromatic structures. The aliphatic structures encompass another 25 to 40%, and different functional groups, the remaining part. Chemical analysis of 14 standard and reference materials from International Humic Substances Society (IHSS) indicates that the average ratio of phenolic to carboxylic compounds in humic substances is approximately 1:4 (Ritchie and Perdue, 2003).

The fulvic acids are composed of approximately 40 to 52% carbon, 2 to 6% hydrogen, 42 to 52% oxygen, and 2 to 6% nitrogen (Waleczak, 1987), and the composition of the functional groups is similar to that in humic acids.

To illustrate the concept of humic acids, we may imagine a large molecule as a nucleus in a complex of associated molecules. This nucleus is surrounded by a number of functional groups such as carbonyl (−CHO), phenol (−OH), carboxyl (−COOH), and amino ($-NH_2$) groups as well as quinones (Fig. 3). These groups can interact with different ions in the soil solution, forming soluble salts (humates) with monovalent alkaline metals (K, Na), almost insoluble salts with bivalent alkaline metals (Ca, Mg), and insolble chelates with multivalent metalloids and heavy metals (As, Cd, Cr, Cu, Fe, Pb, Zn). The amino groups can, in turn, interact with anions, such as MnO_4^-.

Humins constitute a most variable class of compounds, whose only common property is their insolubility in water. The humins, which is the part remaining after extraction of fulvic and humic acids, contain highly polymerized macromolecules, structurally similar to humic acids. The definition of humins (Textbox 1) means that the original litter compounds such as cellulose, hemicellulose, and native lignin may be included in this group. We have already discussed that, for example, in mor humus, original plant compounds such as hemicellulose and cellulose could be shielded by secondary products, which can explain why these are found also in humus-layer samples.

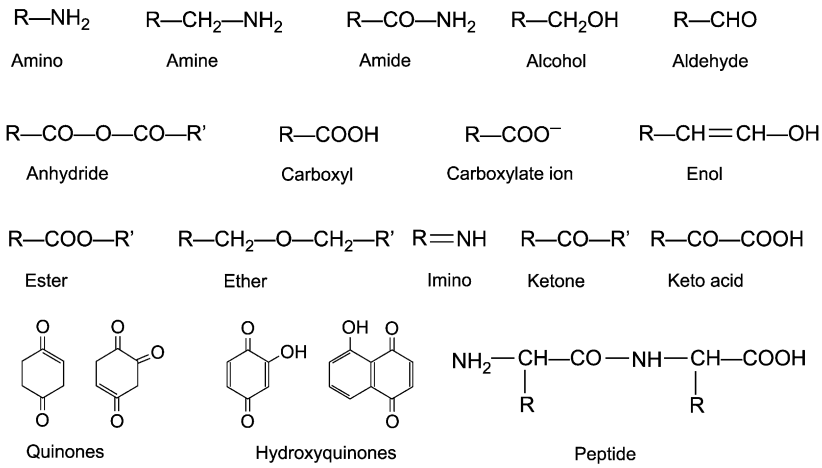

Figure 3 Some basic functional and reactive groups found in humic substances. R indicates an aromatic or aliphatic molecule.

In analytical work on plant litter samples, the extraction of water solubles leaves a nonsoluble residue. We may thus compare the humins and such remaining solid substance as determined for decomposing plant litter. Both are insoluble in water and contain some of the same substances, although the fraction of secondary products in plant litter increases as decomposition proceeds.

In a detailed study on humus in a hardwood stand in the Hubbard Brook Experimental Forest (in New Hampshire in the United States), Ussiri and Johnson (2003) found that extractable humic substances accounted for approximately 50% of the soil organic matter. The largest pool of carbon in the SOM was associated with alkyl compounds, ranging from 33 to 56% of total soil carbon, while the next fraction in size was the carbohydrate carbon (20–45%). The proportion of carbohydrate carbon decreased with soil depth, while that of alkyl and aromatic carbon increased. In their material, the humins appeared richer in aromatic carbon than the fulvic acids, while carbonyl carbon reached higher concentrations in fulvic acids, at the same time increasing with soil depth. The acidity of fulvic acids was dominated by that of carboxylic groups, with about 80% of the total acidity, and was higher than that of the humic acids. Although their studies focused on hardwood stands, they noted that soils of more conifer-rich stands were richer in aromatic structures.

Thermochemolysis of soil samples and humic acids has resulted in the following products: lignin-derived aromatic compounds, nonlignin-derived aromatic compounds, N-heterocyclic compounds, methyl esters of fatty acid, and dimethyl esters of dicarboxylic acids (Chefetz *et al.*, 2002). Based

on these results, the authors concluded that the structures of the compounds in the humic acids' fraction contain large amounts of lignin remains and cuticular materials. The authors also fractionated their material after particle size and found that with decreasing particle size, the humic acids were increasingly richer in lignin-derived units and in fatty acids originating from microbial activity. Also, the contents of aromatic structures of a nonlignin origin were higher in smaller particles.

What has been outlined here is the traditional concept of humic substances. However, in recent papers, this approach is questioned and their authors suggest that specific "humic substances" do not exist, and that soil organic matter is nothing else than a mixture of original organic compounds in various stages of degradation. According to Burdon (2001), this mixture contains different plant and microbial carbohydrates and proteins, partially degraded lignins and tannins, as well as microbial materials such as melanins and other polyketides. Burdon rejects the concept of specific biological and abiotic processes as prime pathways to formation of humic substances. Similarly, Conte and Piccolo (1999) state that humic molecules are associated into large supramolecular structures which are stabilized by weak hydrophobic forces. These associations may be reversibly disrupted into smaller units through interactions with organic and mineral acids. We may compare this to our previous discussion of the concept water solubles versus fulvic acids and humins versus remaining solid substance.

Although the ultimate structures of humic substances still remain in the domain of speculation, the chemistry of the specific single molecules comprising them has been largely discovered after 1970. As these molecules, to a large extent, determine the properties of humic substances, they need developed studies. Some important structural groups identified in humic substances are shown in Fig. 3.

III. ORIGIN OF SECONDARY ORGANIC MATTER—SOME PRIMARY SCENARIOS

A. Introductory Comments

As there are different theories about the main structures of humic substances, there are also different scenarios to how they are formed, for example, whether they are formed biologically or abiotically.

If we accept the traditional, macromolecular structure of humic substances, we also, as a consequence, accept that the major process in which they are formed is probably a polymerization of smaller molecules from partly decomposed organic matter. It is still a question whether this polymerization is mediated by microorganisms in a first step and, in a second

step, the structure is slightly modified by abiotic reactions, resulting in humic substances. The second step then would be based on chemical or "spontaneous" reactions with minor influence of soil microorganisms or even no influence at all. We will discuss different proposed pathways to the formation of humic substances. There are older scenarios as well as newer ones and we should keep in mind that the scenarios described here as "the biopolymer degradation model" and "abiotic condensation model" were suggested as models for formation before the more advanced chemical analytical methods provided a basis for creating newer models. We present these two main traditional scenarios first and describe more recent approaches later.

B. Two Traditional Scenarios

The microbially mediated synthesis of humic substances is frequently referred to in the literature as the "biopolymer degradation model," and assumes that polymerization takes place within the microbial cells through secondary transformations of precursors, such as small molecules originating from lignin, different aromatic structures, peptides, and proteins. The large biopolymers—the product of this polymerization—are then again partially degraded to humic acids in the environment outside the microbial cells and further to fulvic acids (Fig. 4). The most commonly accepted part of this model is the "lignin–protein scenario," which assumes that humic substances originate from partial decomposition products of lignin and protein. One problem with the biopolymer degradation model is that only 10 to 20% of the humic substance structures can be recognized as remains of original organic compounds of biological origin.

An alternative scenario, the "abiotic condensation model," assumes that humic substances originate from repolymerization of small organic molecules, namely remnants from incomplete decomposition of the original polymers, such as lignin. These remnants contain mainly structures that are difficult to degrade, such as very stable aromatic rings. Repolymerization can theoretically follow different pathways and a number of alternative abiotic condensation models are discussed in the literature. One common characteristic of all these models is that the synthesis of humic substances starts with relatively simple molecules of low molecular weight. Gradually, the structures become more complicated as more and more low-molecular units are added. Thus, in contrast to the biopolymer degradation model, humic structures develop, starting from small molecules, developing to fulvic acids to humic acids to humins (Fig. 4). This abiotic scenario is probably the most commonly accepted theory for formation of humic substances. More details on particular models can be found in an article by Hedges (1988).

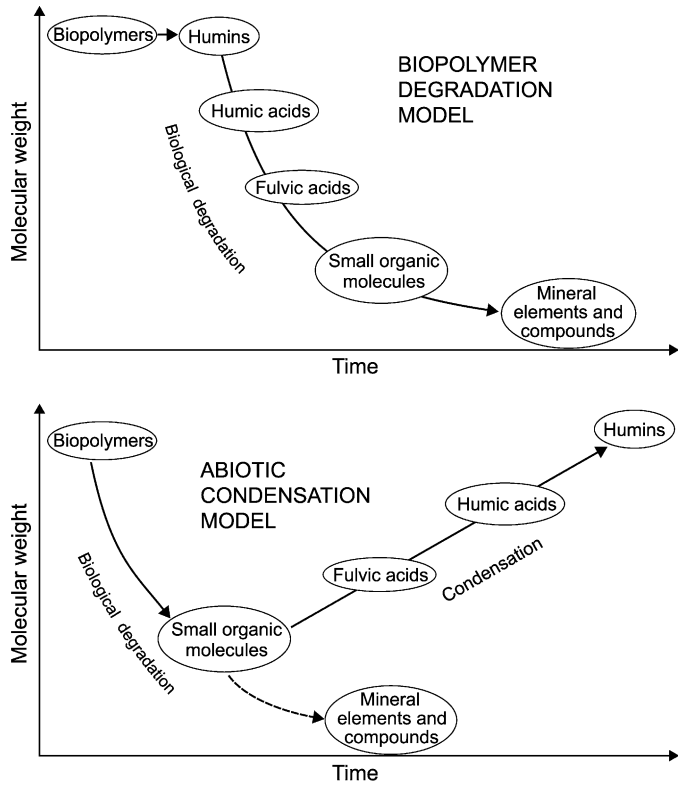

Figure 4 Overviews to two main traditional models for the development of fulvic acids, humic acids, and humins, namely, the Biopolymer Degradation Model and the Abiotic Condensation Model.

Yet another relationship between primary and secondary organic products was proposed by Stevenson (1994). His approach does not solve the question of whether humic substances are the products of degradation or polymerization, but, to some extent, combines both pathways. He postulates that at least some humic substances are the products of both a degradation of primary organic substrates and a synthesis of microbial metabolites (Fig. 5).

C. Some More Recent Approaches to Humic Substances

Some data in more recent humus research seem to confirm the abiotic condensation model. Studies by Zech *et al.* (1992) suggest that different types of forest humus result from different rates of litter decomposition,

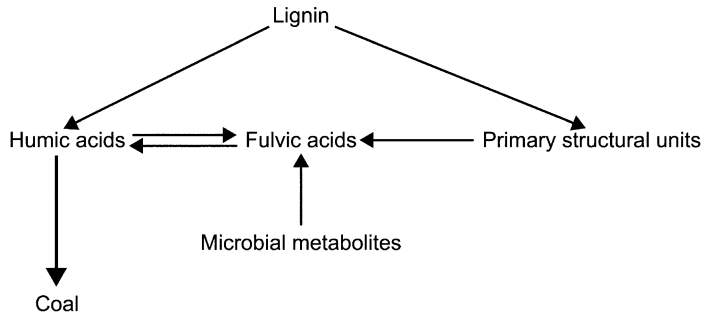

Figure 5 Scenario assuming that humic substances can originate partly from direct degradation of lignin (equivalent to biopolymer degradation model), and partly through polymerization and condensation of partially decomposed lignin units (equivalent to abiotic condensation model) with incorporation of some metabolites of microbial origin.

which nevertheless follow similar pathways. The authors state that "the main features of humification in the investigated forest humus profiles are preferential mineralization of carbohydrates, strong alteration of lignin leading to increasing proportions of substituents in aromatic rings and loss of phenolic groups, increase in carboxyl group contents and accumulation of refractory alkyl components." This does not contradict the statement that soil organic matter consists basically of natural plant and microbial material at different stages of degradation (Burdon, 2001; see also Section II).

Piccolo (2001) points out that an increasing body of information suggests so-called "humic substances" not to be specific polymers, but rather supramolecular associations of relatively small, self-assembling, and heterogeneous molecules derived from the degradation of biological material. This suggestion is supported by the fact that humic substances are stabilized by weak van der Waals and hydrogen linkages rather than strong covalent bonds. Such an aggregation of smaller molecules may lead to formation of large aggregates of humic substances, which constituents are original biopolymers at different stages of decay. If this scenario holds, the characteristics of humus, humic substances, humins, humic acids, and fulvic acids should depend on chemical properties of the plant litter they originate from and the specific degrading microorganisms decomposing this litter species. Such a conclusion leads to a discord with the more traditional approach, according to which stabilized soil organic matter does not generally differ among plant species and development is controlled by climate rather than vegetation type. The newest findings suggest that the traditional concept might be wrong and that, in fact, different types of humus and humic substances develop under different plant cover, while the role of climate is only of secondary importance, perhaps as a factor determining the plant species. For example,

Quideau and co-authors (2001) found substantial differences in soil organic matter composition associated with different plant genera, with no direct effect of climate. Thus, the soil organic matter developed in the forest floor of an oak species stand had characteristics dominated by carbonyl carbon, that under stands of manzanita were especially rich in O-alkyl carbon, while under coniferous trees alkyl carbon was dominating (Table 1). Such results support the idea that humus and humic substances are actually mixtures of natural chemical compounds originating from plants and, to some extent, from microorganisms, and that humic substances are simply more or less loose and random associations of these original molecules and products of their incomplete degradation.

Some of the chemical compounds identified as components of humic substances are linear alcohols, sterols, stanols, and plant-derived triterpenoid alcohols (Berthier *et al.*, 2000). Based on these findings, the authors suggest that alcohols may be incorporated into humic substances by forming esters with carboxylic acids. The presence of stanols, which are the fully saturated sterols, suggests that hydrogenation is a process that also operates in soils. The main processes involved in the formation of humic substances are, according to Lichtfouse (1999): (i) selective preservation of microbial straight-chain biopolymers, (ii) physical encapsulation of nonpolar molecules by weak forces, such as hydrogen bonds, and (iii) chemical binding by covalent bonds.

In a study on humic substances originating from acid soil under temperate climate, Grasset and Ambles (1998) identified a number of molecules from which humic acids and humins were built. Short-chained (mainly C-9) linear dicarboxylic acids, long-chained (C-16 to C-28) linear dicarboxylic acids with a preference for even numbers of carbon atoms, as well as long chains with even numbers of carbon atoms and various aromatic acids, indicating plant origin. In turn, linear monocarboxylic acids (C-12 to C-32), short linear fatty acids, and aliphatic alcohols, accompanied with iso- and anteiso-C-15 and C-17 monocarboxylic acids, indicated bacterial origin. These molecules were linked with ester groups to form long molecular chains.

IV. THE ROLE OF SOM IN SOIL

The role of stabilized soil organic matter in ecosystem function and global carbon balance is a dominant one. Not all SOM is stabilized but the amount of carbon deposited in SOM globally is estimated to be 60×10^{11} tons, which substantially exceeds all carbon stored in living organisms (7×10^{11} tons). In ecosystems, SOM is the carrier of a long-lasting source of nutrients, which are released either at a very low rate following decomposition or very fast as

Table 1 Some site characteristics and distribution of C species in SOM under various vegetation types at different climatic conditions[a]

	Scrub oak	Oak trees and grasses	Manzanita	Manzanita	Coulter pine	White fir and Ponderosa pine
Site characteristics						
Elevation	830	470	850	1240	830	1780
Mean annual temperature (°C)	14.4	17.8	14.4	11.1	14.4	9.1
Mean annual precipitation (mm)	680	310	680	910	680	1010
C species in SOM—fine silt fractions (% total C)						
Alkyl	23.9	16.2	25.2	17.5	29.1	39.5
O-alkyl	42.1	36.5	49.8	49.6	38.1	29.3
Aromatic	18.5	30.0	20.2	26.6	15.1	16.6
Carbonyl	15.4	17.3	4.8	6.3	17.7	14.4

[a]After Quideau *et al.*, 2001.

Textbox 2 The Concepts of Exchange Acidity and Cation Exchange Capacity

Cation exchange capacity (CEC) is a measure of the number of sites on soil surfaces that can retain cations by electrostatic forces. Cation exchange sites are located mostly on surfaces of organic matter and clay. During organic matter decomposition and acidification, CEC usually decreases.
CEC may be measured using different methods, frequently giving differing results. One of these methods relies on using extractants buffered at high pH, for example, ammonium acetate (pH = 7). Such measured CEC is equivalent to soil pH buffering capacity and is frequently referred to as "exchangeable acidity." Nowadays, it is more commonly accepted to measure CEC at the actual pH of a soil.

a consequence of drastic events, such as wildfire. For stabilized SOM, biological decomposition may be extremely slow and it is not yet clear if undisturbed stabilized SOM does decompose and release nutrients, although not-yet-stabilized fractions do. SOM is also a major matrix with a high cation exchange capacity (CEC; Textbox 2). In sandy soils, up to 95% of the CEC is attributed to SOM. Cation exchange capacity in SOM may be as much as five times higher per unit mass than in clay, which means that soil organic matter can hold approximately five times as many cations as clay, including nutrients in available form for soil organisms and plants. To increase the content of organic matter in soil is thus the easiest way to improve its retention of nutrients. Organic matter is also vital for soil structural properties since it forms complexes with clays, leading to a more structured soil matrix. Furthermore, because humic acids readily form strong complexes with metal ions, soil organic matter has an important role in polluted environments, removing large amounts of heavy metals from the directly bioavailable pool. Also, other metals form humates (salts with humic acids). Hence, stabilized soil organic matter provides a large storage capacity for nutrient elements, retaining them for use by plants and preventing them from leaching down the soil profile.

V. WHAT LITTER COMPONENTS MAY BE OF IMPORTANCE FOR THE FORMATION OF HUMUS?

Let us connect to the discussion in Section IV.F, G, Chapter 4. The amount of stable soil organic matter formed from a given litter type or litter species appears to be related to the litter's concentration of lignin, as well as to its concentrations of N and Mn. We also discussed how foliar litter of different species may form stabilized SOM. For wood components, on the other hand, which, in general, have low N levels, it appears that decomposition

patterns may be completely different from those of foliar litter and wood may decompose either quickly and completely or be long-term stored on the ground (see Chapter 4). It appears that the scientific literature so far has not really approached the question of which litter components may dominate in forming humus or even which litter components form humus at all. Generally, there appears to have developed an understanding that all litter fractions from a given species have about the same ability to form stable SOM. In the existing definitions of humus (Bal, 1973), there is no difference indicated between litter components as regards their humus-forming ability, but all are considered equal from this point of view, as were they chemically and structurally uniform. Although de Haan (1977) indicated a connection between some chemical properties of litter and the amount remaining after 10 years, which he called humus, this was not related to real litter fractions, since he used, to a large extent, artificial materials. Still, his study indicated a clear and positive relationship between stored amount and the concentrations of both lignin and N in the incubated materials.

Only recently have new approaches been introduced and given us new insights into this question. The fact that different species of litter influence the type of humus formed, that is, mor, moder, or mull, has, in part, been investigated, but those studies and discussions have been very empirical and have focused on how different leaf and needle species form different types of humus. We lack causal explanations. The observed differences between litter types, for example, needles and leaves of different species, as regards formation of humus, may have their origin in the differences in chemical composition, something that directly influences the decomposing microbial populations and the chemical composition of the formed humus.

Let us recall the earlier discussion about limit values (Section IV.F, Chapter 4) and add the information about chemical components of litter. Berg and Staaf (1981a) investigated the nutrient composition of different kinds of foliar litter in a nutrient-poor Scots pine forest, including that from the low shrubs. They found that most foliar litter components had an N concentration slightly above 0.4%. This also applied to the live, finer roots (Berg and Staaf, 1981). In the same system, woody material, such as rough branches, has lower levels. For example, wood from pine, beech, spruce, and aspen has N-levels between 0.1 and 0.01% (Staaf and Berg, 1989). Concentrations of lignin in the same litter components ranged from approximately 20 to 30% (Berg and Staaf, 1981).

According to the discussion in Section IV.F, Chapter 4, a large part of litter components should form humus, judging from the calculable stable remains. Considering the information concerning the more nutrient-poor woody components, we may conclude that their contribution to humus is more uncertain. We may base a discussion on the degradation of lignin, considering lignin as a key component. Extensive work by Mark Harmon

(Corvallis, Oregon, personal communication) including branches, stumps, and stems, suggests that the decomposition of the N-poor woody material is very dependent on what microorganisms, mainly fungi, are first to colonize the wood. If white-rot fungi dominate as invaders, the decomposition is fast, complete, and leaves minimum remains since the low N level in the wood does not suppress the degradation of lignin. If, on the other hand, brown-rot fungi dominate in the attack, the decomposition will not be complete but the brown-rot fungi have, in practice, through their sheer dominance, prevented ingrowth of the more efficient white-rot organisms. As a result of a brown-rot attack, a fragmented humuslike material is left, a material that apparently has a very low turnover rate and which will be found in the humus layer for a long time. However, such a brown wood powder is not the same material as the SOM formed from foliar litter. How this material differs from the stable remains of foliar litter is not clear as regards stability and transformation of the original material to secondary compounds. Furthermore, considering the definition of humus (Textbox 1), it is not clear from the point of view of classification how the material should be regarded.

In studies on decomposition of wood sticks (N concentration about 0.01%; B. Berg, unpublished), the results were similar to those described by M. Harmon, namely, that the variation within a set of replicate samples could range between just a few percent decomposition and an almost complete disappearance of the sample. From such results, we conclude that there is a large need to investigate the humus-forming ability of woody components. This may be of limited interest for natural systems but in, for example, N-polluted systems, the wood may have a higher N concentration, thus changing the pattern of humus-forming components and, as a consequence, may contribute new additions to humus.

There is thus another pattern for the decomposition of woody components than for the more nutrient-rich foliar litter. The predominance of white-rot or brown-rot fungi in microbial attack may be either random or ruled by environmental factors that give one or the other kind of lignin-degrading organism an advantage. The fact that we see remains of partly decomposed woody material in the humus layer thus should not be interpreted to mean that this is the only kind of decomposition of wood; it also does not mean that woody materials generally form "humus," or even long-lasting organic matter. We must conclude that the magnitude of this more long- lasting fraction with a brown powder is unknown relative to the inflow of woody litter.

The observations described have been confirmed, in part, through investigations of the chemical composition of agricultural harvest remains in different stages of decomposition. The studies encompassed both more nutrient-rich litter and woody materials. Baldock *et al.* (1997) found that relatively N-rich litter of rye and wheat showed an even and continuous

change in chemical properties with the level of degradation, for example, in alkyl- or O-alkyl groups. More nutrient-poor woody material in different stages of degradation showed considerable variation in the levels of these indicators. We interpret this mainly as we have discussed and conclude that each individual fallen branch or stem may be attacked mainly by one type of degrading organism, for example, white-rot or brown-rot, which means either a fast and complete decomposition or an extremely slow one, probably, in part, leading to stable SOM.

Thus, not only the magnitude of the contribution of woody components to the formation of stable SOM is unclear but also the decomposition patterns that rule the relative sizes of the contributions from different litter components are far from known. We may, though somewhat simplified, speculate that ecosystems in which white-rot organisms dominate should give a soil system in which complete decomposition of woody materials should dominate. Likewise, in systems in which brown-rot organisms dominate, a proportionally larger part of the SOM would be based on woody materials, including wood remains.

In the case of fine roots, the picture is even less clear. We have not found any direct studies on decomposition of fine roots towards a humuslike stage. In addition, personal communications of other scientists indicate that traditional decomposition experiments do not give a true picture of the decomposition of this component. Dead, mycorrhizal fine roots of pine, when killed by drying and incubated in litter bags in the humus layer, have shown a strong resistance to decomposition. On the other hand, live mycorrhizal fine roots may be abundant in the soil system one month, disappearing the next without leaving visible remains.

We may summarize this section by saying that more nutrient-rich foliar litter forms humus and that we may distinguish a connection between quantitative aspects and the litter chemical composition. As regards the more nutrient-poor litter components, such as woody waste and woody litter, the picture is more unclear and our knowledge does not yet allow us to quantify the formation of humus from other litter components than the foliar ones, probably because of a lack of knowledge about the ecology of the lignin-degrading organisms.

VI. THE ACCUMULATION RATE OF HUMUS

A. Direct Measurements of Humus Accumulation

The organic matter we call humus accumulates either as a separate organic layer on top of the mineral soil or is mixed with mineral soil to different extents, forming a range of humus forms from mor through different moder

Table 2 Some cronosequence studies in which the accumulation of SOM in organic layers has been followed[a]

Tree species	Stand age range	R^2_{adj}	n	p<	Lit. ref.[b]
Scots pine	7–55	0.819	7	0.001	(1)
Red alder	5–41	0.743	7	0.01	(2)
Monterey pine	3–12	0.888	5	0.05	(3)

[a]The increase is linear against stand age.
[b]References: (1) Ovington (1959), (2) Bormann and de Bell (1981), (3) Forrest and Ovington (1970).

varieties to typical mull forms. In this chapter, we have chosen to describe the accumulation of humus on top of the mineral soil and most of our data originate from mor humus since this humus type creates a system in which it is simpler to quantify the amount.

The accumulation rate of humus may, of course, be measured directly on the forest floor as was done by Ovington (1959) and Forrest and Ovington (1970), but may also be predicted with the use of simple parameters such as estimated litter fall (Chapter 2) and estimated limit values for decomposition (Chapter 4).

We have mentioned in the Introduction that humus accumulates under growing stands (Ovington, 1959; Forrest and Ovington, 1970; Bormann and deBell, 1981; Schiffman and Johnson, 1989) and we may see that the accumulated amounts follow linear relationships against time (Table 2). We have given the classical study of Ovington as an example (Fig. 6). Thus, for a given stand, the accumulation rate was about constant, at least over a stand age. A linear relationship may be general but the slope should depend on the magnitude of litter fall and the fraction of stable remains.

More long-term information comes from the measurements by Wardle *et al.* (1997), which cover periods up to 2984 years as counted from the latest forest fire (Table 3). Direct measurements every three to four years in temperate Norway spruce and common beech forests already show a clear increase between the individual measurements.

B. Accumulation of Humus—Estimates

As discussed in section V, different components may or may not form stable organic matter and we base the present discussion on a long-term accumulation of remains from foliar litter. Humus accumulation rates depend, of course, on both the magnitude of the litter fall and its chemical composition. The magnitude of litter fall gives the quantity in the input

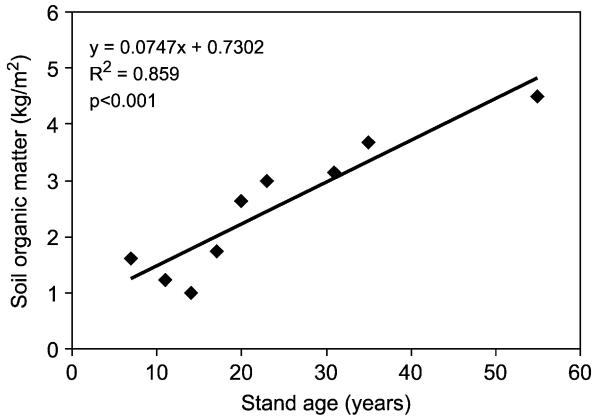

Figure 6 The amount of humus (SOM) increases linearly with time within a given stand. The figure shows the development of ash-free humus amounts with stand age in a chronosequence of Scots pine forests on the same type of soil and within a limited area. Data from Ovington (1959). For stands with other tree species or for Scots pine on nutrient-poor soil, the increase rate may be different.

while the chemical composition determines the substrate quality and the limit value and thus the stable fraction. The limit value is determined to a large extent by the litter's levels of N and Mn (Chapter 4). As has been mentioned, there is a general negative relationship between limit value and initial N level in the foliar litter and a positive one to litter Mn concentration (Fig. 4). Their concentrations thus can be used to model the limit values (Figs. 15 and 16, Chapter 4). This approach to estimating limit values is relatively new, however, and should have a potential for development.

As the present approach to calculating humus accumulation (or carbon sequestration) is rather new, we believe that a description of a particular example has more value than an attempt to express general principles. In general, the annual increase in amount of humus can be estimated as:

$$\text{Annual increase} = (\text{annual foliar litter fall}) \times (100 - \text{limit value})/100 \quad (1)$$

This equation gives the annually formed amount of recalcitrant litter material. Two case studies will give examples on the calculations.

We start by making a budget estimate of SOM accumulation for a period of 120 years in a pine forest and show a validation of the result (Berg *et al.*, 1995). Thus, we created a budget for humus using litter fall and the stable-fraction concept. For this, we use information from a monocultural Scots pine forest (of the Swedish Coniferous Forest Project at a site in

Table 3 Estimated and observed accumulation of soil organic matter in forest floors of known age in Swedish boreal forests[a]

	North Sweden - islands			Jädraås
	n = 14	n = 24	n = 12	n = 1
Mean stand age (yrs)	2984 (340)	2081 (424)	1106 (495)	120
Estimated annual litter fall[d] (kg m^{-2} yr^{-1})	0.081	0.081	0.081	15.2
Estimated accumulated litter fall[d] (kg m^{-2})	242	169	89.6	16.5
Average limit values[b] *(%)*				
Scots pine	86.4 (3.85)	86.4 (3.85)	86.4 (3.85)	89.02 (3.63)[c]
Norway spruce	70.3 (13.1)	70.3 (13.1)	70.3 (13.1)	–
Silver birch	84.7 (7.14)	84.7 (7.14)	84.7 (7.14)	–
Humus				
Measured forest floor mass[f] (kg m^{-2})	49.08	34.62	14.33	1.54
Modeled forest floor mass (kg m^{-2})	47.2	31	14.56	1.67
Missing fraction[e] (%)	3.8	10.5	1.6	8.4

[a]The stands in north Sweden were located on islands and the values are averages. Table from Berg and Dise (2004a,b). Data from Wardle *et al.* (1997) and Berg *et al.* (1995, 2001). Standard error is given in parentheses.

[b]For the north Swedish sites, average limit values were estimated from existing limit values for Scots pine (n = 12), Norway spruce (n = 5); at sites in Sweden north of about 59 °N and available Scandinavian ones for silver birch leaf litter (n = 3; data from Berg and Johansson, 1998).

[c]Average limit value for needle litter decomposition at site Jädraås (Berg *et al.*, 1995).

[d]Litter fall for the Scots pine stand at Jädraås was estimated over a stand age and calculated as described in Section III.B, Chapter 2 (Berg *et al.*, 1995b). Litter fall at Hornavan–Uddjaure was interpolated versus latitude using available Scandinavian data for Scots pine and Norway spruce forests between 59 °N (about north of the line Oslo–Stockholm–Helsinki) and 67 °N (cf. Berg *et al.*, 2001).

[e]Missing fractions as calculated by Berg *et al.* (2001) to be 16, 17, and 6% for the 2984-, 2081-, and 1106-year-old stands. The present calculation considered an equal occurrence of all three species and took into account the fact that Norway spruce invaded the area not until approximately year 2000 BP.

[f]Humus mass is here calculated from Wardle *et al.* (1997). The total C per meter square on the 2984-year islands was 26.8 ± 8.8 kg, from which biomass with 2.25 kg C m^{-2} was subtracted. For the 2081-year islands, the figures were 20.3 ± 8.2, from which 2.99 kg C m^{-2} was subtracted; and for the 1106-year islands, the numbers were 10.7 ± 4.1 kg C m^{-2} from which 3.99 kg C m^{-2} were subtracted. For Jädraås the data is taken from Berg *et al.* (2001).

Central Sweden), for which there existed well-documented background data and site history. The budget was validated using data for amounts of SOM for the same stand. For this forest site, there were extremely good data for litter fall, litter decomposition, and amounts of accumulated soil organic matter on the ground. The soil organic matter (mor humus) referred to is that in the organic layer on top of a very even mineral soil, and the borderline between the humus and the mineral soil was very clear. An important piece of information is that a violent fire took place in the mid-1800s, which burned off the previous organic layer. Thus, the current humus layer in this forest stand has been built up on the ash layer after the fire. As the time of the fire is well documented, the time period for the accumulation of the organic (FH) layer is known very precisely. Furthermore, the ash from the fire was easy to distinguish and thus was support for the quantification.

Litter fall had been measured both in a nearby, younger stand and the main stand for 7 and 10 years, respectively, thus covering the periods 18 to 25 and 120 to 130 years (Flower-Ellis, 1985). The chronosequence thus covered a period of 18 years, which gave a good possibility to adapt a litter-fall model for the older stand. Berg *et al.* (1995) used a logistic function for litter fall as a function of stand age. Using this model, the estimated accumulated litter fall over 120 years was 164,500 kg ha^{-1} (Section III.B, Chapter 2). Root litter was not considered because the main part, namely pine roots, had been observed in the mineral soil at this stand (H. Persson, personal communication) and only a smaller part, mostly lignon berry / cowberry rhizomes and heather roots, were found in the humus layer.

The amount of SOM was 1.54 kg m^{-2} in the combined A_{01} – A_{02} (FH) horizon when the stand was 120 years old (Staaf and Berg, 1977). This value, which gives the ash-free matter, did not include distinguishable litter remains. As the litter's chemical composition is important for the level of the limit value, it is important to emphasize that the litter was chemically similar for almost all litter-forming parts of the trees, with the exception of the crude bark and the nutrients of the woody parts, and also that the main part of the litter from the lower shrubs had a composition as regards N and lignin that was close to that of the pine litter components (Berg, 1981). As the foliar litter fall from the pines completely dominated the litter inflow, Berg *et al.* (1995) made the approximation that the limit value for all measured litter components was similar. The value they used was the average (89%) of nine different determinations of limit values for Scots pine needle litter based on nine separate decomposition studies. The estimated remaining stable organic matter fraction was thus 11% of the needle litter fall. The litter formed in the last 8 years had not yet formed a stable humus and therefore the litter inflow for the past 112 years was estimated. A multiplication of the total accumulated litter fall with the remaining fraction of 0.11 gave the accumulated amount of stable organic matter and was estimated to be 1.67 kg m^{-2}. This

result differed by approximately 8% from the direct measurement (Staaf and Berg, 1977).

The other study encompasses three groups of stands with long-term accumulation ranging from 1106 to 2984 years. Site Hornavan is made up of about 50 small islands located in a remote area in the two lakes of Uddjaure and Hornavan, in Swedish Lapland. All islands are located on till. The location of the stands on small islands ranging in area from approximately 0.1 to 15 ha in the relatively large lakes, has protected the forests and the humus on each island from both human management and fires. Those fires that occurred were caused by thunder and were rare due to the small size of the islands and the distance to the shore. Wardle *et al.* (1997) divided the islands into three groups: those smaller than 0.1 ha, those between 0.1 and 1.0 ha, and those bigger than 1.0 ha. The average time from the last fire until 1997 as determined by ^{14}C analysis on ash layers under the humus layer is 2984 years for 14 islands, 2081 years for 24 islands, and 1106 years for 12 islands, for the <0.1 ha, the 0.1 to 1.0 ha, and >1 ha islands, respectively. We subsequently refer to these groups of forests as the 2984-, 2081-, and 1106-year-old stands, or oldest, middle, and youngest stands, bearing in mind that the age refers to the accumulation time of humus rather than to the age of the trees. Fires were less frequent on the smallest islands due simply to their small size, affording them a lower probability of being struck by lightning (Wardle *et al.*, 1997). The smallest islands thus have the thickest humus, which may reach a thickness of up to about 1.4 m (O. Zachrisson, personal communication). The medium-sized islands have, on the average, less humus mass. The youngest forests (on the largest islands) have thinner humus layers than the other two groups (G. Hörnberg, personal communication; Wardle *et al.*, 1997). We make the reasonable assumption of an undisturbed humus accumulation since the date of the ashes.

The forests on these islands are mixed cultures of Scots pine, silver birch, and Norway spruce (Wardle *et al.*, 1997; G. Hörnberg, personal communication) in different proportions, partly dependent on island size. The annual litter fall was estimated. Because these stands are very old, individual trees would be replaced over the years, but not the entire stand at once, and we can ignore the fact that litter fall in the first 20 years or so of a forest's existence is much lower than litter fall at stand maturity, which we could not ignore in the calculations for the 120-year-old stand. We only need to estimate annual foliar litter fall at maturity to calculate mean annual foliar litter fall. To do this, we use a relationship between annual litter fall at maturity and latitude for Norway spruce ($n = 6$) and Scots pine ($n = 33$), based on data from 39 sites in northern Scandinavia located between 67 and 59°N (Berg *et al.*, 1999b,c):

$$\text{M.a.l.f.} = 10782.3 - 150.8 \times \text{Latitude} \quad (2)$$

where M.a.l.f. stands for Mean Annual Litter Fall (kg ha^{-1} yr^{-1}) at stand maturity (equivalent to Max in the logistic function, Section III.B, Chapter 2), and latitude is given in decimal degrees. We assume that the mean annual litter fall for silver birch is similar to that of the two coniferous species (B. Berg, unpublished data), and we use the same relationship for all three major tree species found on the islands. For the Hornavan forests, the average latitude of 66°10′N gives a mean annual litter fall of 0.081 kg m^{-2} yr^{-1} (Table 3).

The annual litter-fall values are multiplied by the number of years for the different time periods, giving the accumulated litter fall. In the 2984-year-old stands, the accumulated foliar litter fall is 242 kg m^{-2} (0.081 kg m^{-2} yr^{-1} × 2984 years); for the 2081-year-old stands, it is 169 kg m^{-2}; for the 1106-year-old stands, it is 89.6 kg m^{-2} (Table 3).

Wardle *et al.* (1997) determined the amount of humus to be 49.0, 34.6, and 14.3 kg m^{-2} for the three stands, 2984, 2081, and 1106 years old, respectively. In the above-mentioned case study, the site history gave the forest an age of 120 years (preceding section), and for that stand, the corresponding figure was 1.54 kg (Table 3). By using a simple regression model for needle litter fall from pine and spruce based on measurements in 65 stands in the boreal forest of Northern Europe (between 52 and 67 °N), the foliar litter fall was estimated for all four stands using the same method. Then, with the use of the average limit values for needle litter of Scots pine and Norway spruce from studies in northern Sweden (52 to 67 °N; n = 18) and available data for birch leaf litter (n = 3), the magnitude of the annual accumulation was estimated and summarized over the periods corresponding to the determined age for the undisturbed humus (stand age). The SOM accumulations estimated that were was 47.2, 31.0, 14.56, and 1.67 kg per meter square and these figures were in surprisingly good accord with the measured values, especially for the older stands. Thus, the estimation errors were (in percent of the measured value) 3.7, 10.4, 1.8, and 8.4, respectively, and the errors can be at least partly explained by uncertainty in litter-fall data. It must be emphasized that in the validation work (Berg *et al.*, 2001; Berg and Dise, 2004a,b), only data for foliar litter fall were used. The root-litter and woody litter components were not considered for three main reasons: (i) generally, the formation of root litter may be overestimated as a consequence of the indirect methods, (ii) the possibility that mycorrhizal fine roots have a decomposition process that differs from that of the falling litter (see preceding text), and (iii) the decomposition of woody roots and woody litter probably, to a large extent, does not lead to humus. Still, these root and woody components create an uncertainty in the calculations until they are satisfactorily explained.

C. How Reliable are Quantitative Estimates of Humus Accumulation?

It is reasonable to conclude from the preceding section that quantitative estimates of humus accumulation appear to be reliable at least for undisturbed boreal coniferous forests, a group of forests for which estimates have been validated with direct long-term measurements. We may not assume generality over all tree species and systems, though. In the validated systems dominated by Scots pine and Norway spruce, the lack of, for example, earthworms creates an environment without perturbation. Their mixing of organic matter and mineral soil is, in fact, a disturbance that may enhance decomposition. Nevertheless, studies indicate that the concept may be valid also for at least some temperate forest ecosystems. For example, estimates similar to those already presented made for nitrogen-polluted stands of Norway spruce and common beech (Solling, Germany) are confirmed by direct measurements of humus accumulation and may extend the validity of the concept.

This section thus illustrates that there is good support for a calculable long-term net accumulation that may be based on the limit-value model. In the next section, the effects of mycorrhiza, fire, and anthropogenic disturbances on humus accumulation rate will be discussed.

VII. MAY ALL HUMUS BE DECOMPOSED OR JUST A FRACTION?

A. Different Fractions—General Comments

As we mentioned earlier, the SOM can be subdivided into different fractions of differing stability, and a water-soluble fraction in Scots pine SOM has been found to encompass approximately between 5 and 15% of the total SOM mass (Table 4). Still, water solubles should not be regarded as synonymous with easily degradable compounds and their degradability has to be investigated, more or less in each single case. Of three fractions in a Scots pine humus identified by Couteaux *et al.* (1998), the labile one encompassed about 5% of the humus mass as judged from respiration measurements. Also, the humus layer samples used by the researchers (Table 4) consisted of a Scots pine humus with a water-soluble fraction of about 12%.

We cannot exclude that many conclusions based on laboratory measurements of respiration of humus-layer samples (C mineralization) may be based on properties of the more easily decomposed fractions, thus suggesting a very high decomposition rate for humus, whereas the decomposition rates

Table 4 Fractions of different size and stability in far-decomposed Scots pine needle litter and humus from the Scots pine stand of incubation[a]

Fraction	Size [%]	k [% day^{-1}]	Mass loss [% $year^{-1}$]
Far-decomposed litter			
Labile	5	0.124	30
Meta-stable	15	0.087	3–6
Stable	80	$10^{-5} - 10^{-4}$	0.03 – 0.003
Humus			
Labile	5	0.124	30
Meta-stable	15	0.087	3–6
Stable	80	$10^{-5} - 10^{-4}$	0.03 – 0.003

[a]The k-value given by Couteaux *et al.* (1998) has been recalculated to mass loss in % per year for the sake of comparison to decomposition rates of litter. Data from Couteaux *et al.* (1998).

of the solid parts of humus may correspond to the rates of the recalcitrant fractions of Couteaux *et al.* (1998) (Table 4).

B. Four Cases of Turnover of Humus Layers

We make an attempt to describe humus decomposition by distinguishing four cases in which decomposition takes place. Such a division into distinct cases can, of course, always be questioned and developed. The four kinds of decomposition of humus layer samples distinguished by us have been related to a few major influences.

Probably the most common case, a very slow decomposition, takes place in completely undisturbed humus. Humus-layer decomposition rates may increase due to mechanical disturbances that are caused by, for example, perturbation, soil scarification (site preparation), and drainage. It should be mentioned also that the sampling itself of humus layer samples for respiration experiments belongs here and may give considerably increased decomposition rates, which thus do not reflect the natural decomposition rate typical for undisturbed systems. We first describe two contrasting cases for humus decomposition, namely, those in undisturbed and in disturbed systems. Further, there are two recently observed cases with higher activity, one being ascribed to strongly "activated" mycorrhizal fungi.

1. Undisturbed Systems

It has been suggested repeatedly that only part of the organic matter in the humus layer is stabilized (Townsend *et al.*, 1995, 1997; Olsson *et al.*, 1996;

Couteaux *et al.*, 1998) and a good part of the organic substances sampled from a humus layer is considerably easier to degrade than the dominant stable parts of the humus, although we may distinguish different subfractions. Couteaux *et al.* (1998) found in humus a labile pool of about 5%, a ''metastable'' of about 13 to 15%, and a recalcitrant pool of about 80 to 85% (Table 4).

There are few published direct measurements on humus decomposition. For a correct measurement of decomposition rates of undisturbed humus samples in the field, it is required that the samples studied encompass ash-free humus, and not simply the whole humus layer, and that the system is not disturbed prior to the measurements. In such studies, Olsson *et al.* (1996) found mass losses ranging from 0 to 7% for Scots pine forest humus and 17 and 22% for Norway spruce forest humus in a period of 15 to 16 years. This translates to 0 to 0.47% loss yr^{-1} for pine forest humus, and 1 to 1.5% loss yr^{-1} for spruce forest humus.

2. *Disturbed Humus*

There have been many respiration measurements (O_2 consumption or CO_2 evolution) carried out on humus samples but the sampling of humus layers, in itself, means a disturbance of the soil system and its microorganisms. When the humus-layer sample is sorted and, for example, roots removed, the disturbance is even greater. The effect of a disturbance of this kind normally is seen as heavily increased microbial activity, for at least a few days. In order to obtain more realistic estimates of humus decomposition rates, samples are preincubated, usually for up to 2 weeks, to be stabilized. This does not mean, however, that they become so stable that the humus decomposition rate measured in this way corresponds to undisturbed conditions.

In their work, Couteaux *et al.* (1998) found that a slowly decomposing ''recalcitrant'' fraction decomposed at a rate of 1% in 30 to 300 years (Table 4), which means 0.033 to 0.003% per year. In their approach, using respiration measurements, Couteaux *et al.* (1998) (Table 4) investigated both humus layer samples and partly decomposed litter from Scots pine. Using a statistical analysis allowing them to separate the decomposition rates of a labile, a metastable, and a stable (recalcitrant) fraction, they found that, for about 20% of the respired mass, the rates differed strongly between the two pools labile and recalcitrant. The ratio between decomposition rates for the labile and the recalcitrant pools was about 1:0.0001, and the relative sizes of the pools were 5 and 80%, respectively. A conclusion based on these results is that respiration rates measured with the purpose of giving an estimate of field decomposition rates may provide a heavy overestimate since, in fact,

often only the total respiration is measured, which in practice means that only decomposition of the labile part is measured and considered to represent the whole material.

We have chosen the results shown in Table 4 as an example because it represents a new approach for experiments based on respiration measurements. Traditional respiration measurements made on field-collected humus material may be unsuitable for quantification of real decomposition rates. Even if samples are cleaned from fresh and recently dead organic matter and have been preincubated for stabilization, the respiration rates may be so high that it must be assumed that the disturbance made at sampling still has an effect.

We reviewed published respiration rates for samples of humus layers from 30 randomly taken articles, used the values for respiration rates expressed as released CO_2 from the organic fraction of the humus layers, recalculated the respiration rates to percentage mass loss per year, and found a range from approximately 10 to over 100% mass loss, clearly suggesting that the measured rates, at least in several cases, were too high. This observation may also have far-reaching consequences for interpretation of results from studies on temperature dependence of humus respiration rate, including experiments related to the global climate-change problem (Chapter 8). It may be questioned whether the temperature-dependent increase of the turnover rate that is determined in the laboratory is correct also for the recalcitrant part of the humus. The respiration experiments (above) cited from the literature were carried out over relatively short periods and it is, of course, still an open question what fraction of the material was respired. When comparing the above orders of magnitude for mass-loss rates (10 to more than 100% mass loss in a year) with those given in Table 4, we see that they are of the same order of magnitude as those calculated by Couteaux *et al.* (1998) for the labile fraction (about 30% yr^{-1}). The rates of their metastable fraction were about 3 to 6% per year and for the stable fraction, a rate of about 10^{-4} to 10^{-5}% day^{-1}, or about 1% in 30 to 300 years, was determined.

The forest management practice "site preparation" is carried out as a method to "activate the humus" and to start a decomposition process for the forest floor humus to release nutrients. It is based on a very crude plowing or scarification of the soil. We may express this by saying simply that large parts of the humus are aerated. To some extent, mineral soil is placed on top of the humus, thus creating a nutrient release and thereby a heavy stimulation of humus decomposition and a further nutrient release. We cite an example of the effect of site preparation on the decomposition of needle litter. We use the results of Johansson (1987), who found a faster and considerably more extensive decomposition of needle litter buried under a layer of humus in scarified plots where limit values ranged between 90 and 100%. This may be compared to the control, in which they ranged between

57 and 84%. Thus, this may be an indication that under the plowed up mineral soil, less organic matter remained.

On a larger scale, Delcourt and Harris (1980) in their review made a comparison between the effects of the North American cultivation in the eighteenth and nineteenth centuries and today's situation, revealing what happens when the agricultural use of the ground is cut back. During that period, cultivation was a large-area disturbance of the soil, resulting in a large-scale release of carbon. Nowadays, over large areas agriculture has been stopped, the land has in part reforested and the vegetation-soil system is rather undisturbed. The situation is thus reversed and the ground has turned into a sink for carbon.

3. Specific Cases of Disturbances, Namely Mycorrhiza, Fires, and Ditching in Natural Systems

In 1967, Hintikka and Näykki probably were the first to describe how humus layers in a nutrient-poor Scots pine forest were dissolved patchwise in a very short time, leaving just a grey powder. In other words, the same kind of humus layer formed from Scots pine which Couteaux *et al.* (1998) found to have a very low decomposition rate could disappear completely in a very short time. They (Hintikka and Näykki) supported their investigation with field measurements over dissolved humus and also measured extremely high respiration rates from such humus layer samples.

Their observation has so far been suggested to be due to nutrient stress. When the trees are subject to nutrient stress, their mycorrhizas are suggested to be "activated" by a so far unexplained mechanism and function as fungal decomposers. The humus layer is decomposed, which results in an increased release of nutrients as a response to the trees' nutrient stress. The difference in decomposition rate between such activated humus and the more "normal" turnover is dramatic. Still, the mechanisms of the activation remain to be investigated.

Forest fires often result in at least partly burned-off humus layers. Normally, the whole humus layer does not burn and disappear in each fire, but every fire causes a massive release of CO_2 and mineralization of nutrients. We may not exclude that this release of nutrients has an influence on the decomposition of the remaining humus layer. Still, the main effect of repeated fires is, of course, a dramatic change in the accumulation and storage of humus and means that the fire history of a stand is a dominant factor for all evaluations of humus accumulation (Wardle *et al.*, 1997).

Ditching of a soil also often increases the turnover rate of soil organic matter. We may return here to the conceptual model that shows the strong

influence of lignin and lignin-like transformation products (Section IV.C, Chapter 4) on litter decomposition rates. Lignin and lignin-like compounds can not be completely degraded under anaerobic conditions since the organisms able to degrade lignin completely, namely, white-rot fungi and a group of bacteria—actinomycetes—require oxygen. As an effect of ditching, the water surface is lowered and oxygen penetrates to deeper soil layers, leading to an initiation in the degradation of larger polymer aromatic compounds, among them, lignin and partially transformed lignin.

VIII. HUMUS ACCUMULATION AND DECOMPOSITION VERSUS THE CONCEPT "STEADY STATE"

A. Background

The term "steady state" is sometimes applied to the accumulation of humus in soil organic layers, but we have not found any clear definition of the steady state concept in this context in the scientific literature. Usually, only a general and not always clear reference to a kind of equilibrium is made, the details of which are not explained. The use of the term is vague and appears to be based on general assumptions.

The earliest reference we have found to the term "steady state" in the context of soil organic matter is an article by Dickson and Crocker (1953). They use the expression as a generally descriptive concept about humus in a chronosequence of pine stands, which they claimed to be up to approximately 1200 years old. Unfortunately, the study does not show any age determination of the humus and it is not unlikely that the authors used the expression as a general botanical term which referred to the whole ecosystem without a deeper investigation of its relevance for the humus layer.

In the 1960s, the concept became more widely used in the humus literature. It is possible that it was first used as a kinetics concept when Olson (1963) made the assumption about a steady state in the humus layers as a tool when applying his kinetics equation to litter and humus. The paper by Olson is very frequently quoted and that may explain why the steady state concept became more widely used.

It is further possible that the introduction of systems analysis in ecology supported a wider use of the concept for forest ecosystems. It appears that the use of the steady state concept simplifies calculations, which may be a good reason to use it. Still, such a use does not mean that it reflects a reality, but is just a simplifying tool and must be regarded as such.

B. Why Is It an Error to Use the Concept "Steady State"?

It may be of value to state that the two main processes in undisturbed forest systems that determine the amount of stored humus have very little in common. The formation of litter, the inflow of dead organic matter to the ground, takes place via live plants. The factors ruling the formation of litter are those that rule the growth and the general physiology of the photosynthesizing plants. In contrast, the decomposition of litter and humus is ruled by factors that determine the activity of the complex system of heterotrophic microorganisms in the soil. These two systems are, from the point of view of physiology, completely different. The type of energy inflow supporting one system, for example, solar radiation as an energy source for plants, is completely different from the energy inflow to another one, namely, organic carbon compounds as the energy source for microorganisms, and the regulation for this energy flow through N and Mn concentrations (Section IV.B,C, Chapter 4).

We cannot exclude the possibility of a phenomenon of steady state, at least for some ecosystems. Still, it needs to be proven, described, and mechanistically identified for each single type of ecosystem.

In studies and work that are focused directly on the dynamics of the humus layer, the general assumption of a steady state may be erroneous since the phenomenon has not yet been confirmed, is used as an unsupported condition, and, in addition, is used in a diffuse way. We illustrate the problem by analyzing what may happen when using the same term for two hypothetical and different cases. In both cases, we refer to undisturbed systems.

View 1. We may say that a humus layer is in an equilibrium or in a steady state when it is thin, receives a high litter fall, and has a high and complete turnover taking place, for example, within a few years. In such a case, we would observe that the thickness of the layer or the amount of organic matter is generally constant over a longer time period, which is enough to make the steady state concept valid.

View 2. In an extremely different case, we may assume a humus layer that grows, maybe even in a forest stand with a low litter fall, until such a large part of the available nutrients are bound that the tree growth is influenced, litter fall decreases, and the growth of the humus layer goes more slowly or stops completely. In this case, we may also say that a steady state is reached.

These two examples illustrate the lack of clarity of the term *steady state* as it has been used. When the dynamics of a humus layer and a possible humus accumulation is the central topic in a given study, the meaning in one case as compared to the other one is entirely different. In the former case (view 1), the steady state means that no long-term storage takes place, whereas in the

second case (view 2), long-term accumulation and storage is a fact. Considering that humus layers under a growing forest have been observed to grow for at least 3000 years and that even 10,000 years has been suggested, we may expect that humus layers in the forest soil have a large storage potential, which means a stable accumulation for thousands of years and with hundreds of thousands of kilos of humus per hectare before a possible steady state develops. The thick humus layers that we observe today, say, in pine forests, have developed under special circumstances, the main ones probably being that they have been protected from fire and from human influence such as forest management.

As an example, we cite a study in connection with the concept of "critical loads" of nitrogen. Schulze *et al.* (1989) hypothesized that the humus layers generally as well as on a regional level should remain constant. In other words, they should be in and stay in a kind of steady state. The authors simply assumed that the sum of all influencing factors should remain constant over time, and based their arguments on the fact that a certain humus accumulation had taken place after the latest glaciation and that this humus accumulation was the actual growth of the humus layer that had taken place. With our examples, this means that an approach close to view 1 was adopted and that, in practice, no more nitrogen could be stored. The mistake in such an argument is evident since we can actually determine that a growth of the humus layers does take place and so does the accumulation of both C and N. The most likely flaw in their argument is the fact that the prevention of wildfire today is efficient enough to allow the humus layers to grow. We may use the example of Sweden (M.-B. Johansson, unpublished), where it has been found that the measured humus layers, mainly in boreal forest, have increased on the average ca 180 kg C ha^{-1} and yr^{-1} over a 40-year period from the beginning of the 1960s.

However, our argument about the present use of the steady state concept does not exclude the possibility that steady states may be found for humus in some forest systems. Still, for a discussion, the concept needs to be defined.

IX. NITROGEN SEQUESTRATION TO SOM

A. We Can Estimate the Sequestration Rate of N in Stable Organic Matter

The limit value gives the fraction of foliar litter fall that is long-term recalcitrant to decomposition and also the N bound to this limit-value defined fraction should be expected to be long-term recalcitrant. Knowing the amount of litter fall in a forest, the limit value for decomposition and the

concentration of N at the limit value should allow us to estimate the amount of N bound in a recalcitrant fraction (Section IV, Chapter 5). We present a case study for a 120-year-old, well-investigated Scots pine stand in Central Sweden and use data from several studies on litter decomposition and litter N dynamics that have been carried out in that stand. For the case study stand, the N concentration at the limit value was estimated (Fig. 10, Chapter 5) using the average limit values of nine sets of decomposing needle litter.

1. Accumulated Litter Fall and N Sequestration

The average annual needle litter fall in the case study stand was 93.5 g m^{-2}. The average limit value of 89% decomposition was used to calculate the remaining recalcitrant part of the litter as (100-limit value)/100 and, by multiplying with litter fall, we thus estimate the annual amount of needle litter that becomes recalcitrant, giving an average value for this fraction of 10.3 g m^{-2}.

We discussed the concentration of N at the limit value in Section IV, Chapter 5. For our case study, we use the empirical equation (Eq. 2, Chapter 5) to calculate N_{limit} , using average values: $N_{limit} = 0.0991 \times 89.0 + 3.98$ in which 0.0991 is obtained as the average value for nine slopes (NCIR; see Section III, Chapter 5), 89.0 is the average percentage decomposed litter (the limit value), and 3.98 the average initial N concentration (mg g^{-1}) in the shed needle litter. Thus, of the annual litter fall of 93.5 g m^{-2}, 11% remained as recalcitrant fraction and these remains had an N concentration of 12.8 mg g^{-1}. This gives approximately 0.132 g m^{-2} (93.5 g $m^{-2} \times 0.11 \times 12.8$ mg g^{-1}) of N accumulated in recalcitrant organic matter annually. When using the nine decomposition studies to calculate nine individual N_{limit} values, we found that there was a certain variation among the estimates, which ranged from 14.7 to 11.8 mg g^{-1} yr^{-1} with an average of 12.8 mg per gram litter and an SE of 0.33.

The average initial needle litter N concentration was 3.98 mg g^{-1} and with an average needle litter fall of 93.5 g m^{-2}, the total N input to the ground from the needle litter was 0.372 g m^{-2} yr^{-1}. We may use this information to calculate also the amount of N that is not stored, which is 0.372 to 0.132, giving an average annual input of which 0.240 g m^{-2} is releaseable N from the needle litter.

B. We Can Validate the Long-Term Accumulation of Stable Nitrogen

This case study presents an empirical method for calculating the sequestration rate of N in SOM. The accuracy of the method needs to be confirmed and we present a validation using four groups of stands at which the

undisturbed accumulation was measured for periods ranging between 120 and 2984 years. Again, we present this as a case study.

1. Validation Using a 120-Year-Old Scots Pine Stand

The validation was simply a comparison of, on the one hand, the directly measured, and, on the other hand, the calculated amount of N sequestered in the soil organic matter layer (see the example in Section IX.A). The SOM had started to accumulate in this Scots pine stand after a violent wildfire that could be exactly specified in time. An ash layer separated remains of an old organic matter layer and the new organic matter accumulating from the new forest. The new forest was a monoculture of Scots pine growing on sand sediment, giving a very even soil organic matter (O-) layer with a sharp boundary to both the ash layer and to the mineral soil that made it easy to quantify. Twenty replicate humus samples, each of a size of 400 cm^2, resulted in a measured ash-free amount of SOM of 1.54 kg, and an average amount of N of 18.8 g per meter square. This amount originated not only from needle litter but from all litter components combined. We therefore used the value for total litter fall and used the information of a similar initial N concentration in this specific case (Section VI.B), thus assuming similar limit values and similar N concentrations at the limit value.

We used the calculated accumulated litter fall for the whole stand age (16.4 kg m^{-2}, Section III.B, Chapter 2) and applied the average limit value giving a recalcitrant fraction of (11%; Section IX.A). Using the N concentration at the limit value (12.8 mg g^{-1}), we validated the result using measured data. The resulting calculated amount of N in SOM was 23.2 g m^{-2}, to be compared to the measured 18.8 g m^{-2}.

2. Validation Using Humus Accumulated for Between 1106 and 2984 Years

For this validation, we used the sets of islands for which we have described humus accumulation (Table 3; Section VI.B). Average limit values are estimated by using all available limit values for decomposing Norway spruce and Scots pine needle litter from northern Sweden (north of approximately 59°N) and all available data for silver birch (Berg and Johansson, 1998). The average values were Scots pine 86.4% ($n = 12$), Norway spruce 70.3% ($n = 5$), and silver birch 84.7% ($n = 3$) (Table 3).

For the calculations, we used weighted limit values, simply weighting them in relation to the composition of the three different stand-age groups at the site given by Wardle *et al.* (1997). For the oldest stand, the weighted limit value is 80.5, for the middle, it is 81.7, and for the youngest, it is 83.8. These different values reflect the fact that the oldest stands, those on the smallest islands, are dominated by Norway spruce, with a low limit value, and the youngest stands on the largest islands are dominated by Scots pine, with a higher limit value. Multiplying the estimated foliar litter fall by the values for the remaining fraction (100−limit value/100) gives us the estimated forest floor mass (Table 3). Also, the fact that spruce invaded this area first approximately 2000 years before present (BP) was considered. We used the linear relationship between litter N concentration and accumulated mass loss (Fig.1, Eq. 1, Chapter 5) and calculated N concentration at the limit value (Fig. 10, Chapter 5) by extrapolation (Eq. 2, Chapter 5). We used an average value for the limit value (N_{limit}).

The value for initial N concentration (N_{init}) used is the average initial N concentration for stands north of 59°N. For Scots pine, N_{init} is 3.94 mg g^{-1}; for Norway spruce, 5.02 mg g^{-1}; and for silver birch, 10.17 mg g^{-1}. The coefficients (NCIR) (Eq. 2 and Fig. 11, Chapter 5) are calculated as averages for each species and are taken from an earlier study (Berg *et al.*, 1999a). The average NCIR value for Scots pine is 0.0979, for Norway spruce 0.1101, and for silver birch 0.1476. These are used to calculate average N_{limit} values for each tree species of 12.40 mg g^{-1} N, 12.76 mg g^{-1} N, and 22.71 mg g^{-1} N, respectively (Table 5). For the oldest stand at Hornavan, the species-weighted N_{limit} value is 14.34; for the middle, it is 14.62; and for the

Table 5 Estimated and observed accumulation of N in forest floors of known age in Swedish boreal forests[a]

	North Sweden islands			Jädraås
	n = 14	n = 24	n = 12	n = 1
Mean stand age (yrs)	2984 (340)	2081 (424)	1106 (495)	120
Estimated N concentration at limit value (mg g^{-1})				
Scots pine	12.4	12.4	12.4	12.8
Norway spruce	12.76	12.76	12.76	–
Silver birch	22.71	22.71	22.71	–
Measured N in SOM (g m^{-2})	761.0	460.0	163.0	18.8
Estimated N in SOM (g m^{-2})	677.3	453.2	213.2	21.4
Missing fraction (%)	11.0	1.5	30.8	13.3

[a]The stands in north Sweden were located on islands and values are averages. Data from Berg and Dise (2004a,b) and Wardle *et al.* (1997). Standard error is given in parentheses.

youngest, it is 14.64, reflecting a slightly higher relative composition of silver birch in the two younger stands.

Using the limit value concept, total accumulated N is estimated to be 676.8 g m^{-2}, 451.8 g m^{-2}, 212.6 g m^{-2}, and 23.2 g m^{-2} for the four sets of stands (Hornavan and Jädraås) (Table 5), leading to estimated annual N accumulation rates of 0.227, 0.217, 0.192, and 0.193 g N m^{-2} yr^{-1}, respectively.

The actual amount of N accumulated at the forest floor was obtained by multiplying the measured N concentration of the humus by the measured humus mass. This gave total accumulated N values of 761, 460, and 163 g m^{-2} for the oldest to the youngest Hornavan forests, respectively, corresponding to average annual accumulation rates of 0.255, 0.221, and 0.147, g m^{-2} yr^{-1}.

The estimated values for N in the forest floor were compared to the measured values. The difference between measured and estimated total accumulated N is 11, 1.5, 30.8, and 13.3%, respectively. Thus, by applying limit values derived from simple decomposition experiments, we can predict the rate of N accumulation over time scales of hundreds to thousands of years.

When comparing the measured and estimated amounts against the accumulation time, we see that, under these undisturbed conditions, there is no tendency for a steady state to develop within the time frame of 3000 years and the amount of both organic matter and nitrogen accumulates in a forest floor approximately linearly with time (Fig. 7).

X. THE CAPACITY OF SOM TO STORE N

When we know the concentration of N at the limit value for a given litter, we know the amount of N bound in the remaining stable material and we may use this to calculate the capacity of the litter to store N. Thus, we calculate the amount of N that is bound and sequestered in the SOM.

We define the capacity of a given litter type to sequester N (N_{capac}) as the amount of N remaining when the litter has decomposed to the limit value after decomposing an initial mass of 1 g of litter:

$$N_{capac} = N_{limit}(100 - m)/100 \quad (3)$$

in which N_{limit} has been defined earlier (Eq. 2, Chapter 5) and m is the limit value (asymptote) (Eq. 3, Chapter 4). Using this equation, we may use information on litter mass loss and N concentration for decomposing litter to calculate the amount of N that is bound in SOM. We will demonstrate the

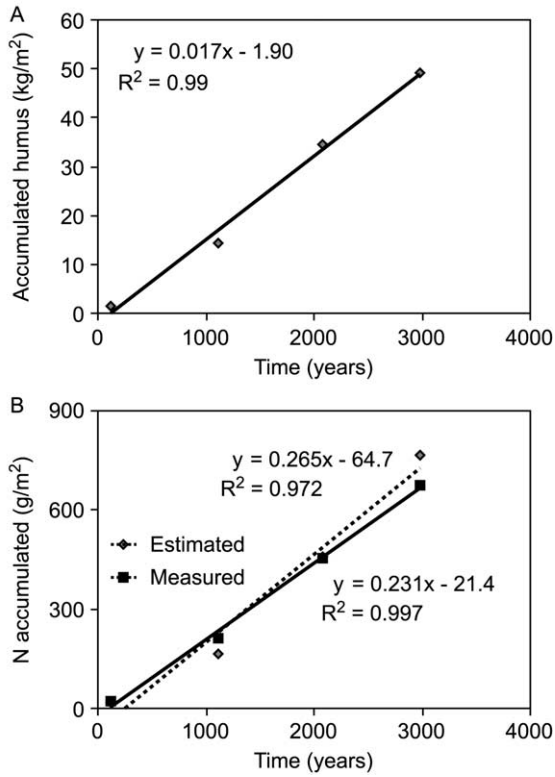

Figure 7 The amount of humus (A) and N in humus (B) accumulated on the forest floor increases linearly with time, as indicated by studies in some Scandinavian boreal forests of known age. Data from Wardle *et al.* (1997) and Berg *et al.* (1995, 2001).

calculations and use some case studies. Such calculations have been made for litter from boreal and temperate forests.

XI. CAN DIFFERENT CAPACITIES TO SEQUESTER N BE RELATED TO SPECIES OR TO THE INITIAL LITTER N CONCENTRATION?

The capacity of the far-decomposed stable remains of litter (or SOM) to store N (N_{capac}) may be calculated using equation 3. We use existing data to calculate N_{capac} for all available data (53 studies indicated on Fig. 8A).

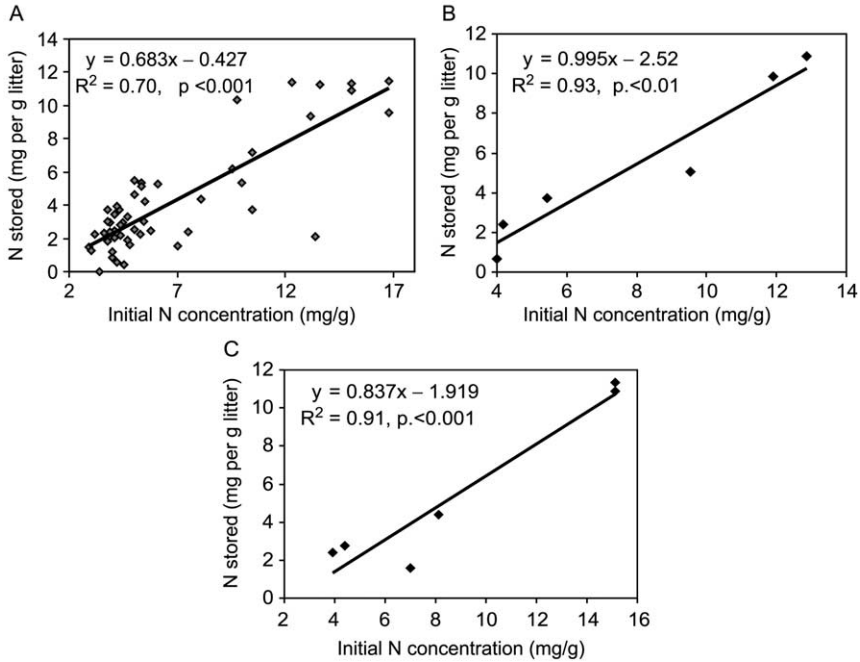

Figure 8 N stored in a recalcitrant form in decomposing litter of different foliar litter species and litter with different initial N concentrations. The stored amount is calculated using Eq. 3 and is different for different litter species and increases with increasing initial litter N. (A) All available data with each point representing a separate decomposition study. (B) Average values for N storage for six litter types, the different N levels being average values for different species. For values and litter species see Table 6. Lodgepole pine (n = 5), Scots pine (n = 20), Norway spruce (n = 14), silver birch (n = 3), common beech (n = 2), silver fir (n = 3). (C) Scots pine needle litter. The different N levels were obtained by using needle litter from N-fertilized trees and green needles. Data from Berg *et al.* (1999a) and from Berg and Johansson (1998).

We found that it was possible to relate N_{capac} to species, in our case, Scots pine, lodgepole pine, silver birch, Norway spruce, common oak, grey alder, silver fir, and common beech. When relating N_{capac} to species (Table 6; Fig. 8B), the lowest storage was found for lodgepole pine litter, with 0.68 mg N sequestered per gram of initial litter. For Scots pine litter, the storage was higher, 2.39 mg N g^{-1} litter; and Norway spruce litter had an even higher capacity with 3.74 mg N per initial gram of litter, which may be ascribed to a higher stable amount remaining (lower limit value) and a high N_{limit} value. For silver birch, the capacity was considerably higher (7.34 mg N g^{-1}) and due mainly to a high N_{limit} value. Common beech and silver fir

Table 6 The capacity of some different litter types to sequester N as based on calculations using limit values and N concentrations at the limit value[a]

Litter type	Average initial N concentration (mg g^{-1})	Average limit value (%)	n	Average N conc. at limit value (N_{limit}) (mg g^{-1})	n	Sequestered N (N_{capac}) (mg g^{-1})	Sequestered fraction of initial amount (%)
Lodgepole pine	4.0 (0.51)	94.91 (5.14)	7	13.6 (1.16)	5	0.68	17
Scots pine	4.19 (0.57)	81.3 (6.11)	23	12.76 (1.63)	20	2.39	57
Norway spruce	5.44 (1.42)	74.07 (13.9)	15	14.46 (2.14)	14	3.74	69
Silver birch	9.55 (2.74)	77.7 (15.6)	4	22.71 (1.19)	3	7.34	77
Common beech	11.9 (4.85)	59.12 (8.51)	5	24.05 (2.45)	2	9.84	83
Silver fir	12.85 (0.66)	51.5 (2.52)	4	21.93 (1.36)	3	10.86	85

[a]From Berg and Dise (2004a). Standard deviation within parentheses.

had even higher capacities with 9.84 and 10.89 mg N g^{-1}, respectively, due to both rather low limit values and high values for N_{limit}.

The capacity to store N may be related to initial litter N concentrations, and using all available data with N_{capac} estimated from each of 53 litter decomposition studies encompassing seven litter species, we obtain a highly significant, positive linear relationship ($R^2 = 0.70$) over the range in initial N concentrations from 2.9 to 15.1 mg g^{-1} (Fig. 8A). In this case study, using the 53 values, we also calculated average values for six litter species for both litter N concentration and N_{capac}. In this relationship, the initial litter N levels were related to N_{capac} (Fig. 8B; $R^2 = 0.93$; $p < 0.001$). Finally, we used a set of experimental Scots pine needle litter from a fertilization experiment (Textbox 4, Chapter 2; Fig. 8C) and included N-rich green Scots pine needles. The values for N_{capac} plotted versus initial N concentration showed the same trend within one species ($R^2 = 0.91$; Fig. 8C).

Nitrogen pollution will produce litter with higher initial N concentrations, which will lead to a higher storage of N. That litter in, for example, N-fertilized stands takes up more N and has a higher N concentration increase rate observed by Berg and Tamm (1994). The higher uptake also results in a higher N concentration at the limit value and a higher capacity to store N in a sequestered form (Fig. 8C).

XII. HOW STABLE IS THE LONG-TERM N STORED IN HUMUS?

That the amount of N stored in humus increased with time (Table 5, Fig. 7B) indicates a certain stability of the compounds holding N. The fact that there was a long-term predictability based on the limit-value concept further supports this.

The stability of stored humus and humus N is, in part, dependent on the composition and activity of the microbial community and factors ruling them. A given humus that has accumulated for a century may be decomposed in a relatively short time if the limiting conditions for the microbial community change. Possibly, nutrient stress for the trees opens a mechanism for a high fungal activity (Hintikka and Näyki, 1967). In that study, the authors found that the stable SOM in the O-layer disappeared in a short time period, leaving just a grey powder. Still, we have reconstructed the amounts of C and N in mor humus stored for almost three millennia, indicating that the stored N has a long-term stability. In all cases, the SOM was located under growing forest stands, a factor that may influence the stability. The study by Hintikka and Näyki (1967) was made in a very nutrient-poor Scots pine forest and the authors speculate that this quick decomposition followed by a nutrient release to the trees was a result of strong nutrient stress.

Wardle *et al.* (1997) concluded that the N sequestered in the oldest humus of the Hornavan stands was less available than that of the younger ones based on experiments on the availability of N to plants. They also found that humus N concentration was related to the age of the humus (N concentration range about 1.0–1.5%). This may be interpreted that there had been a certain turnover of C but that N had been kept in the system perhaps by fixation of NH_3 to organic matter (Nömmik and Vahtras, 1982). Another interpretation is that the oldest islands had a dominant vegetation of birch with higher N levels in the leaf litter for some time before the conifers started to dominate.

Climatic and Geographic Patterns in Decomposition

I. INTRODUCTION

For a long time, climate has been assumed to have a dominant effect on litter decomposition rates on a regional scale, whereas litter quality should dominate on the local level, for example, within a stand. Thus, at a given forest stand and climate, one should expect the mass–loss rates of litter to be related primarily to its chemical and physical properties. Several studies have shown such general relationships (Fogel and Cromack, 1977; Aber and

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Melillo, 1982; McClaugherty *et al.*, 1985; Upadhyay and Singh, 1985; Dyer, 1986). Still, this view is oversimplified. There is a variation in weather, in temperature, and moisture in the litter environment as well as in the litter chemical composition, resulting in a large variation in decomposition rates among years, even within one forest stand. In addition, the substrate changes during decomposition (Chapter 4) and with accumulated mass loss, its chemical composition becomes increasingly different from the initial one, progressively creating a new substrate with new properties. When the decomposition process progresses through time, the factors that regulate the rate of mass loss do change. In turn, the heat and moisture delivery to the litter control the rate at which the decay phases can proceed. Thus, for a given litter type in one climatic regime (say, boreal climate), the early, nutrient-controlled phase may span over a long time, while in other regimes, this phase can pass quickly.

Studies of decomposition dynamics have been performed using different litter types, at sites in different climatic regimes and in different forest types, and thus control by climate versus litter quality is often confounded. Furthermore, often only the decomposition of fresh, newly shed litter is studied, thus overemphasizing the early stage (ct. Berg *et al.*, 1993). At broad, regional scales, climatic variables often appear to regulate decomposition rates, at least initially, whereas litter properties appear, in general, to be relatively insensitive indicators of regional patterns (Meentemeyer, 1984). When the analysis is confined, however, to one or a few sites with similar climates, the influence of litter quality becomes apparent. With the increasing emphasis on understanding the impact of climate change, and the broad-scale patterns of biological processes, the issue of geographic scale versus decomposition patterns versus litter chemical composition becomes critical.

This chapter focuses on litter decomposition in stands with monocultures and we use results from five main transects with either only Scots pine or different pine species and one with Norway spruce in which foliar litter decomposition was studied. The results are possibly contrasting enough to illustrate that different patterns should be expected among species under varying climates. To illustrate this, we have described the effect of climate on different decomposition stages, that is, early stage and late stage separately. In addition, we give results from a transect in which root litter decomposition was studied. We also describe respiration from humus at seven sites from one of the transects.

II. THE MICROBIAL RESPONSE TO TEMPERATURE AND MOISTURE

The communities of soil microorganisms encompass several thousands of species in the soil of a given stand (Bakken, 1997) and have high adaptability to different moisture and temperature regimes. This has, in part, been commented on in Chapter 3. Still, both moisture and temperature can be limiting. At low moisture, say, below 10% water-holding capacity, water

supply becomes so limiting that an increase in temperature does not result in higher microbial activity. Likewise, in an energy-limited system, for example, due to low temperatures, higher moisture does not necessarily result in higher activity. An example of this is the boreal forest.

The microbial response to temperature should be regarded as the sum of responses from all microorganisms. Those bacteria and fungi that have their temperature optima at, say, 15 °C are less active at 10 °C and very little active close to 0 °C. Still, at 0 °C and below, there is a clear heterotrophic activity carried out by psychrophilic microorganisms, which are of completely different species from those active at higher temperatures but normally without differences in function. In a system under a given climate, the microorganisms thus are adapted to the prevailing climatic conditions. Further, the soil of a given forest stand under boreal or temperate climate may have large variation in soil temperature over a year, say, from 0 °C, representing unfrozen soil under a snow cover, to maybe 15 °C at summertime. The different temperatures under different periods support the development and maintenance of a microflora with numerous species that have temperature optima over this whole range of temperatures.

A microbial response to climate variability depends also on the availability of nutrient and carbon sources. The lack of an available carbon source or an essential nutrient as compared to the needs of the microbial community results in a lack of response to an increasing temperature and higher precipitation (Panikov, 1999). Thus, if decomposition is limited by what somewhat unspecifically is called ''substrate quality,'' a change in weather has relatively little effect on the decomposition rate.

III. THE INFLUENCE OF CLIMATE ON EARLY-STAGE DECOMPOSITION OF SCOTS PINE NEEDLE LITTER

A. Early-Stage Decomposition at One Forest Stand over Time

At a given site, there is a clear variation in litter decomposition rates among years, which may be related to variation in annual weather. When local, annually collected Scots pine needle litter was incubated at its own site, the variation among years for the first-year mass loss as determined over 21 measurements ranged from 21.1 to 33.8% (Fig. 1), the highest value being 60% higher than the lowest one. However, there was no difference in annual mass loss between litter incubated in the spring and that incubated in late autumn just after litter fall. Average annual mass losses for both groups were close to the overall average of 27.8% mass loss. This means that the

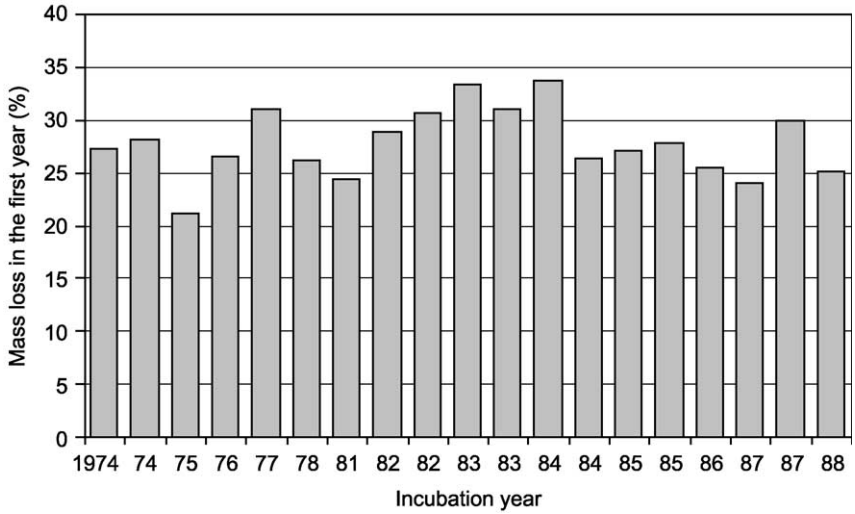

Figure 1 First-year mass loss from Scots pine needle litter incubated annually in a nutrient-poor Scots pine forest over a time range of 23 years, starting when the forest was 120 years of age. The stand was that of the former Swedish Coniferous Forest Project (SWECON), located at Jädraås, Sweden. The first incubation was made in 1973 and the latest in 2000. In those cases, the same year appears twice: one incubation was made in May and one in October. Data from B. Berg (unpublished) and B. Andersson (unpublished). With kind permission of Springer Science and Business Media.

decomposition process is generally not sensitive to the point in time for litter fall.

In the same stand, there are differences in decomposition rates among periods of the year as determined by patterns and intensity in temperature and rainfall. A model for daily soil moisture and temperature was found to predict the early stage decomposition rates quite well over periods of months (Jansson and Berg, 1985), with R^2 values ranging between 0.85 and 0.99, indicating that the variation in climate may dominate the variation in mass-loss at that stand. The predictive power of the two factors, namely, the soil moisture and soil temperature combined, was clearly superior to separate single-factor models (Table 1). The soil climate was modeled over a period of 6 years, representing a substantial variation with respect to soil moisture and temperature and indicating that periods with high and low decomposition rates did not follow any simple pattern. Two summers were characterized as warm with extended drought periods, whereas the other summers were moist. The variations in soil temperatures were much more pronounced between different winters than between summers. Three of the winters had soil temperatures well below zero degrees, which also caused high water

Table 1 Coefficients of determination (R^2) obtained from correlations between observed decomposition rates and different soil climate estimates as independent variable

Independent variable	1st incubation yr n = 9	2nd incubation yr n = 8	Both years n = 17
Actual evapotranspiration (AET)	0.41	0.74	0.55
Soil temperature	0.37	0.77	0.52
Soil water tension	0.78	0.97	0.81
Soil water content	0.68	0.96	0.77
Soil temp and water tension	0.90	0.98	0.89
Soil temp and water content	0.85	0.99	0.87

*From Jansson and Berg (1985). Unified Scots pine needle litter was used and incubated annually.

tension in the soil. During the other winters, the soil was both moister and warmer, mainly because of thicker snow packs, which prevented the upper soil layer from freezing. Under these conditions, the soil water was always unfrozen, which means that decomposition took place under the snow cover. In fact, for one of the one-year periods, the main part of the decomposition took place during the winter when the ground had a snow cover.

As indicated in Table 10, Chapter 2, there was a certain variation in initial litter chemical composition at this site, for example, in N and P values; still, the model based on just temperature and moisture could explain the decomposition quite well, supporting the theory that an annual variation in weather can be responsible for the annual variations in decomposition rate within a stand. It deserves to be emphasized that the response to temperature and moisture was observed mainly for the early stage.

B. Decomposition Studies in Transects with Scots Pine and Norway Spruce

Among studies on decomposition in different climatic transects, in Northern Europe, there are at least five using needle litter and one using root litter. We have indicated them in Fig. 2 and numbered them I thru VI (Textbox 1). The decomposition data from the transects Nos. I–IV and from one for root litter were related to both climate and substrate quality, using actual evapotranspiration (AET) as a climatic index (Meentemeyer, 1978). The main climate indices used in this book are listed in Table 2 with often used abbreviations.

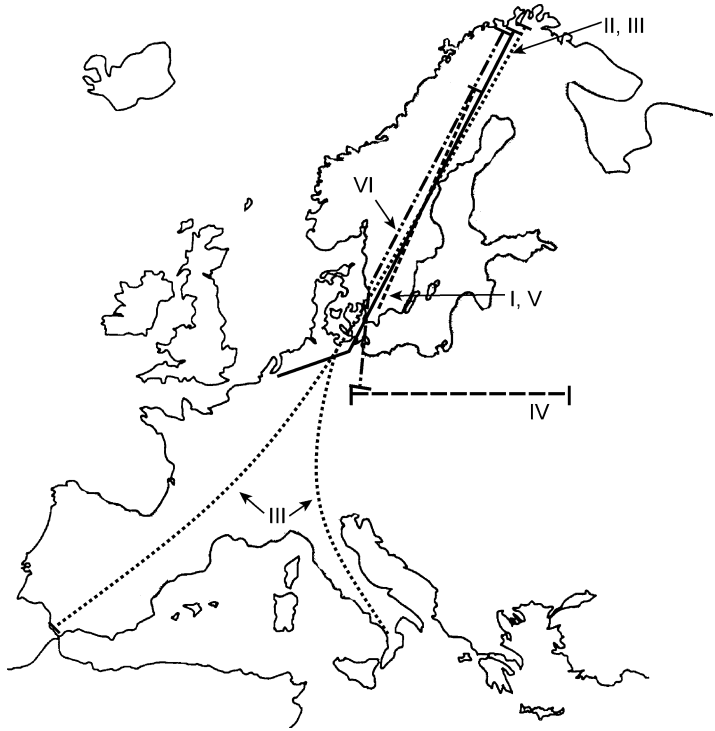

Figure 2 Map of western Europe with transects indicated and numbered from I through VI. Transect No. I in Scots pine forests along Sweden had local needle litter incubated at 20 stands. Transect No. II, in Scots pine forests, had unified needle litter incubated at 13 stands as did transect III with an extension to southernmost Europe, encompassing 39 pine stands. Transect IV was a latitudinal one along 52 and 53 °N, ranging from Berlin in the west (12 °25′E) to the Russian-White Russian border in the east (32 °37′E). Transect V had about the same extension as transect I, but encompassed 14 stands with Norway spruce. A transect (No. VI) with incubated root litter had extension from the Arctic Circle in Scandinavia to Berlin in Northern Germany.

1. Transects with Local Litter in Scots Pine Monocultures

Investigating the data of transect I (Fig. 2) ranging over Scandinavia, Johansson *et al.* (1995) determined the effect of climate and litter-quality variables on mass-loss rates. Using long-term climatic mean values and relating first-year mass loss to climate variables (Table 2), they found that of single climate factors, average annual temperature (AVGT) gave the best

Textbox 1 Description and extent of the climatic transects referred to in the text

The northern end of thre N–S transects was at the Arctic Circle in Scandinavia or northernmost Finland and the extent varied (Fig. 2).

— A transect (No. I) with Scots pine stands in Scandinavia, located mainly on till, in which local Scots pine needle litter was incubated once or twice. Twenty-eight stands at 22 sites were located between 66 °08′N, close to the Arctic Circle and 55 °39′N, close to the latitude of the city of Copenhagen (see also Tables 2, 3, 8, and Figs. 2 and 7).

—A transect (No. II) with Scots pine stands on sediment soil, in which unified Scots pine needle litter was incubated annually for a period of approximately 6 to 19 years. The transect had 13 sites between northernmost Finland (69 °45′N) and central Holland (52 °02′N) and had highly standardized sites with nutrient-poor Scots pine stands on sandy sediments and thus on flat ground. In addition to unified litter at each of these sites, however, a special set of experimental litter was incubated (cf. Table 4; Figs. 5, 6).

—A pine forest transect (No. III), located on mainly sediment soils in which unified Scots pine needle litter was incubated. Transect No. II was included and sites with stands of stone pine, Austrian pine, maritime pine, Corsican pine, and Monterey pine. The transect with, in all, 39 sites ranged across Europe (from northernmost Finland at 69 °45′N to southernmost Spain at 38 °07′N and southernmost Italy 39 °24′N (Tables 4 to 7; Figs. 3, 4, 5).

—A latitudinal (around 52–53 °N) Scots pine transect (No. IV) 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).

—A transect (No. V) with Norway spruce stands located on till soil 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 (Tables 11, 12; Fig. 10).

—A northeast to southwest transect (No. VI) with root litter encompassing pine sites (Scots pine and lodgepole pine) (n = 25) and sites with Norway spruce (n = 12), ranging from the Arctic Circle in Scandinavia to Berlin (at 52 °28′N). Table 13.

fit with an R^2 value of 0.536 (Table 3), and annual actual evapotranspiration (AET) gave almost as good a fit, with an R^2 value of 0.523. Potential evapotranspiration (PET) and average temperature in July (JULT) were also significant whereas annual precipitation did not give any significant relationship. AET has previously been distinguished as a superior climate index at broad, continental scales (Meentemeyer, 1978, 1984; Berg *et al.*,

Table 2 Climatic and substrate quality variables toward which litter mass loss was regressed in the studies of decomposition in the climate transects nos. I–IV and a transect with root litter (no. VI)[a]

Description of variable	Abbreviation
Average temperature for July (°C)	JULT
Average annual temperature (°C)	AVGT
Total annual precipitation (mm)	PRECIP
Potential annual evapotranspiration (mm)	PET
Actual annual evapotranspiration (mm)	AET
Initial concentration of water soluables (mg g^{-1})	WSOL
Initial concentration of mitrogen (mg g^{-1})	N

[a] The climate variables, based on long-term averages were calculated according to Meentemeyer (1978) and Thornthwaite and Mather (1957). See also Berg *et al.* (1993). For convenience, the abbreviations are used in this chapter.

Table 3 Linear relationships between first-year litter mass loss and climate factors in a climatic transect (No. I) from the Arctic Circle in Scandinavia (northeast) to the latitude of Copenhagen in the southwest[a]

Climate factor	Slope (SE)	Intercept (SE)	r	R^2	p <
AVGT	2.728936 (0.497645)	20.86893 (5.812156)	0.732	0.536	0.001
AET	0.134339 (0.02512)	−30.1620 (5.89011)	0.723	0.523	0.001
PET	0.143094 (0.027331)	−37.5219 (5.955117)	0.716	0.513	0.001
JULT	3.870504 (1.786976)	−28.6645 (7.855946)	0.391	0.153	0.05

[a] Local needle litter was incubated at 22 sites. The climate variables tested for are listed in Table 2. On this scale, substrate quality factors (concentrations of N, P, S, K, Ca, Mg, Mn, water solubles, and lignin) gave no significant relationship. From Johansson *et al.* (1995).

1993a,b). That climate indices including temperature give the best relationships in the boreal forest is due to the fact that the processes in these systems are generally energy limited (Berg and Meentemeyer, 2002). That may also explain the fact that AVGT (Table 3) actually gave the best fit in this investigation.

On this geographical scale, Johansson *et al.* (1995) found no relationships between first-year mass loss and substrate-quality factors such as initial concentrations of water solubles, N, P, and lignin. None of these factors was significant, probably because the variation in climate across the 28 boreal (60 °N to 69 °45′N) and temperate (south of 60 °N) forest stands was large enough to overshadow any effect of substrate quality. Thus, for

this litter type and spatial scale, the first-year mass loss supports the traditional image of climate-driven decomposition.

2. Transects with Unified Scots Pine Needle Litter in Scots Pine Monocultures

In another transect (No. II; Fig. 2), needle litter from one Scots pine stand was used (Textbox 1). This litter was called "unified" litter when incubated at other stands. For each single stand, mass-loss measurements were made over a period of between 6 and 19 years using a set of 13 sites in Scandinavia and the northwestern part of continental Europe. The sites of this transect were placed in standardized Scots pine forests, which, in this case, meant monocultures on flat ground and nutrient-poor sediment soils in stands where the only understory was common heather, blueberry, and lingonberry. Of the single climate factors, AET gave a highly significant relationship for first-year mass loss, with an R^2_{adj} value of 0.867 ($p < 0.001$) (Table 4). The good fit may be due to both the unified needle litter and the highly standardized character of the stands.

In this transect, substrate-quality factors alone did not give any significant relationship but the inclusion of N or water solubles as a substrate-quality index improved the relationship to AET somewhat: for AET plus N concentration, an R^2_{adj} value of 0.885 was obtained (Table 4). Addition of other climatic factors added very little to explain the variation. The effect of N may be explained by the fact that although the unified litter originated from the same stand, it was collected over a range of years and the annual variation in N concentration was large enough to give this factor an influence.

Table 4 Linear correlations and regressions between first-year mass loss of unified scots pine needle litter and selected climatic factors, as well as some substrate-quality factors[a]

Eq.	R^2	R^2_{adj}	p
Scandinavian–Northwest European sites (n = 13). Transect II, Scots pine stands only			
Mass loss = f (AET)	0.878	0.867	<0.001
Mass loss = f (AET) + f (N)	0.895	0.885	<0.001
Scots pine sites north of the Alps and the Carpathians (n = 23)			
Mass loss = f (AET)	0.647	0.630	<0.001
Mass loss = f (AET) + f (WSOL)	0.748	0.736	<0.001

[a] Sites were grouped and investigated separately as well as in combinations of groups. For abbreviations, see Table 2. Water solubles (WSOL), actual evapotranspiration (AET), and initial nitrogen concentration (N). From Berg *et al.* (1993a).

3. A Trans-European Transect with Monocultural Pine Stands of Different Species

Unified Scots pine needle litter was incubated at 39 sites with monocultures of pine on nutrient-poor soil (transect No. III; Figs. 2, 3, 4). Across this transect across Europe and with some sites in Georgia (USA), AET ranged from approximately 330 to 950 mm and the stands had a highly standardized character and design. They were all open stands with pine monocultures on nutrient-poor ground and had low ground vegetation. The shrubs ranged from the subarctic/boreal lingonberry and crowberry to subtropical palmettos but were low and characteristic of nutrient-poor stands. The sites ranged over differing climates across western Europe from a subarctic one in northernmost Finland to Mediterranean in southern Spain and a subtropical one in southern Georgia (USA). Unified litter was incubated two or three times a year at the different sites and the first-year mass-loss ranged from about 10% at the northernmost subarctic site close to Barents Sea to 56% at the subtropical one in Georgia.

First-year (early-stage) mass loss was plotted against the best single predictor variable (AET) using all sites, irrespective of climate type. The progression in mass-loss rates from the subarctic site to the subtropical ones is apparent (Fig. 3). Some of the scatter can be attributed to the use of long-term climatic normals rather than information about the actual weather

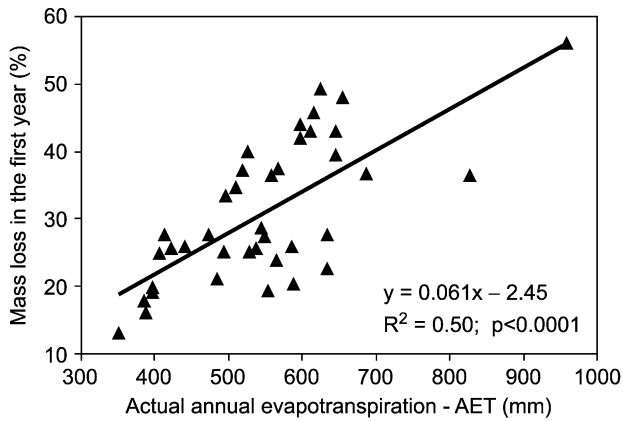

Figure 3 Average first-year litter mass loss for each stand plotted versus actual annual evapotranspiration (AET). The transect was based on 39 pine forest stands and included stands close to the European west coast, relatively exposed to Atlantic climate; stands with characteristics of inland climate (east and south Poland and in the eastern inland of the United States), and finally, sites around the Mediterranean with long dry summers. From Berg *et al.* (1993a) (see Table 5).

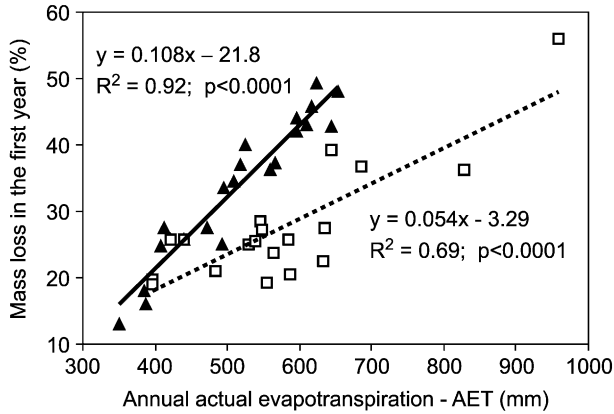

Figure 4 Average first-year litter mass loss versus actual evapotranspiration (AET). The data for transect III (Fig. 3) were subdivided into two transects based on different climate types. Atlantic climate sites with Scots pine monocultures in a transect from Scandinavia to the northwestern parts of the European continent (n = 22) (▲). Sites with relatively dry summers, such as those in a Mediterranean area, and those with inland climate in Central Europe and North America (n = 19) (□). A unified Scots pine needle litter was used (Berg *et al.*, 1993a); cf. Table 5.

during the incubation. For example, the Georgia sites probably had lower mass-loss rates as compared to normal years because the single incubation occurred in an extremely dry year. Over the whole transect (31°28′N to 69°45′N), the best positive correlation was obtained for the relationship between first-year mass loss and actual evapotranspiration (AET), with an R^2 value of 0.50 (Fig. 3), the total annual precipitation ($R^2 = 0.323$), both with $p < 0.001$, and average temperature ($R^2 = 0.203$), statistically significant at the $p < 0.05$ level. Of the other climatic variables, water deficit (DEF) also gave a barely significant correlation (Table 5).

The sites were located under different climates but the climate variables shown in Table 2 indicate just general differences in climate, that is, in long-term annual averages. Still, the distribution of weather events over a year may influence the biological activity of decomposers. For example, at sites with a maritime climate, often-occurring rains create a more even soil moisture level, and milder winters allow the decomposition process to proceed. In contrast, the distribution of weather events under an inland climate as well as under a typical Mediterranean climate is more uneven. Exceptionally dry and warm summers, occurring in these climates create a dry and warm soil, in which biological processes proceed very slowly, if at all. So, we ascribed the variation in first-year mass loss (Fig. 3) to a difference in climate type and subdivided the sites into two groups. One group with 20 stands encompasses

Table 5 First-year mass loss (LOSS) of unified scots pine needle litter as a function of some single climatic factors as well as multiple ones[a]

Equation	R^2	R^2_{adj}	p	Comments
Simple linear regressions (n = 39)				
LOSS = f (AET)	0.509	0.496	<0.001	
LOSS = f (PRECIP)	0.323	0.304	<0.001	
LOSS = f (AVGT)	0.203	0.181	<0.01	
LOSS = f (PET)	0.187	0.165	<0.05	
LOSS = f (DEF)	0.097	0.073	<0.05	DEF gave neg. rel.
Stepwise multiple linear regression (n = 39)				
LOSS = f (AET)	0.509	0.496	<0.001	
LOSS = f (AET) + f (JULT)	0.689	0.681	<0.001	JULT gave neg rel.
LOSS = f (AET) + f (JULT) + f(AVGT)	0.716	0.708	<0.001	

[a]A broad regional scale was used across Europe from a subarctic site close to Barents Sea to south Spain with a Mediterranean climate and included subtropical sites in south Georgia (USA). Transect No. III with 39 pine stands. Actual evapotranspiration (AET), potential evapotranspiration (PET), mean precipitation (PRECIP), mean annual temperature (AVGT), water deficit (DEF), mean temperature in July (JULT). From Berg *et al.* (1993a,b).

sites with Atlantic or maritime climate and the other group with 19 stands encompasses sites with dry summers, that is, sites with Mediterranean and inland climate. In the following text, we discuss these two cases.

Part of the variation seen in Fig. 3 may also be caused by variation in local site conditions and in litter quality. Although the litter originated from the same site (unified litter), there were some differences in chemical composition among years. The concentrations of N ranged from 2.9 to 4.8 mg g^{-1}, those of P from 0.19 to 0.33, and those of S from 0.29 to 0.78 mg g^{-1} (Table 10, Chapter 2).

4. Sites with Atlantic or Maritime Climate versus Sites with Dry and Warm Summer Climate

Atlantic and maritime climates normally mean relatively rainy summers and not very cold winters and, in Europe, this climate type encompasses practically all Scandinavia and northwestern Europe. Northwestern Spain and a main part of Portugal have an Atlantic influence on the climate. The 20 sites with an Atlantic climate had similar responses of litter mass loss to AET (Fig. 4), as had data from two Finnish sites. All of them had low water deficit with the exception of a site in Portugal, which is, however, located very close to the Atlantic coast. With these similar responses, the 22 first-year mass loss values were combined. An analysis of mass-loss data and climate indices

resulted in a very good fit of regression of the first-year mass loss on AET, with an R^2 value of 0.92 (Fig. 4). This relationship was not improved by the addition of other climatic or substrate-quality factors.

A combination of the mass-loss values for the sites characterized by dry and warm summers resulted in a set of sites in Central Europe, in the American Midwest, and those with the Mediterranean climate. A linear regression of the first-year mass loss versus AET gave, also in this case, a clearly significant relationship ($R^2 = 0.69$) (Fig. 4). Again, the relationship was not improved by climatic factors that would indicate seasonality or by substrate-quality factors (Table 6).

The two relationships obtained for (i) the Atlantic climate sites and (ii) sites with warm and dry summers were, however, significantly different (Fig. 4). It seems that the pattern and temporal distribution of temperature and precipitation were also of importance. The results shown in Fig. 4 show that general broad-scale models of climatic control of pine needle litter mass-loss rates can be devised. The results also show that different regions have differing responses that may be related to climate patterns. This means that the slopes and intercepts of the relationships can vary (Fig. 4). In this comparison, climatic variables which respond to seasonality and continentality (for example, July temperatures) were included, but none of them could help to explain the lower decomposition rates at the Mediterranean and inland-climate sites.

Effects of climate patterns may be direct or indirect. We have already mentioned the direct effect of the weather pattern on decomposition rate.

Table 6 Linear correlations and regressions between first-year mass loss of unified Scots pine needle litter and selected climatic factors, as well as some substrate-quality factors[a]

Equation	R^2	R^2_{adj}	p
Scandinavian-NW-European plus Atlantic sites (n = 22). Stands with monocultures of Scots pine, Austrian pine, Monterey pine, and maritime pine.			
Mass loss = f (AET)	0.916	0.912	<0.001
Mediterranean sites plus Central European sites plus North American sites (n = 17). Stands with monocultures of Scots pine, stone pine, Monterey pine, and red pine.			
Mass loss = f (AET)	0.753	0.736	<0.001
Mass loss = f (AET) + f (WSOL)	0.766	0.750	<0.001
Mass loss = f (AET) + f (JULT)	0.761	0.745	<0.001

[a] Sites were grouped and investigated separately as well as in combinations of groups. Transect No. III was divided into two climatically different groups. For abbreviations, see Table 2. Water solubles (WSOL), mean temperature in July (JULT) and actual evapotranspiration (AET). From Berg *et al.* (1993).

Increasing continentality may result in indirect effects caused by a gradually changing ground vegetation, in terms of shrubs, herbs, etc. (Roo-Zielinska and Solon, 1997, 1998). Such differences in ground vegetation may also index the ground climate and other environmental conditions for decomposition.

5. *Latitudinal Transect*

In a different approach, Breymeyer and Laskowski (1999) investigated a latitudinal transect (No. IV; Fig. 2) with an increasing degree of continentality along the longitude 52–53 °N, ranging from Berlin in the west (12 °25′E) to the Russian/White Russian border in the east (32 °37′E). Their experiment indicated that along the gradient of oceanic–continental climate, with only minor differences in average annual temperature among sites, almost 40% of the variability in decomposition rate was explained by the degree of continentality, expressed as annual temperature amplitude, temperatures of the coldest and warmest months (January and July), and annual amplitude of precipitation. The relationship with precipitation amplitude is particularly interesting since this index is not usually used in studies on litter decomposition. The results from this transect support the results stated previously (shown in Fig. 4), that the temporal distribution of temperature and precipitation is of clear importance for the decomposition.

IV. THE EFFECT OF SUBSTRATE QUALITY ON MASS-LOSS RATES IN SCOTS PINE TRANSECTS

A. Early Stages

Although climate is often the dominating factor over large geographical regions determining the early-stage decomposition rate, at smaller scales, other factors may become important, at least for some litter types (Section V.B). At a given site, it has been shown that litter decays at rates that, to a large extent, are dictated by their chemical properties (Berg and Staaf, 1980; Berg and Ekbohm, 1991), at least when litter with varying substrate quality is incubated in parallel in the same time period. However, litter chemical properties are related both to climate and to the site's edaphic conditions (Section VI.C, Chapter 2), and the decomposer organisms, in their turn, may be specific to the ecosystem type. Predictions of decay rates for a range of sites, therefore, cannot be made with confidence only on the basis of the effect of substrate quality for one site since the decay dynamics at a given site includes the combined effects of both climate and litter-quality variables.

In one of the transect studies (transect No. II; Fig. 2; Textbox 1), litter of different qualities was incubated at 11 of the 13 sites, representing four different litter types. These sites were located in northwestern Europe in boreal and temperate climate. For each site, the litter-quality variables important for the early stage (concentrations of N, P, and water-soluble constituents) were regressed against annual mass loss. Most of the regressions were significant at $p < 0.1$, even if the number of different litter types at each site was low ($n = 4$). Examination of the intercepts and slope coefficients for each regression equation at each site suggested a consistent change in coefficients, which is influenced by climate (Dyer, 1986).

The set of intercepts and slope coefficients for the 11 sites was regressed against each of the climatic variables listed in Table 2. 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 the site's precipitation. Thus, the slopes of the relationship (first-year mass loss versus quality) appear to be driven by the gross water supply (precipitation) and the intercepts by climatic heat, here expressed as PET.

We may thus express and quantify the influence of climate on the effect of substrate quality on decomposition. Within this climate transect, at the warmer and wetter stands, the effect of higher N and P concentrations becomes emphasized as temperature and moisture become less limiting. The expanded model for the influence of initial concentrations of P at any particular site may be illustrated as a nomogram (Fig. 5). We illustrate here only the effect of phosphorus and use Eq. 1 (Table 7). Figure 5 shows, in a different way, a conclusion regarding the effect of climate on litter-quality influences and is drawn from analyses of observations of mass-loss rates covering a large geographical region. It can be seen (Fig. 5) that a small shift in climate can produce a larger change in early-stage decay rates than even large differences in litter quality, simply because the quality can be expressed in a higher mass-loss rate when climate is less limiting. Thus, it is not surprising that in this type of system, quality variables are important at local scales but their influences are apparently less significant when viewed at broad spatial scales. The equations presented here show a method for predicting the influence of litter quality across a broad area of North European pine forests.

These relationships were obtained for northern Europe (Fig. 5; Table 7) and suggest that most of the regional variation in early-stage mass-loss rates in mainly boreal Scots pine forests is driven by temperature/heat constraints. As precipitation increases, the differences in mass-loss rates for litter of differing P concentrations become larger. It has to be stressed, however, that all sites used in this investigation were located in the zone with Atlantic climate (see preceding text; Fig. 4) and the corresponding relationships for other climate regions, for example, Mediterranean and typical inland climates, may be different.

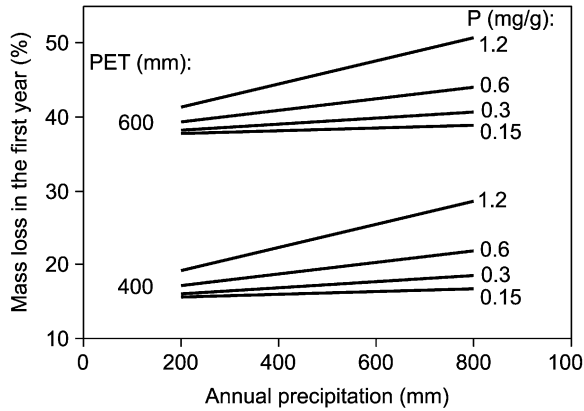

Figure 5 Nomogram constructed from Eq. 1 in Table 7. The figure provides predicted mass-loss rates for PET values of 400 and 600 mm over a range of annual precipitation from 200 to 800 mm at four initial concentrations of P: 0.15 mg g^{-1}, 0.30 mg g^{-1}, 0.60 mg g^{-1}, and 1.20 mg g^{-1}. From Berg *et al.* (1993a).

Table 7 Linear models for the influence of initial concentrations of P and N on initial needle litter decomposition rate at any particular Scots pine site in a boreal climatic (cf. transect No. II; Section IV.A)[a]

For P

Mass loss (Phos) = (−29.3 + 0.111 (PET)) + (0.749 + 0.013(PRECIP)) (P) (Eq. 1)

where the first statement in the parentheses is, in reality, a new intercept determined by a site's PET (mm) and the second term is a new slope coefficient driven by annual precipitation (mm). The third term is the individual litter's P concentration.

For N

Mass loss (Nitr) = (127.3 + 0.100(PET)) + (−0.067 + 0.0022) (PRECIP)) (N) (Eq. 2)

where the first statement is again determined by site PET, the second by precipitation, and the third by the litter's N concentration.

[a] From Berg *et al.* (1993a). Potential evapotranspiration (PET), mean precipitation (PRECIP), initial phosphorus concentration (P), initial nitrogen concentration (N).

B. Decomposition over a Transect with Scots Pine Monocultures—The Late Stage

Lignin concentrations increase during decomposition of foliar litter (Section II.A, Chapter 4), and litter decomposition rates are negatively related to raised lignin concentrations (Section IV.C, Chapter 4). The rate-suppressing effect on litter mass-loss rates acting through increasing lignin concentrations can be described by a negative linear relationship, which, for some species of pine needle litter, may start already at 20% mass loss. In earlier work Meentemeyer (1978) and Berg *et al.* (1993a) related mass-loss rates to

lignin concentrations and demonstrated a variation in lignin effects on decomposition rate with geographic location.

We may calculate slopes for the relationship between the increasing lignin concentration and annual mass loss, both at a single site and over a climatic transect. This was done for each of 16 stands located along a 2000-km-long climatic transect with local litter (part of transects I and II; see Fig. 2). At 11 of 16 sites, statistically significant relationships were found. The steepest slopes were obtained for the southern sites, which were warmer and wetter and thus had initially higher mass-loss rates than did the more northern ones (Fig. 6). In fact, for two dry and nutrient-poor northern sites, the slopes became so shallow that the R^2 values became very low (Table 8). Thus, whereas the slope for the site in northern Germany (Fig. 6) with AET 559 mm was −0.250, a value of −0.023 was determined close to the Arctic Circle in Scandinavia (AET = 385 mm), and the slopes for the sites in south and central Sweden were in between (Fig. 6). The ranges of lignin concentrations used for the relationships are given by the extension of the lines in the figure.

Johansson *et al.* (1995) related the slopes to climatic factors for the corresponding stands, performed a second set of linear regressions, and found that the best fit was that between the slope and AET (Fig. 7), with an R^2_{adj} of 0.528. Also, other climatic variables gave significant relationships, for example, PET and annual average precipitation with R^2_{adj} values of 0.413 and 0.405, respectively. This is good support for the conclusion that the relationship between litter mass-loss rate and litter lignin concentration at a site is dependent directly or indirectly on the climatic factors,

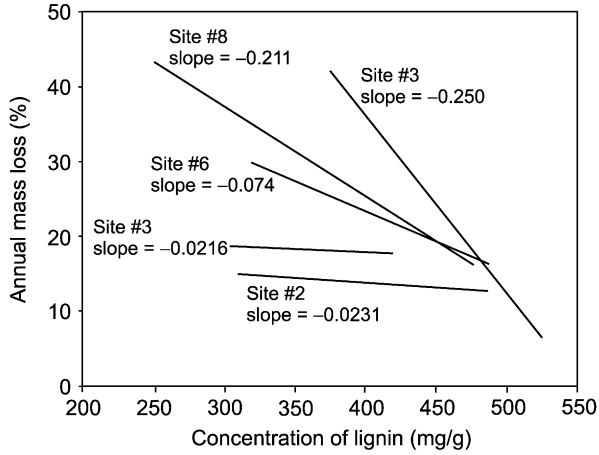

Figure 6 Annual litter mass loss for Scots pine litter plotted versus litter lignin concentrations at the start of each incubation year. Plots ranged from the Arctic Circle in Scandinavia to Lüneburger Heide approximately 100 km south of the city of Hamburg (Germany). From Johansson *et al.* (1995).

Table 8 Calculated slopes for the relationship between annual mass loss and lignin concentration in litter at the start of each one-year period[a]

Site No/name	AET (mm)	Slope	SE	R^2	r	n	p <
2	387	−0.0231	0.0144	0.076	−0.276	33	n.s.
3:1	385	−0.02159	0.0421	0.036	−0.189	7	n.s.
3:2	385	−0.060	0.0597	0.173	−0.416	9	n.s.
3:3	385	−0.132	0.0209	0.278	0.527	8	0.05
4:23	407	−0.0815	0.0217	0.453	−0.673	19	0.01
6:51	472	−0.0734	0.0240	0.227	−0.476	34	0.01
17:2	454	−0.1751	0.0473	0.774	−0.880	6	0.05
18:2	436	−0.1874	0.0551	0.794	−0.891	5	0.05
103:1	470	−0.045	0.0593	0.055	−0.235	12	n.s.
102:1	515	−0.107	0.0353	0.568	−0.754	9	0.05
105:1	486	−0.166	0.043	0.650	−0.806	10	0.01
101:1	484	−0.148	0.0518	0.577	−0.760	8	0.05
107	491	−0.166	0.043	0.650	−0.806	8	0.01
8	509	−0.230	0.0516	0.665	−0.815	12	0.01
10:1	519	−0.228	0.0533	0.901	−0.949	4	n.s.
13	559	−0.250	0.0334	0.846	−0.920	12	0.001

[a] Data from a transect with local and unified Scots pine needle litter incubated at sites ranging from the Arctic Circle to central Lüneburger Heide approximately 100 km south of Hamburg (Germany). From Johansson *et al.* (1995).

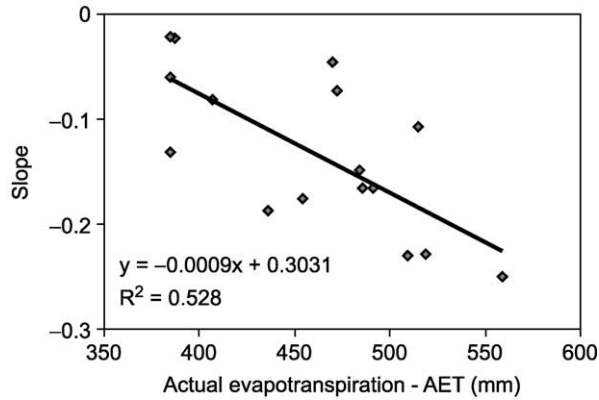

Figure 7 Using data from Table 8, slopes for the relationship between mass loss rate for decomposing local Scots pine needle litter were plotted versus AET for 16 Scots pine sites in a climatic transect (No. I), ranging from the Arctic Circle to northern Germany.

especially AET, although this relationship so far is empirical and the causal explanation is missing.

We may speculate that the causal relationship of the lignin concentration versus. mass-loss rate could depend on the increase in litter N concentration (cf. Sections III.C, Chapter 3, and IV.D, Chapter 4). The fact that the mass-loss rates were affected more strongly by increasing lignin concentrations at warmer and wetter climate (steeper slopes) means that the degradation of lignin and ligninlike compounds was more hampered at stands with such climate. It has been found that the N concentration in decomposing litter increases more quickly in litter incubated in stands located at higher AET, which may be a partial explanation. We may see this as an extension of the model presented in Section IV., Chapter 4. Still, we emphasize that although it appears very likely that the N transported into the litter has this effect, it still must be proved.

An experiment by Dalias *et al.* (2001) may confirm the observation of a negative climate-related effect on late-stage decomposition rates. They investigated the effect of different temperatures on the degradability of a litter substrate. Using humus from five coniferous sites in a transect from 43°07′N at the Mediterranean to 64°00′N in North Sweden, they incubated a ^{14}C-labeled straw material at 4, 16, and 30°C. They let the humus decompose to the same level of mass loss as measured through released $^{14}CO_2$. The material was reincubated and the release of $^{14}CO_2$ showed that the highest mineralization rate took place in samples that had been conditioned at 4°C and the lowest in those conditioned at 30°C (Fig. 8). Their interpretation was that when litter decomposed under higher temperatures, its residual compounds became more recalcitrant.

C. Respiration from Humus from Scots Pine Stands in a Pan-European Transect

Decomposition of SOM or humus which we consider to be stabilized is a not a very clear concept. Published reports on measurements encompass either respiration of undisturbed humus in the field, as measured directly on the ground, or samples that are taken from the organic layers and thus disturbed. In the first case, respiration from, for example, mycorrhiza will influence the outcome by a heavy increase of CO_2 release as compared to the heterotrophic one from decomposers (Högberg *et al.*, 2001). We still do not really know whether respiration from humus samples taken into the laboratory means respiration from water-soluble material only and we do not know its origin. For example, we do not know to what extent the pool of soluble material in humus originates from root exudates or leachates from litter. In spite of this, respiration studies on humus, even carried out in the

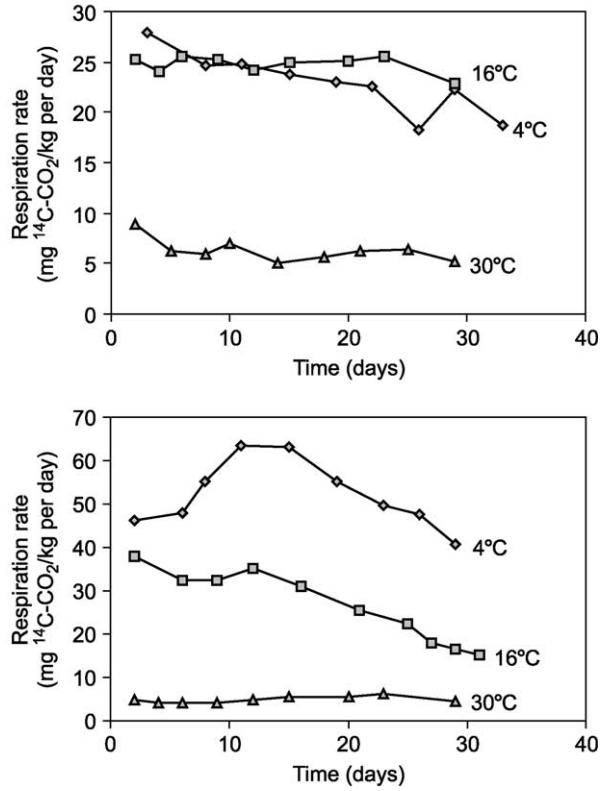

Figure 8 Average daily respiration rate (mg per kg organic matter per day of $^{14}CO_2$) from decaying wheat straw. The straw, which was originally incubated in humus at five coniferous sites in a climatic transect, was partly decomposed under the different climate conditions. A reincubation was then made at 4, 16, and 30 °C in the laboratory and decomposition was allowed to proceed until, in all cases, the same mass loss was reached (measured as $^{14}CO_2$). The wheat straw was then reincubated at a standard temperature of 23 °C and the respiration rate was compared for the straw that had been incubated at different temperatures. The highest respiration rate was found for litter that had been incubated at the lowest temperature. We have given just two of five figures as examples; still, they show the main result. From Dalias *et al.* (2001).

laboratory, often are used to quantify humus decomposition rates and thus CO_2 release from forest floors.

We have been conservative about discussing respiration studies in this book and, as regards a climate influence on respiration from humus, we have selected a work of (Niklińska *et al.*, 1999) carried out in seven Scots pine stands of transect III (Textbox 1) to illustrate the respiration from as

uniform humus as possible over a climate transect. As we have discussed, respiration rates measured over a relatively short time, for example, under laboratory conditions, may reflect mainly the mineralization of a labile part of soil organic matter (Table 10, Chapter 4), which is a main conclusion of the work by Couteaux *et al.* (1998). The study sites were located at latitudes from 42°40′N in the Pyrenees (Spain) to 66°08′N close to the Arctic Circle in northern Sweden. All stands had a well-developed mor-type humus layer.

The samples were incubated at the sites' average air temperatures for the growing season, and the respiration rates were recalculated per one gram of organic matter to account for differences in contents of mineral soil among the samples. The average respiration rates for 14 weeks of incubation were related to the growing season average temperature for all sites. As should be expected, the samples from the northern stands with lower annual average temperature had lower respiration rates than did the stands with higher temperature.

The humus respiration rates were also measured at 5, 10, 15, 20, and 25 °C, at 50% WHC (water-holding capacity). Thus, the temperature range covered and exceeded in both directions the growing season temperatures characteristic for the study sites (Table 9). Throughout the temperature range, the samples from the two southernmost stands (La Viale and Biescas) had the highest respiration rates, while the lowest were represented by Brandstorp and Ołobok, which are located approximately in the middle of the transect (Fig. 9).

The so-called Q_{10} values for respiration indicate how much the respiration rate increases when the incubation temperature increases by 10 degrees. Normally, these Q_{10} values decrease with increasing temperatures and as the temperature optima of the decomposing microorganisms come closer to the incubation temperature. The calculated Q_{10} values for the respiration rate ranged from about 1.0 at the highest temperatures to more than 5 at an increase in incubation temperature from 10 to 15 °C in the northernmost samples (Table 10). For those stands for which the humus samples Q_{10} values were below 1.0 (Brandstorp and Jädraås), the optimum temperature was apparently exceeded when incubation temperatures were over 20 °C, and the low increase in respiration rate with temperature for humus from the other plots ($1 < Q_{10} < 1.5$) indicates that in those cases also, the highest incubation temperature was close to the optimal one (Table 10).

In samples from more northern sites, respiration rates remained approximately constant throughout the whole 14-week incubation period. In the southern end of the transect, rates decreased over time. To determine the factors responsible for the between-plot variability in the respiration rates, a multiple regression analysis with incubation temperature (T), pH, total N (N_{tot}), and C:N as independent variables was performed. All four factors appeared significant (T, $p < 0.0001$; pH, $p < 0.0001$; N_{tot}, $p = 0.004$; C:N,

Table 9 Main characteristics of seven Scots pine sites used in a transect study ranging from Northern Sweden to Northern Spain (Niklińska *et al.*, 1999)[a]

Forest stand	Latitude longitude	Altitude (m a.s.l.)	Ann. mean temp. (°C)	Avg. temp. for growing season (°C)	Ann. mean precip. (mm)	AET (mm)
Harads	66°08′N 20°53′E	58	0.6	9.8	470	387
Jädraås	60°49′N 16°01′E	185	3.8	11.5	609	472
Brandstorp	58°03′N 14°08′E	155	6.2	11.1	930	491
Czerlonka	52°41′N 23°47′E	165	5.7	12.0	594	545
Ołobok	52°22′N 14°36′E	60	8.1	13.9	604	549
LaViale	44°11′N 03°24′E	920	8.2	13.5	793	565
Biescas	42°40′N 03°20′E	800	10.6	17.7	793	661

[a]Sites Harads, Jädraås, and Brandstorp ranged from northern to southern Sweden, sites Czerlonka and Ołobok were located in Poland, La Viale in southern France, and Biescas in northern Spain.

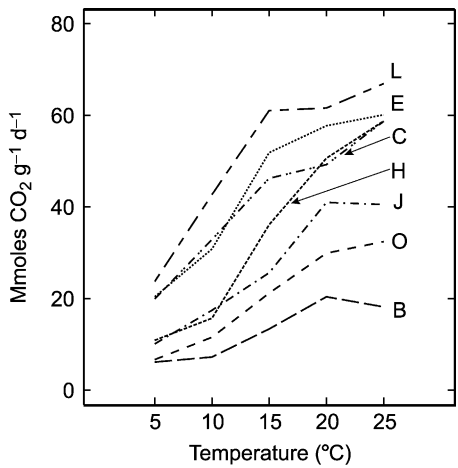

Figure 9 Respiration rates of humus samples originating from seven sites along a climatic transect from Pyrenees (E) to northern Sweden (H). The samples were incubated in a laboratory at different temperatures and respiration rate is calculated per g organic matter. H, Harads; J, Jädraås; B, Brandstorp; C, Czerlonka; O, Ołobok; L, La Viale; E, Biescas. For details on site characteristics, see Table 9. From Niklińska *et al.* (1999).

Table 10 The Q_{10} Values of humus samples originating from seven Scots pine forests growing under different climates (cf. Table 9), calculated using 5 °C temperature intervals[a]

Forest stand	Temperature range (°C–°C)	Q_{10}
Harads (northern Sweden)	5–10	2.07
	10–15	5.28
	15–20	1.96
	20–25	1.35
Jädraås (central Sweden)	5–10	2.98
	10–15	2.15
	15–20	2.56
	20–25	0.98
Brandstorp (southern Sweden)	5–10	1.39
	10–15	3.40
	15–20	2.33
	20–25	0.80
Czerlonka (eastern Poland)	5–10	2.73
	10–15	1.98
	15–20	1.13
	25–20	1.42
Ołobok (western Poland)	5–10	3.01
	10–15	3.36
	15–20	1.99
	20–25	1.18
LaViale (south France)	5–10	3.24
	10–15	2.04
	15–20	1.02
	20–25	1.18
Biescas (northern Spain)	5–10	2.28
	10–15	2.83
	15–20	1.24
	20–25	1.08

[a] After Niklińska *et al.* (1999).

$p = 0.0214$), and the common regression model was:

$$CO_2 = -226.7 + 1.79T + 39.3pH - 14.01N_{tot} + 0.28(C:N) \quad (1)$$

where CO_2 is measured in mmoles CO_2 per gram organic matter daily, N_{tot} is total N concentration in the humus sample (mg kg^{-1}), and C:N the C-to-N ratio in the humus sample.

Thus, the respiration rate increased with increasing temperature, pH, and C:N, and decreased with increasing concentration of total N. In terms of the standardized regression coefficients (β), the most important factor was temperature ($\beta = 0.67$), followed by pH ($\beta = 0.45$), N_{tot} ($\beta = -0.21$), and

C:N ($\beta = 0.19$). This multiple regression model explained approximately 71% of the total variability in the respiration rate.

The study thus shows that there are substantial differences in microbial activity among sites of different climates. However, the study did not show clear adaptations of the microbial communities to temperature regimes characteristic for the climates considered therein. For example, the respiration rate of samples originating from the coldest climate had Q_{10} value 1.35 for the highest temperature range studied, while those from the warmest site had $Q_{10} = 1.08$, indicating that the optimal temperature for microbial activity was exceeded at relatively low temperature. The study also emphasized the importance of substrate-quality factors, namely, pH, N_{tot}, and C-to-N ratio.

Our interpretation is that respiration studies such the one presented show the respiration rate of mainly the labile fraction of the humus. Over a climatic transect, we cannot exclude that, even within a given ecosystem such as the Scots pine ecosystem, the soluble or labile components in humus may be different in terms of substrate quality.

We have included a transect study by Bringmark and Bringmark (1991) who made respiration measurements on humus in a climate transect along Sweden with forest stands from the latitude of the Arctic Circle to that of the city of Copenhagen 66° 08' N to 55°39'N) and found higher respiration rates for the northern humus samples as compared to the southern ones when incubated at the same temperature and moisture. The relationship between latitude and respiration rate was positive and highly significant with $R^2 = 0.41$ ($n = 166$).

V. THE INFLUENCE OF CLIMATE ON DECOMPOSITION OF NORWAY SPRUCE LITTER IN A TRANSECT

A. General Comments

Norway spruce needle litter is a substrate with properties very different from those of different species of pine needle litter (see Chapter 4) and over a climate transect (No. V), these differences were reflected as a switch from control by climate to control by substrate quality. Thus, in a north–south transect from the Arctic Circle (66°08′N) in Scandinavia to the latitude of Copenhagen (55°39′N), climate indices did not show any significant relationship to the first-year mass loss. The annual average temperature ranged from about −1 to 7 °C and AET from 371 to 545 mm. For pine needle litter, such a difference in climate would increase the first-year mass loss by a factor of 3 to 4 (Fig. 4).

B. Climate Versus First-Year Mass Loss

The lack of a climatic influence on the decomposition of Norway spruce litter, both for the first year of incubation and later, makes it differ greatly from previous studies using other litter types, such as Scots pine needles (Fig. 4). In other words, the decomposition rate of Norway spruce litter (see following text) was not related to site-specific energy and water inputs to the Norway spruce ecosystem but to other factors. For Norway spruce litter, site climate, based on long-term averages, was not related to decomposition rate, although the variation in AET in the 1600-km-long NE to SW transect ranged from 371 to 545 mm. This suggests that climate is not an important control of litter decay rates in Norway spruce stands.

For some of the Norway spruce plots in this transect, 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. Nevertheless, in nearby Scots pine stands (paired stands of Scots pine and Norway spruce), the initial decomposition rate clearly was regulated primarily by climate.

In contrast to Scots pine, spruce trees produce dense canopies and soil microclimate in spruce forests is poorly described by local temperature, precipitation, and water-balance variables. In a transect study, Berg *et al.* (2000) found no effect of canopy cover and basal area when used as additional indices on soil climate to describe litter decay rate. In contrast, the decomposition of Scots pine litter incubated in a pine stand follows ground microclimate fluctuations very well (Table 1). Ground climate in the spruce forests may not be related as closely to macroclimatic factors and averages as in the adjacent pine forest. Under the dense spruce canopies, water could be limited due to interception, in which case, temperature differences would have little or no effect. This appears to be a reasonable conclusion since decomposition of Scots pine needles in spruce stands was also unrelated to climate. Still, we cannot exclude the possibility that other factors may be involved, say, substrate quality and possibly a different composition of microflora as compared to Scots pine stands.

The fact that dead Norway spruce needles may stay on the branches for long periods and become leached and partly decomposed before being shed means that the early phase was shorter or nonexistent, and that at least part of the litter collected from trees may have been in a late phase of decomposition already. This means that the concentrations of compounds such as lignin will be higher as compared to directly shed litter (Chapter 4) and concentrations of water solubles lower. Furthermore, leaching of the substrate means that concentrations of mobile ions such as K will be lower (Laskowski *et al.*, 1995). Thus, a dominant influence of the substrate cannot be excluded.

Table 11 Linear relationships of first-year mass loss of Norway spruce needle litter to single climatic and substrate-quality factors[a]

Equation	r	R^2	p
LOSS = f (Mn)	0.570	0.325	<0.05
LOSS = f (AET) + f(Mn) + f(Mg)	0.644	0.415	<0.05

[a] The litter, collected locally, was incubated in a climate transect (No. V) ranging from the Arctic Circle to the latitude of Copenhagen (n = 14), with a range in AET from 371 to 545 mm. All climate and substrate quality variables listed in Table 2 were tested for. Mn and Mg stand for initial concentrations of manganese and magnesium.

One out of eight substrate-quality factors, namely, initial Mn concentration, correlated positively with first-year mass loss of Norway spruce needle litter ($R^2 = 0.325$; $p < 0.05$, Table 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, the role of Mn being that of a coenzyme in Mn peroxidase (Chapters 3 and 4).

C. Lignin-Mediated Effects on Litter Decomposition Rates during Late Stages of Decomposition

1. Individual Sites

Using litter mass-loss data from a transect study (No. V; Fig. 2), we may compare annual mass loss for spruce needle litter to current litter lignin concentrations. For Scots pine needle litter, the same approach resulted in slope coefficients for the negative relationships between changes in lignin concentration and annual mass loss (Table 8) that were related to site AET (Figs. 6 and 7). For Norway spruce needle litter, the lignin 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 site (14 in all), describing the effect of the increasing lignin concentration on litter mass loss. Thus, data were treated like those for Scots pine and the values included were those of the assumed late stages (years 2, 3, 4, and 5). Lignin concentration correlated negatively with litter decay rate for 7 out of the 14 stands and we may combine these into one group (Group 1; Table 12a). For the remaining seven stands (Group 2), no such relationship was seen (Table 12a).

For the seven sites with significant relationships to lignin, no relationship was found between slope and climatic variables. Thus, for Norway spruce

litter, there was no relationship like that for Scots pine needle litter, for which the slopes were related to AET (see Section IV.B; Fig. 7).

When we compared all lignin concentration versus mass loss slopes for the Norway spruce litter (n = 14) to the initial chemical composition of the litter,

Table 12a Equations for the relationship between annual mass loss in years 2 to 5 and lignin concentrations at the start of each year in decomposing Norway spruce needle litter incubated at 14 sites in Scandinavia (transcet V)[a]

Site	Slope	Intercept	r	n	p
Significant relationships (Group 1)					
5	−0.09631	56.5266	−0.709	18	<0.001
111	−0.07393	48.2824	−0.851	13	<0.001
113	−0.09399	57.0367	−0.973	5	<0.01
10	−0.11077	65.05364	−0.96	5	<0.01
114	−0.10636	65.16445	−0.969	5	<0.01
104	−0.10874	66.37035	−0.955	5	<0.05
102	−0.03942	38.60125	−0.930	4	<0.1
Non-significant relationships (Group 2)					
109	0.04882	2.90427	0.801	4	n.s.
108	0.035722	15.61122	0.197	5	n.s.
112	−0.03309	38.60966	−0.911	3	n.s.
103	0.013382	19.7723	0.207	5	n.s.
100	0.037064	12.28549	0.386	5	n.s.
101	0.021138	12.904	0.351	4	n.s.
105	0.002265	28.00804	0.063	5	n.s.

[a] n.s. stands for p > 0.1. Data from Berg *et al.* (2000).

Table 12b Linear regressions for groupwise combined data from Norway spruce needle litter divided into two groups as based on the lignin-mediated effect on decomposition rate[a]

	Significant relationships (Group 1; n = 38)			Nonsignificant relationships (Group 2; n = 33)		
	r	R^2	p	r	R^2	p
Lignin	−0.775	0.600	<0.001	–	–	n.s.
Water sol.	0.673	0.453	<0.001	–	–	n.s.
Nitrogen	−0.608	0.370	<0.001	–	–	n.s.
Phosphorus	−0.498	0.240	<0.01	–	–	n.s.
Potassium	0.330	0.109	<0.05	–	–	n.s.
Magnesium	0.554	0.307	<0.001	–	–	n.s.
Manganese	0.316	0.100	<0.1	0.526	0.277	<0.01
Calcium	0.281	0.079	<0.1	–	–	n.s.

[a] The Group 1 and Group 2 relationships are presented in Fig. 10. Comparisons were made to substrate-quality factors.

the best fit (positive relationship) was found for the correlation with Ca concentration ($R^2 = 0.895$). This means that the higher the initial concentration of Ca and the higher the slope coefficient, the lower the effect of lignin on litter decay rates.

2. *Groupwise Combination of Data*

If there was no effect of climate on litter mass-loss rates, the data from different stands over the whole transect could be combined. Thus, we combined the data for all sites in Group 1 to one set, and those for all sites in Group 2 to another one. Using linear regression, the two groups (Group 1 and Group 2) were analyzed separately. For the Group 1 litter ($n = 38$), there was a highly significant and negative relationship between annual mass loss and concentrations of lignin (Fig. 10A) and N, and a positive one for concentrations of water solubles (Table 12b). For the time being, we have neglected the significant relationships for which we have no casual explanation.

For Group 2 ($n = 33$), the annual mass loss was regressed against the same potential rate-regulating factors, namely, concentrations of nutrients, lignin, and water solubles. In contrast to Group 1, only the relationship to Mn concentration appeared significant ($R^2 = 0.277$; $p < 0.01$; Fig. 10B; Table 12b). In both groups, the intervals for lignin concentrations were similar, with 227 to 524 mg g^{-1} for Group 1 and 286 to 513 mg g^{-1} for Group 2. However, the data combined in Group 2 had a wide range of Mn concentrations (0.41 to 7.7 mg g^{-1}; Fig. 10B), while for the Group 1, the range was clearly narrower (0.3– 3 mg g^{-1}).

3. *All Data Combined*

When relating all annual mass-loss data for late stages (Group 1 plus Group 2) with Mn concentrations, thus using the whole Mn concentration interval from 0.3 to 7.7 mg g^{-1}, we found a highly significant and positive relationship between Mn concentrations and annual mass loss ($R^2 = 0.372$; $n = 59$; $p < 0.001$). The effects of Mn on lignin degradation have been discussed before (Sections III.C, Chapter 3, and IV.E, Chapter 4). In a next step, when all the Norway spruce data for late stages (Group 1 plus Group 2) were combined with all Norway spruce data from an experimental site ($n = 95$), the relationship still held and the Mn concentration correlated positively with annual mass loss ($R^2 = 0.356$; $p < 0.001$).

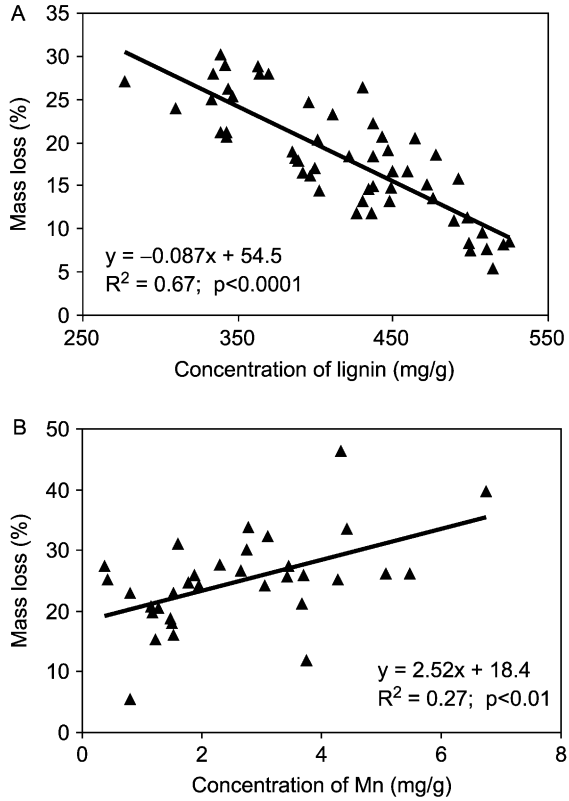

Figure 10 Annual mass loss plotted versus substrate-quality factors at the start of each year for local Norway spruce needle litter in late decomposition stages. The litter was incubated in a climate transect (14 sites) ranging from the Arctic Circle (66°08′N) in Scandinavia to approximately the latitude of Copenhagen (55°25′N). (A) Mass loss versus lignin concentration at start of each year. Data was taken from the sites where lignin was regulating the rate (cf. Table 12a). (B) Mass loss versus litter Mn concentration at the start of each year for those sites for which no relationship with lignin concentration was seen in the late stages (cf. Table 12a,b).

VI. A SERIES OF LIMITING FACTORS FOR DECOMPOSING LITTER

A. Factors Influencing Lignin Degradation Rates

The concentrations of a few nutrients in litter may influence the prevailing microflora and its succession in decomposing litter, and thus the microbial degradation rate of lignin, as well as of the litter substrate as a whole. The

effects of concentrations of N (Eriksson *et al.*, 1990) and Mn (Hatakka, 2001) have been discussed earlier. Lignin degradation rates may limit the overall litter decomposition rates if one or more of the essential elements required for microbial degradation of lignin is lacking.

A high concentration of N may suppress the degradation of lignin but, as has been discussed, in an N-rich environment, the microorganisms present may be insensitive to high N concentrations (Eriksson *et al.*, 1990). We cannot exclude that raised concentrations of heavy metals (during the decomposition process) may suppress the lignin degradation. Laskowski and Berg (1993) found for unpolluted stands that the concentration of heavy metals increased so heavily during the decomposition process (Fig. 2, Chapter 8) that they reached concentrations that might be inhibitory for the decomposition rate. Such effects of nutrients and heavy metals may be complex, and the composition of the microbial community, including the lignin-degrading fungi, depends greatly on concentrations of nutrient elements.

If the degradation of lignin and lignin-like compounds is the primary rate-regulating process in the late decomposition stage, factors such as nutrients that influence lignin degradation will, in their turn, influence the decomposition of the whole litter to an extent that depends on their concentration and biological availability. This applies at least to Mn and N.

Thus, we may argue that for pine needle litter and some deciduous litter types, the rate retardation in the late stage was primarily related to raised lignin concentrations, an effect that Berg *et al.* (1982), Berg and Ekbohm (1991), and McClaugherty and Berg (1987) related to raised litter N levels. In a climatic transect, the differing effects of lignin with climate can possibly be related to a difference in increase rate for N concentration in litter. This is a speculation but it is, in part, supported by the data in Fig. 11 (Berg and Matzner, 1997).

For the litter of Norway spruce, the effect of lignin on litter mass-loss rate was related to Mn concentrations. At high Mn concentrations, the microbial lignin degradation may be enhanced. Thus, lignin concentration itself appears less important than the litter concentration of Mn. Only when Mn concentrations were at a low level could we expect that litter mass loss would be related to lignin concentration. As the concentration of Mn in litter may depend on soil properties, such as pH and richness in Mn (Berg *et al.*, 1995), the availability of Mn in the mineral soil could be an important site property for the degradability of spruce needle litter.

That Fe is of importance for lignin degradation is well known (Eriksson *et al.*, 1990). We have not discussed the effect of Fe on decomposition rate for two simple reasons. First, we do not consider Fe to be limiting for the degradation of lignin in the systems studied and reported by us. Second, on the level of litter decomposition, too few data exist to allow a meaningful discussion.

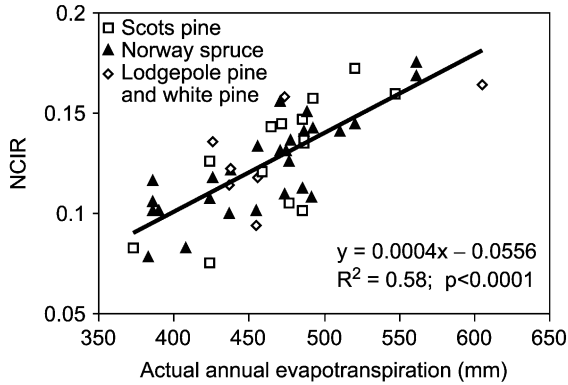

Figure 11 A linear relationship between the slope for the increase in N concentration in decomposing foliar litter with accumulated mass loss (nitrogen concentration increase rate; NCIR) and AET. The linear increase in N concentration in decomposing litter (Fig. 11 and Table 5, Chapter 5) may be relatively constant for local litter at single sites but, as studied in a climatic transect, the slope of the relationship is related to climate, here indexed as AET. From Berg *et al.* (1998).

VII. THE INFLUENCE OF CLIMATE ON DECOMPOSITION OF ROOT LITTER

A study of coniferous root litter decomposition was undertaken in a climatic transect (No. VI) across a region ranging from the Arctic Circle (approximately 66°08′N) in Scandinavia to the city of Berlin (approximately 52°N) in northeastern Germany. The study was made in coniferous monocultural forests using 37 stands at which local root litter of three coniferous species had been incubated, that is, Scots pine, lodgepole pine, and Norway spruce. In an analysis of all data combined, the linear relationships between the decomposition rate, climatic factors, and root chemical composition were significant but explained only to a small extent the variability in decay rate. In spite of the considerable climatic difference among sites, there were no strong relationships 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 was the most rate-regulating factor for all litter combined, but the R^2_{adj} was only 0.186, explaining only less than 19% of the variability in decomposition rate along the transect. Also, substrate quality influenced the decomposition rate to some extent: for the whole region, initial lignin concentrations gave a significant negative relationship with a value for R^2_{adj} of 0.142. When

Table 13a First-year mass loss of local pine roots from Scots pine and lodgepole pine as a function of climatic and substrate quality factors[a]

Equation	r	R^2_{adj}	n	p <
Climatic factors				
LOSS = f(AVGT)	0.612	0.346	25	0.01
LOSS = f(PET)	0.563	0.287	25	0.01
LOSS = f(AET)	0.553	0.276	25	0.01
LOSS = f(JULT)	0.454	0.171	25	0.05
Substrate quality factors				
LOSS = f(N)	0.536	0.232	17	0.05
Climate and substrate quality factors combined				
LOSS = f(AVGT + N)	0.603	0.322	17	0.05
LOSS = f(AVGT)	0.592	0.308	17	0.05

[a] The litter was incubated in a climatic transect (No. VI) from the Arctic Circle in Scandinavia to the latitude of Berlin. From Berg *et al.* (1998). Mean annual temperature (AVGT), potential evapotranspiration (PET), actual evapotranspiration (AET), mean temperature in July (JULT), and initial nitrogen concentration (N).

Table 13b First-year mass loss of local Norway spruce root litter at a broad regional scale as a function of some single climatic and substrate quality factors[a]

Equation	r	R^2_{adj}	n	p <
Climatic factors				
LOSS = f (JULT)	0.661	0.381	12	0.05
LOSS = f (AVGT)	0.588	0.281	12	0.05
LOSS = f (AET)	0.497	0.172	12	0.1
Substrate quality factors				
LOSS = f (P)	0.569	0.239	10	0.1
LOSS = f (Ca)	0.568	0.238	10	0.1

[a] From Berg *et al.* (1998). Mean annual temperature (AVGT), actual evapotranspiration (AET), mean temperature in July (JULT), initial phosphorus concentration (P) and initial calcium concentration (Ca).

combining average temperature and lignin concentrations, the R^2_{adj} value was 0.262. Thus, the two most important factors controlling litter decomposition combined explained only about 26% of the total variability in root decomposition rate.

The root data was divided into the two main groups of pine and spruce. For the separate groups, the values for R^2 increased but still the average temperature dominated and for the pine group the R^2_{adj} reached a value of 0.346 (Table 13a). Also, N concentration in the fresh pine root litter was

significant ($R^2_{adj} = 0.232$) for the first-year mass loss. For the root litter of Norway spruce, the average temperature in July was the strongest rate-regulating climatic factor (Table 13b), with an R^2_{adj} of 0.381. A combination of July temperature and the initial P concentration in the litter gave for spruce root litter an R^2_{adj} value of 0.713, thus explaining as much as about 71% of the variation.

These results indicate that the most important factors for the decomposition of pine and spruce root litters are different. Berg *et al.* (1998) concluded that the decomposition of spruce root litter was more dependent on energy input as compared to that of pine and that, for both groups, energy was the main rate-regulating factor, with N being the next most important factor for pine root litter decay and P for spruce. These results may be compared to those of Silver and Miya (2001), who compiled data on root decomposition on a global basis and found Ca concentration to be the main factor related to first-year mass loss. Their substrate-quality factors were mainly the same as those investigated in our transect but the climate indices were different. Still, we may not expect that, for example, temperature should be a factor of major importance in their globally based data set since the transect No. VI data set was based on energy-limited stands in a mainly boreal climate.

VIII. LITTER CHEMICAL CHANGES AS RELATED TO CLIMATE

A. Development of Litter N Concentration with Climate in Decomposing Scots Pine Needle Litter (Transects I and II)

In decomposing foliar litter, the N concentration increases, usually in a linear relationship to accumulated litter mass loss. Such relationships may be compared by their slopes, indicating nitrogen concentration increase rates (NCIR), as discussed in Chapter 5.

For local natural Scots pine needle litter and a unified Scots pine needle litter preparation, the relationship between NCIR and AET has been investigated across a climatic transect, with AET ranging from 380 mm to 520 mm. There was a highly significant relationship for Scots pine ($R^2_{adj} = 0.640$, $n = 31$, $p < 0.001$), indicating that the N concentration in decomposing litter increases faster (relative to mass loss) under a warmer and wetter climate. That relationship was significant for both local and transplanted needle litter combined as well as for local needle litter only ($R^2_{adj} = 0.517$, $n = 18$, $p < 0.001$). As we discussed already in Section VI.C, Chapter 2, the initial N concentrations in Scots pine needle litter varied over a large region

and could be related to the climatic index AET. Over a large group of litter species and for litter collected over a broad region, the initial N concentration had, however, only minor influence as a regulating factor on NCIR.

Also, for Norway spruce litter in a climatic transect, the NCIR values increased with increasing AET values and the relationship was highly significant ($R^2_{adj} = 0.534$, $n = 14$, $p < 0.01$). There was no relationship to initial N concentrations. This means that for both Scots pine and Norway spruce, the climatic factor was more important for the buildup of N concentration in litter than was the initial N concentration. In an analysis combining all available coniferous litter species the relationship between NCIR and AET was also highly significant ($R^2_{adj} = 0.58$, $n = 47$, $p < 0.001$; Fig. 11). Deciduous litter species departed from the general pattern exhibited by coniferous ones. Thus, Berg *et al.* (1995) judged that climate, as measured and indexed by AET, is a significant factor affecting the rate of N concentration increase (the NCIR) in decomposing leaf litter. As these increases were related to accumulated mass loss rather than time, the results mean that, at a given litter mass-loss value, a litter decaying in an area with higher AET will have a higher N concentration and contain more N than one decaying in an area with lower AET. We refer, of course, to similar ecosystems.

B. Development of Litter "Lignin" Concentration with Climate in Decomposing Needle Litter

For Scots pine, clear differences have been found between northern and southern sites in Scandinavia as regards the slope of the lignin concentration increase rate (LCIR; Section V, Chapter 4). A unified litter preparation with identical chemical composition was incubated over the climatic transect No. II. In the decomposing litter, the lignin concentration increased at different rates. Thus, different LCIR values were related to climate using the climate index actual evapotranspiration (AET). The LCIR for Scots pine needle litter gave a highly significant positive relationship to AET with $R^2_{adj} = 0.545$, and $p < 0.001$ for $n = 30$ (Fig. 12). A separate investigation for Norway spruce litter indicated that the relationship between LCIR and AET held also for this kind of litter ($R^2_{adj} = 0.546$, $n = 14$, $p < 0.01$).

This empirical finding may be interpreted so that the higher the AET value, the more favorable are the climatic conditions for the initial, early stage decomposition. We may speculate that with climate less limiting, the fast-growing fungi would have an advantage over more slowly growing lignin degraders. In colder climates, the lignin degraders thus would grow relatively better as compared to, say, those fungi degrading holocellulose, which would result in more lignin being degraded at the sites with lower

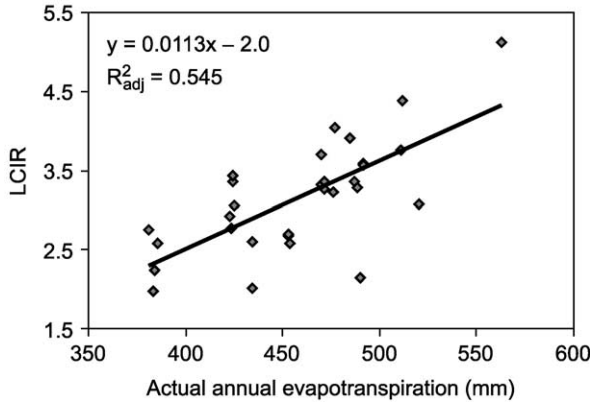

Figure 12 A linear relationship between the climatic index actual evapotranspiration (AET) and the slope of lignin concentration versus accumulated litter mass loss (lignin concentration increase rate; LCIR) in decomposing litter of Scots pine. From Berg *et al.* (1997). Adapted with permission from the Scandinavian Journal of Forest Research.

AET. The result would be that the higher the AET, the more the lignin concentration increased per unit mass lost. In other words, for litters decomposing at sites with higher AET, the amount of lignin occurring in decomposing litter at a particular percent of mass loss is larger than for the same litter at sites with lower AET values.

An alternative and speculative explanation may be connected to the increasing N levels in the same litter types (see preceding text). The increase rate in litter N levels (NCIR) is also positively related to AET and would be higher under warmer and wetter conditions. That implies that N is more quickly mobilized, thus increasing the relative N concentration in the soil and allowing a higher transport to the litter. Furthermore, the higher the litter N concentration, the faster the adsorption to remains of lignin (Stevenson, 1994). Such an explanation is possible since the N concentration apparently is limiting to the adsorption process of N (Axelsson and Berg, 1988).

Anthropogenic Impacts on Litter Decomposition and Soil Organic Matter

I. INTRODUCTORY COMMENTS

In the world of today, with severe anthropogenic impacts on almost every single aspect of many ecosystems, our view on litter decomposition would be incomplete without considering, at least briefly, how these impacts are reflected in this process. In this chapter, we describe the fate of pollutants such as heavy metals, organic compounds, and acidic precipitation, on litter and soil and give an overview of the present knowledge about their effects on decomposition processes. Finally, we will discuss possible effects of global warming and changes in water regimen on litter decomposition.

The term *anthropogenic impacts* covers a broad range of human activities leading to various effects on soil processes. Intensive agriculture and forestry frequently cause massive losses of the most fertile, surface soil layer but, on the other hand, reasonable management can turn infertile soils into arable acreage. These problems are mostly the domain of intentional activities and have been extensively studied by agriculture and forestry practitioners. Here, we concentrate on anthropogenic impacts of specific importance for organic matter decay in forest ecosystems; impacts that usually are unintentional and undesired.

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Although not yet fully understood and explained, some of the impacts of pollutants on the degradation of dead organic matter are relatively well known. On the other hand, only poor data exists on the effects of changes in water regimen resulting from forest management practices and even less is known about possible effects of such a global phenomenon as climate change on decomposition processes. Despite this lack of knowledge and understanding—or, rather, because of that—these processes deserve special attention and it was our intention when preparing this book to include a review of the present state-of-the-art in research in this area.

II. FATE OF POLLUTANTS IN LITTER AND SOIL

A. General Background

Depending on type and chemical composition, pollutants may undergo different fates and have different transfer routes in an ecosystem. For example, heavy metals are deposited mainly with dust particles while nitrogen and sulfur oxides react with water in the air and reach the soil as acidic precipitation. When deposited in a gaseous state on soil and plants, they finally also react with water, for example, in soil solution, and turn to acids. Metals, as well as NH_4^+ and H^+ ions, may accumulate in ecosystems where they can create a threat to an ecosystem in the long run, even at moderate input rates. Organic pesticides are intentionally sprayed in ecosystems where, after reaching the soil, they can be stored for some time, degraded through different physicochemical and microbial processes, or leached to the groundwater. The fate of a pollutant in an ecosystem largely determines how harmful it can be to the function of the ecosystem.

Generally, pollutants reach ecosystems with wet and dry deposition, mostly with rainfall and snow and—to a lesser extent—through so-called *interception* (horizontal deposition; Fig. 1). This latter route, relying on horizontal transport of pollutants with clouds and fog, may be important in mountains and coastal areas, where significant amounts of water are deposited in that way. After reaching a forest canopy layer, part of the water evaporates from leaf surfaces so that the amount of water reaching forest floor as *throughfall* and *stemflow* (Fig. 1) usually is significantly lower than the amount deposited as *bulk deposition* (deposition above the canopy layer plus interception). Water chemical composition also changes dramatically during its passage through the forest canopy: for example, NH_4^+ and H^+ ions are, in part, absorbed directly into leaf tissues while others, such as K^+ or Mg^{2+}, are usually leached out from leaves. Many elements are neither absorbed nor leached but their concentrations in throughfall increase due simply to evaporation of water. As a result of these processes, the water reaching the forest floor is rich in a number of chemical components and, in

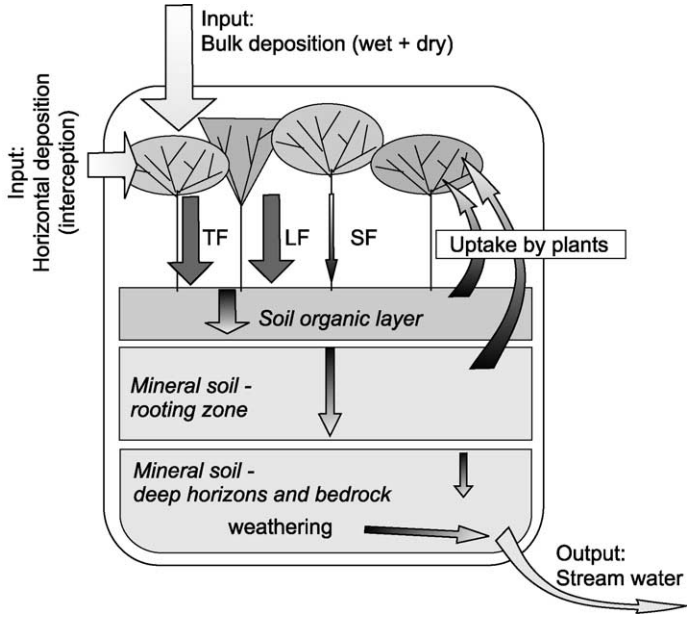

Figure 1 Main routes of input and transfer of chemical elements in forest ecosystems. TF, throughfall; LF, litterfall; SF, stemflow.

industrialized parts of the world, the input of some of them can be significant in comparison to the amounts released by natural turnover. An ecosystem may be reached not only by nutrients, but also by elements normally not involved in biological processes—so-called *xenobiotics*, for example, heavy metals such as cadmium or lead. A fraction of the elements reaching forest floor is leached down the soil profile, eventually leaving the ecosystem with streams or groundwater. The remaining part, however, accumulates in organic layers and—to a lesser extent—in mineral soil layers. Some heavy metals such as Pb or Cd, being potentially toxic to organisms, may endanger the two main ecosystem processes, production and decomposition.

B. Acidic Precipitation

Acidification of atmospheric precipitation has become one of the most serious and widespread threats to ecosystems, originating from human activities. Although natural, unpolluted rainfall is also slightly acidic due to atmospheric CO_2 dissolving in the rainwater and forming carbonic acid, its pH does not drop below 5.6, which is approximately the equilibrium point for CO_2 in water at normal atmospheric CO_2 concentration. Increased concentrations of sulfuric and nitric oxides in the atmosphere, originating from burning fossil fuels, result in formation of sulfuric and nitric acids in

water in clouds, fog, and raindrops. This, in turn, increases the concentration of H^+ ions by as much as 1 to 2 orders of magnitude (pH drops to 4.5–3.5). A large number of these hydrogen ions (50 to 70%) are intercepted by forest canopies due to the substitution of alkaline ions (K^+, Mg^+, Ca^{2+}) in leaves (Lindberg *et al.*, 1986; Stachurski, 1987; Bredemeier, 1988). In fact, at stands rich in alkaline nutrients, the rainfall may be completely buffered during its passage through the forest canopy (Meiwes and Koenig, 1986). On the other hand, in the long term, such a decrease in precipitation pH, especially in stands on pure granite sand, leads to increased leaching of nutrients, not only from leaves but also from the surface soil layers, leading finally to premature foliar litter fall (Lawrence and Fernandez, 1991) and/or decrease in tree biomass production (Orzeł, 1985).

Changes in litter chemical composition can be expected to be reflected in decomposition processes. As we have shown in previous chapters, decomposition is often initially faster in litters rich in the main nutrients. Acidic precipitation may cause increased leaching of alkaline nutrients (K, Ca, Mg) and such chemical elements as are more soluble under acidic conditions, such as Mn. Such changes in litter may lead to changed decomposition patterns, which would be indirectly related to acidic precipitation. Based on the discussion in Chapter 4, we may expect that the higher litter N levels following N deposition and the leaching of Mn from foliar litter would create a litter that leaves larger recalcitrant remains. Thus, we may hypothesize that at least moderate acidic precipitation, in general, should decrease the extent of the organic matter decomposition in ecosystems and cause a higher humus accumulation rate.

C. Heavy Metals

The old statement made by Paracelsus,[1] "*sola dosis fecit venenum,*" means that only the dose makes the poison. This important observation can be regarded as one of the foundations of toxicology and ecotoxicology. From this point of view, distinguishing toxic metals from nontoxic ones does not make much sense. In fact, all metals, even nutritional ones, may become toxic above a certain concentration threshold. When researchers today focus their attention only on a few selected heavy metals, this is not because of their special toxicity but rather due to the simple fact that only a limited number of heavy metals are emitted to the environment in amounts that endanger normal functions of organisms and ecosystems. The general effects of some of them (Pb, Cu, Hg, Zn) on organic matter decomposition are relatively well

[1]Philippus Aureolus Theophrastus Bombastus von Hohenheim, 1493-1541, German alchemist and physician born in Switzerland.

recognized. However, this does not mean that other heavy metals will not become important in the future, for example, if the pollution patterns change.

One of the major problems with several heavy metals is their high affinity to soil organic matter and to mineral particles. Because of this, they tend to accumulate in soil and—even at moderate inputs—may eventually exceed the toxicity threshold to soil microorganisms and invertebrates. The discovery made by Paracelsus almost five centuries ago acquires new meaning as regards the dose: in the long run, not only the input rate of metals (the dose) to an ecosystem is important but also the rate of their accumulation in soil, which, to a large extent, depends on soil properties. Soil properties also determine the chemical form in which metals are present, which is as important for their toxicity as the magnitude of the input and the accumulation rates. It has been shown in a number of studies that it is mostly the ionic form of metals which is toxic to invertebrate and microbial decomposers, mycorrhiza, and plants.

Because concentrations of some heavy metals increase during litter decomposition (Fig. 6, Chapter 4) (Rühling and Tyler, 1973; Berg *et al.*, 1991b; Laskowski *et al.*, 1995), they can reach relatively high concentrations in more decomposed fractions of forest litter, even in clean and moderately polluted ecosystems. Laskowski and Berg (1993) made a similar finding for Fe, Zn, Pb, and Cd in unpolluted Scots pine and oak–hornbeam forest stands. In the Berlin area, Kratz and Bielitz (1989) found that, after 19 months, decomposition concentrations of lead in leaf and needle litter had increased 3- to 14-fold, and those of Cd 1.3- to 6.5-fold.

Furthermore, a net accumulation has been seen and McBrayer and Cromack (1980) and Staaf (1980) found significant accumulation of Fe, Zn, and Cu in unpolluted decomposing litter in beech and oak forests. Net accumulation of heavy metals in soil and litter can be strongly modified by the pH in the soil environment (Livett, 1988). Generally, soils at approximately neutral pH and with a high content of clay minerals and/or organic matter can immobilize large amounts of heavy metal ions. A consequence is that the amount of heavy metals can increase considerably without necessarily affecting ecosystem functions, unless a decrease in soil pH occurs. Under such conditions, with neutral pH, the heavy metals are inactive from a toxicological point of view. However, a drop in pH below approximately 6.0 to 5.5 will cause a rapid increase in solubility of most heavy metals. For instance, Christensen (1984) found that decreasing pH by two units increased the solubility and lowered the equilibrium isogram for cadmium by more than 75%, and Boekhold and Van der Zee (1992) proved that the effect of pH on the behavior of Cd is the most important among all so-far-investigated soil factors. In an experiment by Tyler (1978), less than 10% of the total amount of cadmium and less than 20% of total amount of zinc was leached from soil using a solution of pH 4.2. Decreasing the solution pH

by one unit (to 3.2) resulted in leaching of more than 40% of the cadmium and above 55% of the zinc. Kabata-Pendias and Pendias (1979) have reported zinc mobility in acid soils to be 10-fold higher than at pH above 6.4. In their study, lead is clearly the least mobile heavy metal and only about 10% was leached even at a pH of 2.8. Christensen (1984) identified another important mechanism triggering desorption of Cd from soil: higher concentration of zinc or calcium in a leaching solution significantly increased the solubility of cadmium in soil solution.

The importance of heavy metal accumulation in soils and a possible delayed deleterious effect on ecosystems was recognized many years ago. Some authors suggested that metals accumulated in soil organic layers may become a sort of "time-bomb" which will be triggered by acidification or other as yet unknown phenomena. As a consequence, by the end of the last century, some countries proposed extremely restrictive limits on "allowable" total inputs of heavy metals, aiming at a "zero accumulation of heavy metals in soils." Although this may seem excessive (as we noted before, some heavy metal accumulation can be observed also at low pollution levels), it can be argued that even at very low accumulation rates, toxic concentrations will be reached eventually. The problem was discussed in 1996 by Witter, who wrote that:

"With the possible exception for Cd, there is apparently no scientific evidence at the moment to suggest that zero accumulation of metals in soil is required to adequately protect soil productivity, the environment, and human and animal health. A policy which steers towards zero accumulation may therefore seem excessively cautious. It is, however, also a policy which recognizes the practically irreversible nature of elevated heavy metal concentrations and their effects in soil, the deficiencies in the evidence currently available with which to establish safe metal loadings for soils, as well as the need to preserve the agronomic value of soils for many years to come. It is argued that the use of restrictive annual metal loading rates can be used to effectively ensure that maximum soil concentrations or cumulative pollutant loadings, considered to be safe are not reached in the foreseeable future."

D. Accumulation of Heavy Metals in Decomposing Litter—A Case Study

As an example of research on heavy metal dynamics in decomposing litter, we will use the studies by Laskowski *et al.* (1995), made in two mixed stands of Scots pine and common beech and two mixed stands of common oak and hornbeam of low to moderate pollution levels. In the stands studied, litterbags with natural, mixed foliar litter were exposed on the forest floor in the autumn. The incubation time and collection dates were adjusted to expected

decomposition rates in these two types of forests: the bags were collected every third month for 3 years in the pine-beech forests and every month for 2 years in the oak–hornbeam forests. Decomposition rate was measured as dry mass disappearance and the litter was analyzed for concentrations of Fe, Cd, Pb, Cu, and Zn. The decomposition rate constant k was estimated for each litter type using a single exponential model:

$$W_t = W_0 e^{kt} \tag{1}$$

where W_t is litter dry mass at time t, W_0 is litter mass at the start of the incubation. The dynamics of chemical elements during decay were analyzed using a polynomial regression model:

$$Y = B_0 + B_1 t + B_2 t^2 \tag{2}$$

where t is time in days, Y the concentration of an element and B_0, B_1, and B_2 constants. Equation 2 is the simplest model that allows for testing both the inear and the curvilinear relationships between time and the concentration of the element. Actually, in order to relate the concentrations of elements to the stage of decomposition rather than to absolute time, the time vector was standardized by multiplying time by the decomposition constant k for each litter type. Thus, eventually the regression model used in the analysis was:

$$Y = B_0 + B_1 kt + B_2 (kt)^2 \tag{3}$$

In order to make the dynamics of particular elements more comparable among different ecosystems, all element concentrations (Y) were expressed relative to carbon (C) content in litter, Y/C. Regressions revealing significant B_1 and nonsignificant B_2 were interpreted as linear relationships. Significant B_2 with nonsignificant B_1 resulted in an apparent parabola, while significance of both terms could be interpreted in two ways. The first possibility is a parabola-like relationship, and when, after an initial change in concentration, no clear trend was observed, these regressions were interpreted as indicating the stabilization in the concentration of an element.

The decay of pine–beech litter was much slower than that of oak-hornbeam: after 1080 days, the decomposition reached 57 to 67%, while in oak–hornbeam forests, approximately 65 to 70% decomposition was reached already after 660 days of incubation. The decomposition rates are representative for temperate forests (Dziadowiec, 1987; Blair, 1988a,b; Cameron and Spencer, 1989). We may expect that the patterns of chemical element dynamics observed during decomposition probably is valid for a broad range of forest ecosystems under this climate type.

The initial concentrations of heavy metals were rather low by European standards (Table 1) and all four forest stands could be considered relatively unpolluted. Nevertheless, even at a moderate anthropogenic atmospheric

Table 1 Initial and final concentrations of heavy metals in decomposing mixed local foliar litter of common oak and hornbeam (OH1 and OH2) and of mixed foliar litter of Scots pine and common beech (PB1 and PB2)[a]

		Fe	Mn	Zn	Cu	Pb	Cd
Forest	Stage	mg kg^{-1}					
OH1	Initial	396	1170	48.3	13.70	7.27	0.458
	Final	3584	2061	168.8	12.77	35.55	1.980
OH2	Initial	3055	1348	139.0	12.11	18.84	0.819
	Final	17445	2651	365.1	28.07	58.87	3.064
PB1	Initial	679	1023	70.8	5.02	17.60	0.760
	Final	2086	1896	470.1	22.76	57.50	3.061
PB2	Initial	642	702	79.8	22.34	18.49	1.105
	Final	2995	606	304.0	19.60	93.17	2.668

[a]From Laskowski *et al.*, 1995.

input of heavy metals, the concentrations of Fe, Zn, Pb, and Cd substantially increased during decomposition (Table 1, Fig. 2). In terms of net release rates, the heavy metals studied could be ordered as follows in relation to the amount of organic matter remaining:

Oak–hornbeam 1: Cu $\geq$ Organic matter $>$ Zn $\geq$ Cd $>$ Pb $>$ Fe
Oak–hornbeam 2: Organic matter $>$ Cu $>$ Zn $\geq$ Pb $>$ Cd $>$ Fe
Pine–beech 1: Organic matter $>$ Pb $\geq$ Cd $\geq$ Fe $\geq$ Cu $\geq$ Zn
Pine–beech 2: Cu $\geq$ Organic matter $>$ Cd $>$ Pb $\geq$ Zn $\geq$ Fe

Thus, at the end of the incubation, not only concentrations but also absolute amounts of Fe, Zn, Pb, and Cd in the litter increased at all plots. Such an accumulation of these heavy metals during litter decomposition was also found by other authors. For example, Dziadowiec and Kwiatkowska (1980) noticed a net accumulation of Fe and Al in decomposing mixed leaf litter, and Staaf (1980) found a net accumulation of Fe, Zn, and Cu in beech leaf litter. An increase in the concentrations of Al, Fe, and Zn in oak leaf litter was observed by McBrayer and Cromack (1980), and of Fe and Pb in beech and spruce litter by Parmentier and Remacle (1981). These observations show that an increase in concentration and even a net accumulation of some heavy metals occurs as litter decomposes toward humus and that this increase may be a general phenomenon in forest ecosystems. Because the cited studies were carried out in regions not exposed to a direct influence of industrial pollution, we may conclude that this metal accumulation is a natural process in undisturbed forest ecosystems. As this is the case, increased deposition rates in industrialized parts of the world may lead to concentrations high enough to cause undesirable changes in ecosystem processes.

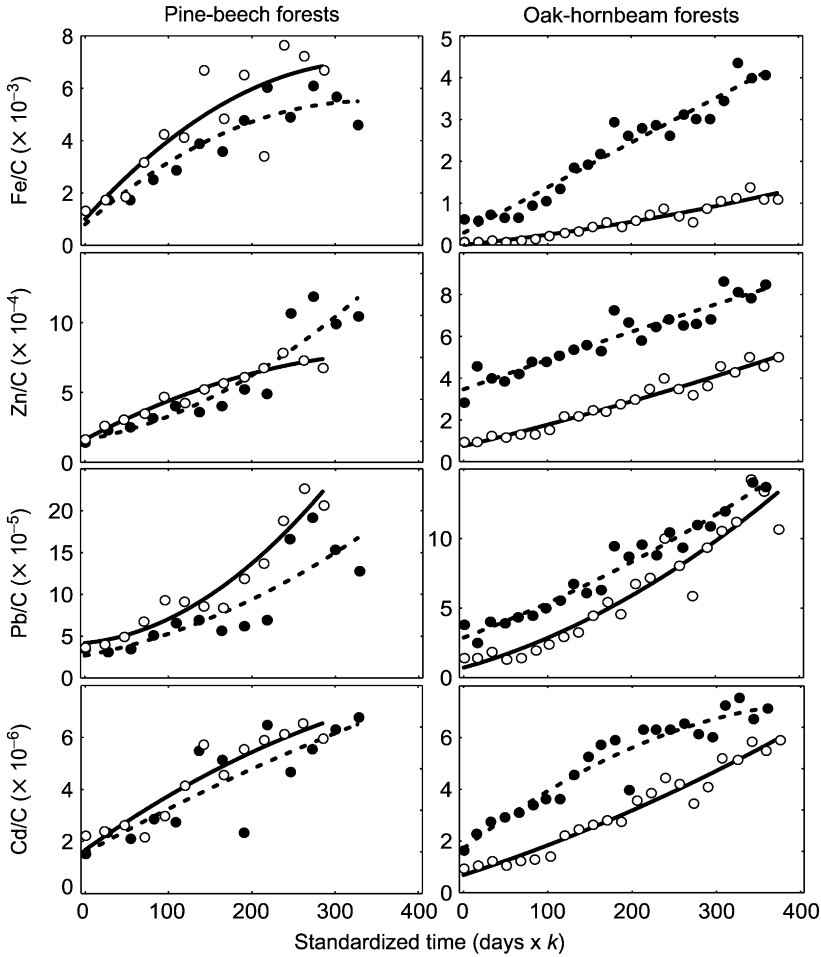

Figure 2 Dynamics of heavy metal concentrations (expressed as heavy metal-to-carbon ratios) in decomposing mixed local foliar litter in forest stands with mixed Scots pine and common beech and stands with common oak and hornbeam. Time is expressed as standardized units obtained by multiplying days of incubation by the decomposition rate constant k (Eq. 2). Different points and line styles indicated separate stands of the same forest type (after Laskowski *et al.*, 1995a).

E. Sources of Heavy Metals in Litter

The increases in concentrations of some nutrients and heavy metals during litter decomposition may be explained by immobilization of the amounts already present in litter by the increasing microbial biomass and binding to humic substances. This, however, cannot explain the increase in absolute

amounts of metals and a net accumulation of any chemical element requires an external source. To explain net increases in amounts of sulfur and phosphorus, Blair (1988a) suggested two possible processes: input with throughfall and biological translocation by fungal mycelium from deeper soil layers. The same processes were proposed by McBrayer and Cromack (1980) for Al, Fe, Zn, Ca, and N, and Berg *et al.* (1991b) stressed the importance of microbial transport of heavy metals, for example, from the humus layer.

As we mentioned at the beginning of this chapter, heavy metals reach ecosystems via wet and dry deposition, frequently measured as total (''bulk'') deposition. In order to estimate the actual input of heavy metals and other elements to the forest floor, it is indispensable to measure the amount and chemical composition of throughfall as well as of litter fall because a large proportion of heavy metals can be deposited on leaf surfaces. For example, in studies on heavy metal input to common beech and Norway spruce forests, annual deposition rates measured as bulk precipitation above forest canopy were: 7 to 13 mg m^{-2} Pb, 0.16 to 0.24 mg m^{-2} Cd, and 0.22 to 0.44 mg m^{-2} Cr (Schultz, 1985). However, annual input rates to the forest floor, measured as the sum of heavy metals in deposition with throughfall and litter fall, were: 13 to 32 mg m^{-2} Pb, 0.35 to 0.54 mg m^{-2} Cd, and 1.5 to 2.2 mg m^{-2} Cr. Thus, canopy interception accounted for approximately 50% of the total Pb and Cd inputs and 70 to 90% that of Cr, with the interception effect being larger in the Norway spruce stand than in that with common beech. Additionally, at least in some forest types, a significant part of the wet deposition may reach the soil as stemflow, which in monocultural beech forests may reach as much as 30% of the total water input (Bredemeier, 1988). The amount of stemflow is dependent on the trees' branch anatomy and is consequently different among species. As a contrast, in monocultural spruce forests, stemflow does not exceed 5% of the total water input and may in practice be neglected (Likens *et al.*, 1977; Zieliński, 1984).

In a detailed study on heavy metal transfer through an ecosystem with Scots pine and common beech in southern Poland (Grodzińska and Laskowski, 1996), the yearly input of zinc with bulk deposition (above canopies) was estimated to 47.7 mg m^{-2}. The input to the forest floor had increased to 63.3 mg m^{-2} as the sum of throughfall, litter fall, and stemflow. Of that, 4.6 mg m^{-2} was retained yearly in the soil organic layer (OL + OH + OF) and the remaining 58.7 mg m^{-2} was leached down the soil profile. However, only 2.3 mg m^{-2} left the watershed with stream water, indicating a strong accumulation of zinc in the ecosystem at 45.4 mg m^{-2} (Fig. 3). Similar observations were also made for copper, lead, and cadmium: all these heavy metals accumulated in the soil organic layers (7.2, 1.21, and 0.21 mg m^{-2} yr^{-1}, respectively), and in the ecosystem as a whole, with 8.95, 4.7, and 1.12 mg m^{-2} yr^{-1} , respectively (Fig. 3).

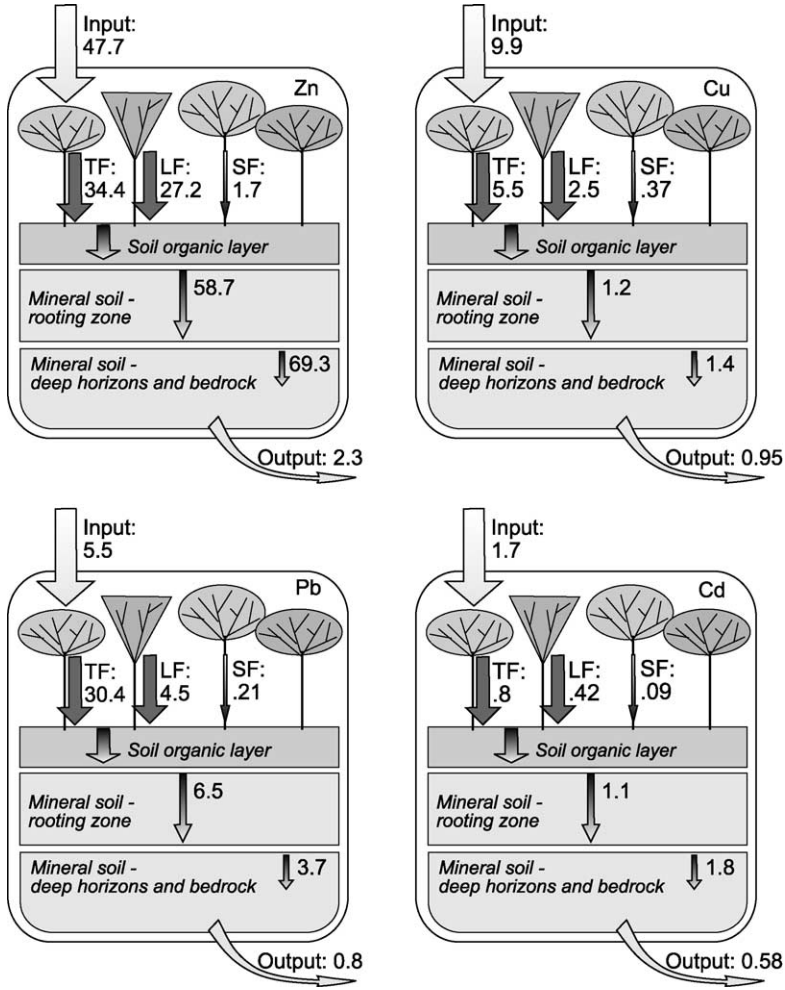

Figure 3 Transfer of Zn, Cu, Pb, and Cd in a stand with mixed Scots pine and common beech (mg m^{-2} yr^{-1}). TF, throughfall; LF, litterfall; SF, stemflow. From Grodzińska and Laskowski (1996).

In an attempt to find an explanation for the increase in absolute amounts of heavy metals in decomposing litter, the amount and chemical composition of throughfall were measured at four mixed stands (2 stands with common beech/Scots pine and 2 stands with common oak/hornbeam), where litterbags were incubated (see previous section; Laskowski *et al.*, 1995). The input of elements with throughfall appeared sufficient to explain the increase in amounts of all heavy metals except for Fe. In the litter at one of the

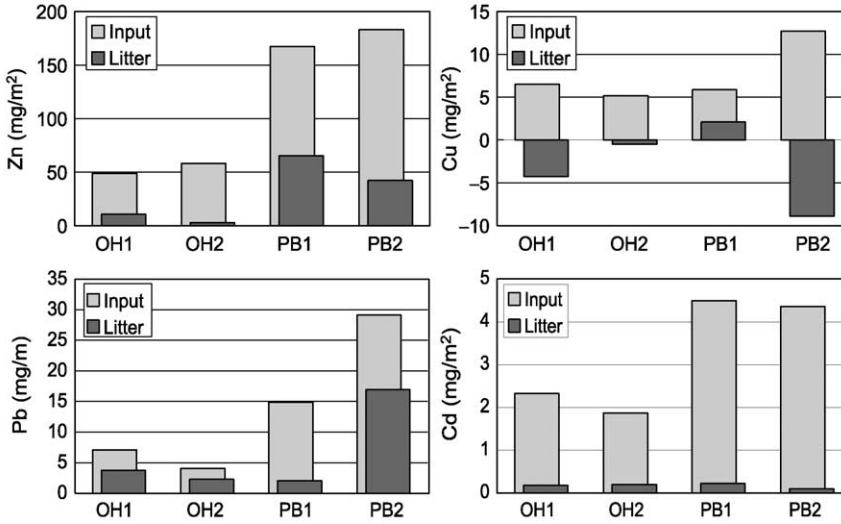

Figure 4 Net change in absolute amount of Zn, Cu, Pb, and Cd in decomposing litter. The input of the heavy metals with throughfall shown is that during the whole litter incubation period. Of the four stands, two were mixed Scots pine and common beech (PB) and two stands were mixed common oak and hornbeam (OH). From Laskowski *et al.* (1995).

oak–hornbeam stands, the amount of Fe increased during decomposition by 21.7 mg per litterbag, while the input with throughfall was 4.7 mg per litterbag area. The difference was even larger for litter incubated at the other oak–hornbeam stand, where Fe increased in amount by 77.4 mg per litterbag, and the input with throughfall was only 3.1 mg per litterbag area, leaving a major part to be transported by mycelium from the soil and/or to mineral contamination. For the two stands with Scots pine and common beech, the amounts of accumulated Fe were clearly in accord with input by throughfall and none of the pine–beech litter bags had visible traces of mineral soil. The inputs of other heavy metals that is, Zn, Pb, and Cd in all four stands and Cu in one Scots pine-common beech stand, was much higher than the amounts that accumulated in the litter (Fig. 4).

It seems, thus, that the absolute amount of heavy metals in litter can increase during decomposition due to three processes: (i) biological transport of metal ions by fungal mycelium from deeper soil layers, (ii) deposition of metals with throughfall, and (iii) contamination of litter with inorganic soil caused by, for example, soil fauna. However, in forests with mor humus layers, contamination with mineral soil is less likely.

F. Organic Pollutants

Organic pollutants cover an extremely broad range of chemical compounds and we give just a brief overview of the different groups. Organic pollutants have some important characteristics that allow us to distinguish them clearly from such pollutants as heavy metals and to describe the most general processes they may undergo in ecosystems. From some points of view, the most important difference between heavy metals and organic chemical compounds is the fact that the latter can be degraded to simpler and less toxic compounds or even completely decomposed and mineralized, like any natural organic compound. A number of organic pollutants can actually be used as a source of carbon and energy by soil microorganisms. Thus, we may expect that in contrast to heavy metals, organic pollutants would not accumulate as efficiently nor as permanently.

Some of the most common organic pollutants are pesticides, which are frequently sprayed in forests as a regular forest management practice. From a chemical point of view, the term *pesticide* is not much more precise than the general term "organic pollutant." Actually, this broad class of chemicals covers even some inorganic compounds, such as one of the most widely used fungicides—the Bordeaux mixture ($CuSO_4 + Ca(OH)_2$ in H_2O). Fungicides constitute one large subgroup of the pesticides and examples of organic fungicides are chinons and their derivatives and phenylmercury acetate. Two other large subgroups are herbicides and insecticides. On a global scale, herbicides are the most commonly used pesticides and are mostly represented by derivatives of chloroaliphatic and phenoxyacetic acids. Finally, insecticides encompass the most divergent group of pesticides from a chemical point of view. Besides some inorganic compounds that are no longer used on a large scale, they include a number of organic chemicals acting on different physiological functions. The best known and the most controversial is DDT—presently forbidden in many countries due to its low degradability and high lipophilicity, both of which lead to high accumulation rates in organisms and increase in concentration along trophic chains (biomagnification). DDT represents a chemical class of *chloroorganic* insecticides to which lindane, aldrine, and dieldrine also belong. They are all highly lipophilic, have a tendency for bioaccumulation, and have similar biochemical and physiological properties. The next large group of insecticides are *phosphoroorganic* compounds, such as the commonly used dimethoate or malathion. Other frequently used groups of insecticides are the *carbamates*, such as isolan and sevin, and the *chloronicotinyles*, such as imidacloprid.

Although the residence time of pesticides in humus and soil differs widely, they are usually decomposed and ultimately mineralized. For more information on toxic properties and detoxification pathways of pesticides, see Cremlyn (1979).

In soil, including its biologically most active parts—humus and litter—transformations of organic pollutants include both microbial degradation and physicochemical reactions. Physicochemical transformations take place through reactions with mineral and organic soil components and are promoted by changes in temperature and humidity. These abiotic transformations include processes such as oxidation, reduction, hydrolysis, photolysis (at the soil surface), dehydrochlorination, and conjugation. Humic compounds, abundantly present in soil, are rich in carboxyl ($COOH^-$), hydroxyl (OH^-), and carbonyl ($C = O$) groups (Section VI, Chapter 6). They are all highly reactive and interact readily with other organic compounds present in the soil, including organic pollutants. Their reactions may be catalyzed by some minerals and metal ions (for example, Cu^{2+} and Mn^{2+}).

Scheunert (1992) distinguishes two main groups of biotic transformations of pesticides in soil: (i) metabolism, by which pesticides are degraded by microorganisms which use them as an energy and carbon source, and (ii) co-metabolism, by which pesticides are degraded without actually being used for energy or as a carbon source. Probably, most pesticide degradation processes in soil take place as co-metabolism. Although Scheunert considers degradation of only pesticides, these two alternatives apply also to other groups of organic pollutants.

Our knowledge about degradation of organic pollutants in soil is far from satisfactory, but it is commonly assumed that no single microorganism is capable of processing the entire degradation pathway from original compound to full mineralization; the complete mineralization probably requires a whole array of microorganisms specialized in different degradation steps. The final mineralization products are such compounds as CO_2, CO, H_2O, H_2S, NH_4^+, Cl^-.

Next to microbial and physicochemical degradation, the most important processes that organic pollutants undergo in the soil subsystem are accumulation, leaching, and evaporation. Determining for their mobility are two counteracting processes, that is, adsorption and desorption. Organic pollutants are bound in soil to both minerals and organic compounds. They interact with humic and fulvic acids and are adsorbed on such minerals as montmorillonite, vermiculite, illite, kaolinite, and chlorite. We may relate retention and adsorption to three main types of chemical bonds.

- *Covalent bonds*, a stable bond based on shared electrons by an atom in the pollutant and one on the surface of, say, the mineral. Since this type of bond is stable, the particles are effectively retained in soil.
- Physical adsorption resulting from the van der Waals electrostatic forces between pollutants with polar molecules and the surface molecules of soil particles; the van der Waals forces are weak and, as a result, the retention time of organic pollutants absorbed in this way in soil is usually short and they can be easily released to the environment.

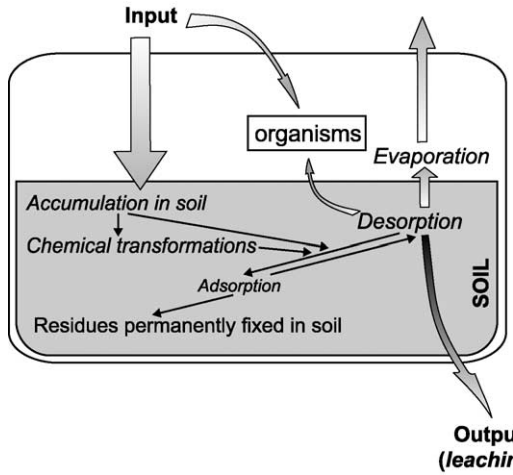

Figure 5 An overview to transports and transformations of organic pollutants in soil. After Scheunert (1992), modified.

- *Hydrogen bonds* in which two strongly electronegative atoms are linked through a common hydrogen ion; their strength is intermediate between covalent bonds and the weaker van der Waals forces.

Organic compounds and the products of their transformations which may be dissolved in the soil solution are leached from soil with rainwater. The leaching from an ecosystem may be dominated—depending on the landscape—by surface flow (mostly in mountains and foothills) or percolation down the soil profile (Fig. 5).

III. EFFECTS OF POLLUTANTS ON DECOMPOSITION

Because of its crucial importance for ecosystem functioning, litter decomposition has been subject to many studies concerning effects of industrial pollution at the ecosystem level. In the following sections, we describe how some major classes of pollutants—heavy metals, organic compounds, and acidic precipitation—affect the decomposition. Each class will be discussed separately and empirical examples from laboratory experiments and field observations will be given.

A. Heavy Metals

As we have mentioned, regardless of their biological role, all heavy metals are potentially toxic. In fact, some heavy metals, such as mercury or copper

and a metalloid such as arsenic, have been used as toxins for centuries to protect crops against pests and molds. Although the general toxic properties of heavy metals have been known for a long time, only recently was some knowledge gained on their influence on the organic matter decomposition. In an early study, Rühling and Tyler (1973) found a significant retardation of litter decomposition in Scots pine forests under the influence of industrial emissions. They suggested that in acidic soils like those used in their study, heavy metals such as Cu, Zn, Cd, Ni, and Pb may be responsible for the observed suppression of the decay. In some studies, the increase of litter accumulation in areas influenced by industrial emissions has been related directly to high concentrations of heavy metals (Coughtrey *et al.*, 1979; Bengtsson *et al.*, 1988, Grodzinski *et al.*, 1990). In 1974, Babich and Stotzky suggested that this effect results from heavy metal toxicity to soil microorganisms responsible for organic matter degradation. In fact, the toxicity of Cd to microorganisms was confirmed later in laboratory experiments by Giesy and Aiken (1978). Also Hattori (1991) showed a suppression of soil microbial activity as a consequence of Cd contamination. Today, it appears obvious that the direct cause of the retardation of litter decomposition in metal-polluted ecosystems is the toxicity of heavy metals to soil microorganisms in general (Giesy and Aiken, 1978; Nordgren *et al.*, 1983; Rühling *et al.*, 1984) and to invertebrates (Strojan, 1978; Bengtsson and Rundgren, 1984).

The retardation of decomposition leads to accumulation of dead organic matter in the forest floor and—as a probable consequence—exclusion of increasing amounts of nutrients from normal biogeochemical cycling in an ecosystem. Such an accumulation may be fast and, after only a few decades of pollution, the amount of organic matter accumulated on the forest floor can be doubled. For example, in heavily polluted regions, Strojan (1978) found that the amount of organic matter had accumulated to as much as 213% of that in the control area. Killham and Wainwright (1981) estimated a 35% reduction in litter decomposition rate in the vicinity of a coke plant releasing a mixture of heavy metals. In most of these studies, the levels of heavy metals in litter were very high, exceeding the levels in litter at unpolluted sites by up to three orders of magnitude. Against the background of available data, Smith (1981) found evidence of heavy metal toxicity for litter decomposition only at high pollution loads. One of the few exceptions was the work by Zieliński (1984), reporting decreased litter decomposition rates in ecosystems affected by moderate pollution levels. Also, Rühling and Tyler (1973) demonstrated that under specific circumstances—in acidic forest stands—the rate of litter decomposition could be suppressed also by moderate concentrations of heavy metals. This was supported in a laboratory experiment (Laskowski *et al.*, 1994) in which the rate of respiration from litter decreased significantly at moderate Zn pollution.

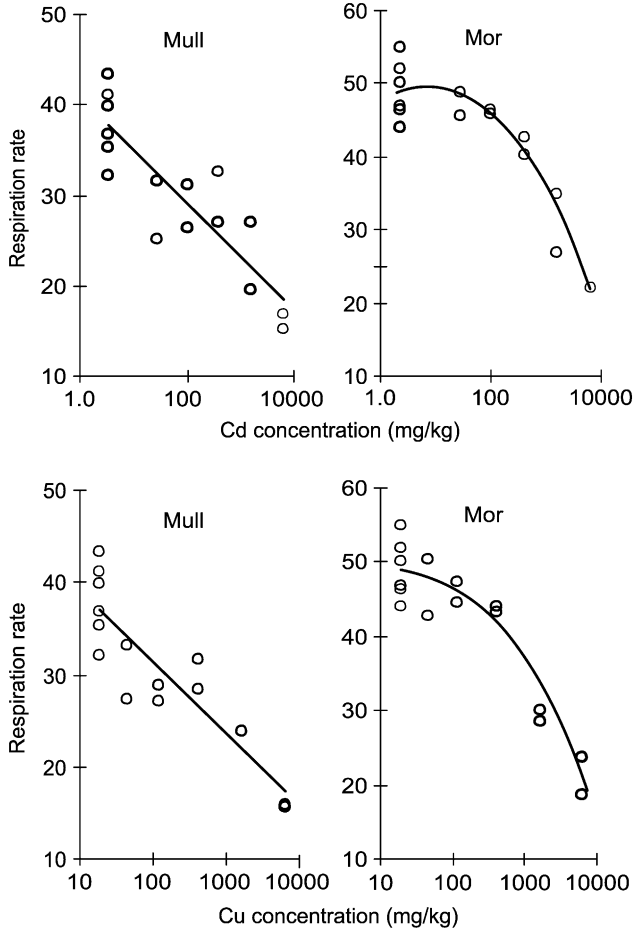

Figure 6 Effects of heavy metals on respiration rate from two forest humus types—mull and mor. Rate is given as mmol CO_2 kg^{-1} organic matter. From Niklińska *et al.* (1998).

Niklińska *et al.* (1998) studied the effects of the addition of four heavy metals, Cu, Zn, Cd, and Pb, on the respiration rate from mull and mor humus originating from two ecosystems typical for the temperate climatic zone, namely, mixed stands of Scots pine and common beech and mixed stands of common oak and hornbeam. The estimated EC_{50} values for the respiration rate (50% inhibition) in the mull humus were (in mg kg^{-1}): Cu, 3980; Zn, 5890; Cd, 6310; and Pb, 26,300 (Fig. 6). In the mor humus, the effect was similar, with the EC_{50} values Cu, 3770; Zn, 5380; Cd, 6300; and Pb, 23,310 mg kg^{-1} (Fig. 6). Although these concentrations are rather high

and can be found only in extremely polluted areas, significant effects on the respiration rate were found also at much lower concentrations. For example, the estimated EC_{10} values (10% inhibition) for the mull humus were: Cu, 29.1; Zn, 538; Cd, 12.9; Pb, 140 mg kg^{-1}. Such concentrations are common for large areas surrounding metal plants, smelters, and mines as well as along highways. As mentioned above, also unpolluted systems may concentrate heavy metals to inhibiting levels. Thus, Bringmark and Bringmark (2001) found a significant correlation between respiration rates from forest litter and concentrations of lead in soil organic layers at concentrations not much higher than those typical for uncontaminated areas.

B. Acidic Precipitation

This kind of pollution is of major concern over large areas of the industrialized world. Acidification may affect the decomposition process directly through the effect of H^+ ions to some decomposers and the deterioration of soil conditions for others. Most soil organisms prefer approximately neutral pH and the active microbial population dominating in a given soil system is adapted to the conditions of that system, including its pH. As a result, the rate of litter decomposition generally decreases with increasing acidification. Under natural conditions, in unpolluted ecosystems, such relationships between soil pH and decomposition rate can be seen. However, soil acidification due to anthropogenic activity may be too fast for microbial communities to adapt to new, changed conditions.

Indirect effects of acidic precipitation include increased leaching of nutrients from soil organic matter and upper mineral soil layers and mobilization of heavy metal ions, which, in their turn, can suppress decomposition due to their toxicity to soil organisms (see preceding text). Such effects were observed by, for example, Johnson *et al.* (1991) in forests subject to high atmospheric deposition of N and S in the Appalachians (USA). The high input rate of these two elements, together with extremely acidic soils, very low N and S retention, and high N mineralization rates, resulted in soil solutions dominated by NO_3^-, SO_4^{2-}, H^+, and Al. The pulses of high Al concentrations in soil, resulting from the pulses in NO_3^- and SO_4^{2-}, reached levels known to suppress the uptake of base cations and root growth. Highly acidic soil conditions lead also to increased leaching of N, P, Ca, and Mg, thus deteriorating the soil. Increased concentrations of hydrogen and aluminium ions in soil together with decreased nutrient availability may affect decomposer communities negatively and decrease the decomposition rate in affected ecosystems.

Wolters (1991) studied effects of simulated acid rain on soil biotic processes in a beech forest on moder soil in the Solling area in Germany. The acid

treatment reduced CO_2 production, microbial biomass in the OF layer, and leaching of NO_3^-. The suppressing effect was particularly strong in the early decomposition stage. A similar reduction of microbial CO_2 evolution from litter due to acidic conditions was observed by Moloney *et al.* (1983). CO_2 production was further suppressed by the presence of Pb and Zn, which indicates the importance of increasing heavy-metal mobility and availability under acidic conditions. In fact, Nouri and Reddy (1995) observed a significant increase in Cd, Pb, and Mn solubility in litter after treatment with simulated acid rain of pH 3.5.

Hågvar and Kjoendal (1981) performed an acidification experiment on field- and greenhouse-incubated litterbags. The litterbags were acidified with artificial acid "rain" (diluted H_2SO_4) of pH 4, 3, and 2, while application of groundwater (pH 6) in the field and simulated rain of pH 5.3 in the greenhouse were used as controls. The strongest acidification (pH 2) resulted in significantly lower decomposition rates in the early decomposition stage. Corresponding tendencies were observed in the late decomposition phase in both the greenhouse and the field experiments. Application of pH 2 water also increased the leaching rate of Ca, Mg, and Mn in both field and greenhouse experiments. Watering with a weaker acid (pH 3) did not affect the decomposition rate or leaf chemical composition significantly, and no effects on decomposition rates were observed in the pH 4 treatments.

Similar effects may be caused directly by SO_2 when occurring in high atmospheric concentrations. The SO_2 is readily dry-deposited to forest litter where it is oxidized to sulfuric acid. Ineson and Wookey (1988) observed a suppression of the respiration rate from litter by SO_2 concentrations commonly encountered in air, even in rural areas. A substantial drop in litter pH resulted also in enhanced leaching of cations, especially Ca and Mg.

From numerous studies, it thus appears that acid precipitation usually leads to a decrease in decomposition rates of dead organic matter. Although different authors report significant effects at different rainfall pH values, the phenomenon seems to be general and well supported. Differences among results of different studies may simply reflect the variability in soil characteristics as well as differences in composition of microbial communities.

C. Organic Pollutants

The effects of organic pollutants on litter decomposition are less clear and differing results have been obtained in different studies. This is not surprising, considering the size of this group of pollutants and its numerous classes of chemicals (previously mentioned). Even the two groups most commonly used in horticulture, namely herbicides and insecticides, are tremendously variable and encompass easily degradable compounds with

half-lives in soil in the range of days and weeks, as well as such resistant compounds as organochloric pesticides like DDT or dieldrin. However, even organochloric pesticides can be degraded in soil, both abiotically and through microbial decomposition, although their half-lifes count in years—between 2 and 15 years for DDT (U.S. Environmental Protection Agency, 1989; Augustijn-Beckers *et al.*, 1994). Newer types of pesticides are usually degraded much faster, as in the case of the fungicide benomyl with a half-life of 32 days or the insecticide diazinon, with a half-life of only 8.9 days (Vink and van Straalen, 1999). Thus, in case of organic pollutants, it is rather difficult to find some common principles regarding their fate in soil and, in consequence, their effect on soil organisms and litter decomposition.

For example, Hartley *et al.* (1996) studied effects of weed control in orchards in New Zealand, and usually combines herbicides and mowing or cultivation. The authors compared effects of a number of different treatments, including the use of the herbicide terbuthylazine, on soil respiration, cellulose degradation, and bacterial and fungal biomass. It appeared that terbuthylazine had no detectable effects on CO_2 production or cellulose decomposition rate over two growing seasons following the application. Similarly, Vink and van Straalen (1999) did not find any effect of benomyl on the respiration rate and dehydrogenase formation in microcosms containing a mixture of different leaf litter species. However, it decreased the nitrification rate at high concentrations. In contrast, diazinon, at a concentration of 400 mg kg^{-1}, reduced respiration and nitrification rates as well as dehydrogenase formation.

From several studies, it appears that pesticides usually do not affect microbial communities significantly, but may have effects on the soil fauna. As the importance of the latter group for litter decomposition differs among ecosystem types, the effects of pesticides and similar organic toxicants on litter decay may be expected to vary similarly. For example, after application of lindane in pine forests of North Carolina, the abundance of mites, springtails, and other soil arthropods was substantially reduced and did not return to pretreatment conditions for at least 2 years (Hastings *et al.*, 1989). In a forest system, Perry *et al.* (1997) detected no significant effects of diflubenzuron on the total number of invertebrates or counts by trophic categories of litter and soil invertebrates. Only the densities of spiders and springtails were significantly reduced in the treated forests. Whether such changes affect litter decomposition remains unknown.

To summarize this section, there is no proof that pesticides and similar organic compounds that are not classified as pesticides have significant effect on forest litter decomposition rate, with the possible exception of unrealistically high doses of chemicals or in ecosystems where the mediating role of soil invertebrates in organic matter decay is especially important.

D. Effects of Climate Change

1. General Comments about Existing Scenarios and Methods

There is still (in 2005) only general agreement among scientists as regards possible climate-change scenarios. However, all tend to agree that the accumulation of organic matter in soil is crucial to the atmospheric CO_2 balance and, as a consequence, also for global temperature levels. The effects of a climate change will result in clear changes and modifications in the complex of processes that determine the store of soil organic matter but today there is no generally accepted picture of the net outcome, even for one forested ecosystem. One reason appears to be that some of the scenarios presented are based on studies that are likely to be methodologically less correct. Further, some scenarios of the effects on the soil systems presented today may appear confusing to most readers since they often are based on assumptions that are not always made clear. For example, it is often assumed that all litter mass is decomposed biologically, which also means that all SOM finally is decomposed and that the amount of humus mainly is built up by an SOM fraction that is decomposing. Thus, the amount of stored humus is dependent on a balance between litter input and the amount of decomposing SOM.

Raised CO_2 levels in the atmosphere have been suggested to decrease the N concentrations in litter (see review by Cotrufo *et al.*, 1998), and a lower decomposition rate until the litter is decomposed has been assumed. A problem with such an effect is that N is far from the only nutrient/compound influencing decomposition rates and patterns and the decomposers need a balance among at least N, P, and S. A further problem is that the effect of N is actually reversed in the course of decomposition, hampering the decomposition process instead of enhancing it (Sections III.C, Chapter 3, and IV. C, Chapter 4). A lower N level may mean a lower decomposition rate in the early stage but a more complete decomposition in the limit-value stage. Also, Mn has an effect on decomposition and its concentration has been related to the limit value (Sections III.C, Chapter 3, and IV.C, Chapter 4) but the effect of a changed CO_2 concentration on this nutrient is not known. We do not question the effect of CO_2 on litter N concentrations in newly shed litter, but merely express a concern that it may be overexploited.

The methods used to study the decomposition may be critical and measurements using litter bags incubated over years yield results that may be interpreted very differently from those obtained from respiration studies. We may consider the observations made by Couteaux *et al.* (1998) (Table 10, Chapter 4), pointing out the different decomposition rates of different main fractions in decomposing litter and humus. A relatively small labile fraction respiring at least approximately 1000 times faster than the main recalcitrant

fraction is likely to dominate the measured rates. One possible conclusion is that scenarios based on CO_2 release rates from humus reflect mainly the properties of such a labile fraction rather than those of the whole humus.

Furthermore, decomposing foliar litter has no standardized behavior over ecosystems and there is no unified nor general decomposition pattern. Thus, a scenario based on properties of decomposing litter and its chemical composition developed for a boreal pine forest may have very little in common with that of a temperate oak forest. Also, properties of a temperate spruce forest soil probably have little in common with those of a subtropical eucalypt forest.

2. A Climate Scenario and a General Approach to its Effects on Soil C Dynamics

We will discuss a possible scenario for soil C dynamics, based directly on the content in this book. It belongs mainly to the group of "negative feedback scenarios," suggesting that the climate scenario results in an increased net accumulation of soil organic matter. We have selected a general scenario of a climate change with an increase in annual average temperature of +4 to 5°C and about 40% increased precipitation, a scenario predicted for Scandinavia and the Baltic basin, and restrict our discussion to that region, although the principle discussed may have wider application. We apply an increase of 4°C in mean annual temperature, evenly distributed over the year, and an increase in precipitation of 40%, also evenly distributed over the year, thus simplifying an existing prediction (Johannesson *et al.*, 1995). Annual actual evapotranspiration (AET) has been calculated (Meentemeyer, 1978) for several representative sites in Scandinavia and mainland Europe for which we had data on initial chemical composition of litter, quantitative litterfall, as well as for limit values. Applying the previously defined climate change, AET was calculated for the sites, and we obtained an average increase in AET of 27%, with only a minor variation about the mean.

Since the forested systems in Scandinavia are energy limited, a rather constant change in AET resulted. A basic assumption is that, in spite of climate change and temperature increase, the decomposing litter leaves recalcitrant remains (Couteaux *et al.*, 1998; Berg *et al.*, 2001). Litter decomposing in a long climate transect has been shown to give limit values at the Arctic Circle (AET 370–380 mm) as well as in the temperate zone (at an AET of 560 mm), which makes our basic assumption valid over at least two climatic zones. For our discussion, we thus use the rather new finding that climate apparently does not influence litter decomposition rates in near-humus stages and possibly not at the limit value (Fig. 6, Chapter 7) nor the limit value. Thus, the once formed humus is stable, meaning that it is not

decomposing in undisturbed systems. This has been confirmed for boreal and some temperate systems.

We discuss the scenario starting from changed properties of litter fall, thus including some aspects of changed climate on the vegetation. We use data from climate transects, keeping the type of ecosystem—in our case, Scots pine forests—constant over a range of climates. Even so, we cannot exclude that the same type of ecosystem located at different latitudes and under different climates may react as differently to a temperature increase as different ecosystems under the same climate. We present the scenario stepwise: (i) the effect of climate on litter chemical composition, and (ii) the effect of a changed chemical composition on the limit value and thus on the size of the recalcitrant remains.

3. Litter Chemical Composition versus Climate Scenarios

The climate as such has an effect on litter chemical composition, for example, warmer and wetter climate may give higher levels of N, P, and S (Berg *et al.*, 1995) (Section VI.C–D, Chapter 2,), an effect that has been traced back to green needles for Scots pine (Oleksyn *et al.*, 2003). Changed levels of N have been observed as a general phenomenon also in transcontinental transects, encompassing large groups of broadleaf and coniferous species (Liu *et al.*, 2004) and has been related to actual evapotranspiration (AET) as a climate index (Berg and Meentemeyer, 2002). Our transect had a range in AET values ranging from about 380 mm at and north of the Arctic Circle and to approximately 600 mm, covering the range that we used in our scenario. The litter level of N at the Arctic Circle, about 3 mg g^{-1} at an AET value of approximately 380 mm, was the lowest level in our transect, and its concentrations can increase at least three times at higher AET, that is, from about 3 to 9 mg g^{-1}. Thus, a climate change with an increase in temperature and precipitation will give a litter richer in N, P, and S (Berg *et al.*, 1995), which may increase initial decomposition rates but also results in a lower limit value.

4. Limit Values versus a Climate Change

We use the observation that under warmer and wetter climate (i.e., at higher AET), the N concentration increases in foliar litter, which results in a higher fraction of recalcitrant organic matter. We continue using the climate scenario previously mentioned (Berg and Meentemeyer, 2002) and focus our discussion on a Scots pine transect from the Arctic Circle in Scandinavia to the northern part of the European continent. The temperature range in this transect well covers the range suggested for the climate scenario.

If we accept the given relationships, suggesting that plant litter formed at sites with higher AET will have a higher N concentration, such litter would reach a lower limit value during decomposition (Fig. 16, Chapter 4), leaving more recalcitrant material. This is provided that the Mn concentration does not increase and, in fact, empirical data indicate the opposite. Combining available data on increased litter N concentrations, calculated limit values, and the climate index AET estimated for a set of sites, Berg and Meentemeyer (2002) regressed limit values for the local litter against AET, thus limit values obtained from decomposition experiments using local Scots pine needle litter at each site. The negative relationship was highly significant and indicates that within this range of AET values, the limit values fell from about 90% decomposition to less than 80%, increasing the recalcitrant fraction by a factor of two.

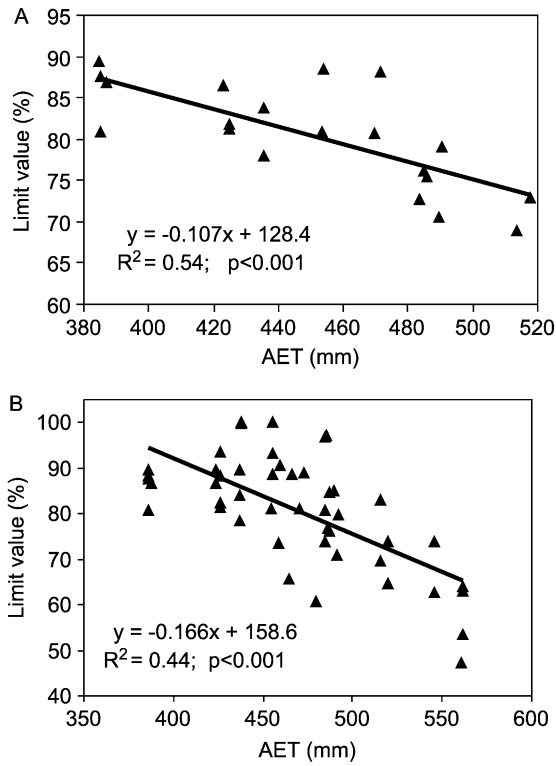

Figure 7 A relationship between limit value for litter decomposition and actual evapotranspiration (AET). The litter originated, in all cases, from the site at which decomposition was studied. (A) Scots pine litter decomposing at sites throughout Sweden. (B) Available data for foliar litter on a European basis, including Scots pine, lodgepole pine, Norway spruce, silver birch, silver fir, and common beech. From Berg and Meentemeyer (2002).

We apply an increase in AET of 27% in the Baltic basin (see previous text) to the functions based on Scots pine data (Fig. 7A). The graphs are based on decomposition of local litter from trees grown under different AET, thus shedding litter with naturally different N levels, which then produces different limit values. The graph of AET versus limit values shows the resulting effect of raised N levels, causing a lower limit value for decomposition.

For our comparison, we use the AET value of 470 mm for a given site, at which the AET would be 588 mm after the assumed climate change. In order to compare the effect of just a changed substrate quality on humus accumulation, we used, in a first step, the arbitrary value for litter fall of 2000 kg ha^{-1} for both climate situations. Such an assumption is not entirely correct since a changed climate would also result in a higher litterfall. For Scots pine, an increased AET (Fig. 7A) gives an increase in needle litter N and the limit value decreases from 79.1 to 68% (Table 2), which means that the annual humus accumulation will increase from 416 to 640 kg ha^{-1}, namely, a bit more than 50% (Table 2). A climate change may lead to a change in tree species and, if we instead use the function (Fig. 7B) for all available data covering several tree species, the annual increase would be about 100%. This leaves us with the estimate for Scots pine as a lower estimate.

In the forest, this would not lead to any drastic change to the eye. An example, in a period of 112 years, the accumulated humus at a Scots pine site was 15,400 kg ha^{-1} (Section VI.B, Chapter 6), giving a humus layer of about 6 cm thickness. A scenario based on the Scots pine data (Fig. 7A) would increase the humus accumulation rate by 54% and, if we transfer the effects of a higher humus accumulation over a 112-year period, the result would have been a humus layer of about 10 cm and an amount of about 23,000 kg humus per hectare.

As regards an increased litter fall, we may speculate about its magnitude. Even if the climate becomes less limiting for tree growth rate and litter fall, other factors, such as available nutrients, may become limiting. Thus, when using the climate scenario and including Scots pine needle litter fall, we give a potential effect. An increased litter fall would result in an increase in litter fall of about 80%. Multiplying with the higher fraction remaining gives an annual sequestration of 1150 kg ha^{-1} yr^{-1} to be compared to 416 kg ha^{-1} today and to 640 kg ha^{-1} if we do not consider the increase in litter fall. This is, of course, a potential increase since tree growth rate and litter fall may be limited by other factors, as has been mentioned.

5. *Are There Climate-Change Effects in a Labile Fraction of the SOM?*

Predicting the actual effect of global warming on decomposition of litter and soil organic matter is complicated by the fact that different fractions in the

Table 2 An estimate of potential annual increase in humus layers (relative increase) using functions based on Scots pine data only and all available data[a]

AET (mm)	Limit value (%)	SOM accumulated (kg ha^{-1} yr^{-1})	Relative increase (%)
Scots pine data			
470	79.1	416	
588	68.0	640	54
All available data			
470	79.4	412	
588	58.1	838	100

[a]For this comparison, which illustrates the effect of a changed substrate quality, we used an example of a site with AET of 470 mm which, after a climate change, increased to 588 mm and a constant annual litterfall of 2000 kg ha^{-1}. From Berg and Meentemeyer (2002).

stored humus may vary and similar fractions may have different properties when the ecosystem varies. To overcome some of these problems, we prefer to use a study from a climatic transect of Scots pine, which also allows a certain comparison to the litterbag studies.

Still, respiration from humus samples from the same type of Scots pine ecosystem but at different latitudes may react differently to temperature increase. An example is measurements of respiration rates from humus samples from seven Scots pine stands located along a climatic transect across the European continent from the Pyrenees mountains in Spain (42°40′) to northern Sweden (66°08′) (transect No. III, Chapter 7). In that study, the average temperatures for the growing season ranged from about 8 to 18°C. The effect of temperature on respiration rate was investigated in the temperature range from 5 to 25°C (Niklińska *et al.*, 1999), thus covering our scenario well. The average Q_{10} values for the respiration rate ranged from about 1.0 at the highest temperatures to more than 5 at 10 to 15°C in the northernmost samples, exhibiting not only large differences between different temperature ranges but also among samples originating from sites located at different latitudes (see Section IV.C, Chapter 7). As we have mentioned, the respiration rate from a labile fraction may be up to 1000 times higher than that from the intermediate or resistant fraction (Table 10, Chapter 4). At the same time, in a scenario based on a Scots pine transect, we may consider the fractions of the pools of labile material (<5%), intermediate (<20%), and recalcitrant material (70–90%) in far-decomposed litter and humus. Thus, the labile, alternatively labile plus intermediate fractions represent a small to relatively small fraction of the humus and an increase in respiration rate may represent a limited fraction.

Applying the scenario suggested previously increased the respiration rates for Scandinavia and the Baltic basin considerably, in general, by 50 to 90%

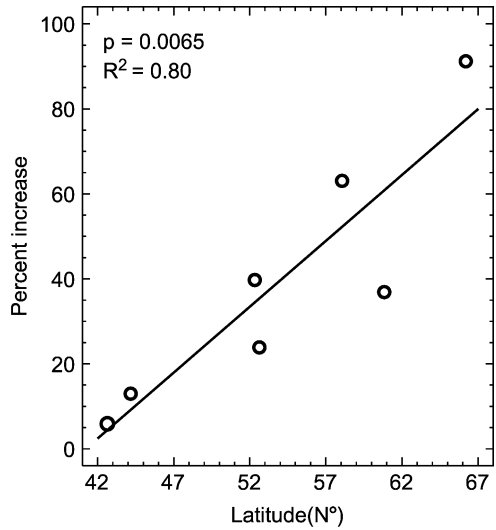

Figure 8 A relationship between latitude and the estimated increase in soil microbial respiration rate due to a 2°C increase in temperature over Europe. Note that due to different average temperatures at different latitudes as well as different sensitivity of decomposing microorganisms originating from different latitudes to temperature increase, the predicted increase in respiration rate is not uniform in the transect and is highest at the highest latitudes. From Niklińska *et al.* (1999).

(Fig. 8). If this respiration rate represents labile material only, we expect that such a fraction in the humus may be smaller after a temperature increase. On the other hand, with a microflora that slowly adapts to a higher temperature, the effect may be reduced. Considering the size of this labile fraction though, we may consider that an increase in decomposition rate of the labile fraction will have less direct effects on the carbon balance.

E. Changes in Water Regimen

Among different anthropogenic influences on soil/humus subsystems and organic matter decomposition, pollution effects have been studied extensively. Still, due to the high sensitivity of the decomposition rate to humus and litter moisture, changes in water regimen may be also of high importance. For the last hundred years, profound changes in water regimen have been made in a number of ecosystems due to, for example, ditching of forest systems or mining, thus sinking the water table. Such activities lead to sinking groundwater level and—as a consequence—decreasing surface soil and litter moisture. Unfortunately, such phenomena, occurring in heavily industrialized regions, are usually accompanied by significant pollution, with

toxic chemicals making it difficult to separate effects of decreased moisture and pollution on litter decomposition rate. As the global warming, discussed previously, is predicted to be linked with an increase in precipitation during the growing season, it may also affect litter decomposition through changes in soil moisture (see the previous paragraph).

Unfortunately, although litter decomposition is highly sensitive to moisture, the direct effects of changes in water regimen are little known. We predict, though, that with an increased precipitation, there is a potential for a higher initial mass loss rate for litter, unless temperature or nutrients would be limiting. Still, the effects may be different at late stages of decomposition.

Methods in Studies of Organic Matter Decay

I. INTRODUCTORY COMMENTS

Although the book has been devoted so far solely to litter decomposition processes, described mostly using case studies from boreal forests, we recognize that the reader may require some insight into methods used more broadly in soil biology. Thus, in this last chapter, we present an overview of a range of field and laboratory methods to study decomposition. Since the book is addressed mainly to students and younger scientists, we also discuss briefly some methods of data analysis and presentation in the latter part of the chapter. They all represent more general techniques and conventions used in data handling and we discuss advantages and disadvantages of using particular models and methods rather than giving detailed formulas for calculating statistics, which may be found in relevant textbooks. Our impression from many years of teaching at the university level is, however, that it is easy to get lost in the plethora of statistical methods and ways to present data graphically, and we hope that this short guide is helpful.

As decomposition of organic matter is a set of most complex biological, physical, and chemical processes, a broad range of research techniques and tools is required to study it. Depending on the research problem, techniques

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may be needed to expose plant litter in the field or to apply atomic absorption spectrometry (AAS), nuclear magnetic resonance (NMR), chromatography, or isotopic analyses. Some of these methods are fields of studies in themselves and it would be impossible to cover them all in detail in this book. Our intention is to present in detail those methods that are used solely in decomposition studies, and to mention briefly some more general techniques to make the reader familiar with other possibilities and what to look for when more detailed studies are required. We also try to pinpoint the pitfalls and indicate some solutions that pertain especially to the studies of organic matter decomposition. Thus, this chapter can be used as a reference for specific litter decomposition techniques; however, for more general methods, specialized handbooks will be indispensable.

Generally, research techniques might be divided between *in situ* and *laboratory* methods. However, a number of methods can be used equally well, with only minor modifications, both in the field and in a laboratory, although the interpretation of results may be different between laboratory and field techniques. From the point of view of research questions, we distinguish between studies on *decomposition rates and patterns* and *studies on chemical changes*, although they are frequently performed in parallel. One might also differentiate between *direct* and *indirect* methods. An example of the first group would be studies with litter bags, while the latter could be represented by, say, calculation of decomposition rates from litter fall/organic matter accumulation balance. There is probably no single good classification of the research techniques used in decomposition studies. For the purpose of this book, we decided to describe the methods grouped into two major classes, with studies on *decomposition rates, patterns, and chemical changes* in one group and *analytical techniques* in another. The first category contains detailed descriptions of a number of *in situ* (field) and laboratory methods. Analytical techniques will be presented in a general guideline to assist the researcher in choosing the most appropriate tools for specific studies and avoiding common problems. Finally, we present a brief overview of mathematical decomposition models and some useful statistical methods.

II. INCUBATION TECHNIQUES

A. *In Situ* (Field) Methods

1. General Comments

Standard field methods include incubation of plant litter using the "litter-bag" technique and microcosms. The rate of organic matter degradation can also be measured as the amount of organic carbon mineralized and evolved

from soil as carbon dioxide (respirometry). Other methods may also include the use of isotopes such as ^{13}C, ^{14}C, and ^{15}N, often labeling specific molecules. Depending on the problems to be studied, different methods are preferred. For example, the classical litter-bag technique is the method of choice when the decomposition rates and patterns of different plant species are to be compared and when chemical changes are studied. To measure the maximal extent of litter decomposition or the potential accumulation of resistant material, an important point is to follow the decomposition for as long as possible.

The litter bag technique does not allow for estimating total release of carbon from organic matter or humus of the forest floor. Thus, if this is the study subject, the respirometric techniques would be preferred. Regular respirometry, in turn, does not allow us to distinguish between the CO_2 originating from dead organic matter and that evolved by roots and mycorrhiza—in this case, isotope labeling, for example, using ^{14}C, may be of use.

The aim of this section is to provide help in choosing the most suitable methods for field studies of particular decomposition processes.

2. *Litter-Bags*

This is one of the most commonly used field techniques. Despite its relative simplicity, it is a very powerful method indeed, allowing us to address a wide range of problems connected with plant litter decomposition. It is also frequently used as a first, indispensable step in more detailed studies—for example, on dynamics of organic compounds and chemical elements during litter decomposition (see Chapters 4 and 5). Because of the abundance of directly *in situ* measured data which may be gathered using this method, it has become a sort of standard in decomposition studies: a quick search through the database of the Institute of Scientific Information for "litter-bag" resulted in 198 articles published in the 9 years from 1996 through 2004, and these include only the articles in which the term occurred in the title, in the abstract, or as a keyword.

Essentially, a litter-bag is exactly what the word says—a bag containing some plant litter. Such a bag is filled with weighed dry litter, exposed to field conditions for a specific time period, brought back to the laboratory and—after cleaning from contamination with ingrown roots, small soil invertebrates, or mineral particles—the remaining contents are dried and weighed. This allows us to calculate the rate and follow the pattern of one of the most crucial ecosystem processes—the decay of dead organic matter. Thus, important information about an ecosystem can be obtained with that simple method. This determination of mass loss is a first step

in a study but the basic one since it allows us also to quantify the dynamics of the litter chemical components.

Although incubation of litter in litter-bags is a simple method, it still requires good and detailed planning for each single study. There are no general rules regarding the litter-bag size, mesh type, or material from which it is made. In practice, a typical litter-bag measures from 10 × 10 cm to 20 × 20 cm and is made of flexible but biologically resistant polyester net. Nylon is an alternative, but since nylon contains nitrogen, we cannot exclude that this material is suboptimal in many studies, for example, if litter nitrogen should be studied. The mesh size should be adjusted depending on type of litter and the aim of studies; for example, by using different mesh sizes, one can exclude particular groups of soil invertebrates from degradation processes. However, the size of the litter is the main factor that determines the mesh size. For needles of spruce or larch, a fine mesh size is required, 0.5 mm or less. With leaf litter of broadleaf species, larger mesh sizes can be used. Still, litter of several deciduous species is fragmented in the late decomposition stage and, in order to prevent such fragments being lost, a fine mesh size may be needed. Most frequently, a mesh size of approximately 0.5 to 1 mm is used. This allows a number of small invertebrates that are active in organic matter degradation (micro- and mesofauna) to participate in the process, at the same time excluding most of the macrofauna, such as worms, which might drag large parts of litter from the bag.

A litter-bag usually contains a small amount of dry litter—approximately 1 to 10 g, depending on the study's needs. Larger amounts in a small bag are not advisable since they make the bags pillowlike so that they do not adhere to soil surfaces correctly. A bag should be stitched firmly with a thread made from polyester or nylon but not a natural material such as cotton, which would decompose rather quickly. To account for possible losses during transportation, etc., it is advisable to pack each litter bag in a separate envelope. This allows us to retrieve any small parts of leaves that may have fallen from a bag. In some cases, for example, spruce needles, the lost parts can be even returned to the litter bag without reopening it.

Preparing litter for litter-bag incubation is a compromise between weighing accuracy and retaining the litter in a natural stage. The accurate estimation of mass loss—that is, the main aim of the study—is possible only if weighing errors are minimized and this is achieved in most studies other than on litter decomposition by simply weighing the material that is dried to constant mass at 105°C. Unfortunately, drying litter at that high temperature results in the loss of its microbial communities. In addition, the fiber structures change and several volatile compounds, such as terpenes, may be lost, leading to a mass loss not due to decomposition. The changed and collapsed fiber structures and the loss of some chemical compounds may delay and change the colonization of the litter with new microflora and affect

the decomposition rate and pattern. As a consequence, litter must never be dried at high temperatures before the field incubation.

In practice, this tradeoff between weighing accuracy and retaining original litter structure and microflora is usually resolved by drying litter at room temperature. Only a few subsamples are dried at higher temperature and they are used only to calculate the correction factor for recalculating room-temperature dried mass to "water-free" dry mass. However, as has been mentioned, at high temperatures, some volatile compounds may evaporate, thus underestimating the real litter weight. Consequently, we recommend that litter is dried at room temperature to an even moisture level. This is usually reached within 2 to 4 weeks. Subsamples should be dried at temperature in the range of 75 to 85°C, a range in which most volatile organic compounds normally would not disappear. The temperature used for drying should be the same both before and after the incubation. Note that the concept of a volatile compound is a relative one. Some litter types, such as eucalypt leaves, may release volatile compounds at our recommended temperature or even below, and it is simply impossible to give generally valid recommendations.

In litter-bag experiments, large numbers of bags need to be handled and, considering the time needed for each study, the basic necessary information must be given and stored in a way that makes it still available when a shift in personnel takes place. We suggest two alternative ways of organizing the litter-bags and the information. In a first approach, the litter for each litter-bag is weighed individually, the weight is stamped on a piece of plastic tape (such as, Dymo tape) together with a simple code for the litter moisture. Different tape colors allow for differentiation between, for example, litter types, soil treatment, and ecosystem type. With this approach, each bag contains all the essential information needed for identifying the bag and calculating the mass loss. The Dymo tape may follow each litter sample through the handling process after sampling the incubated bags, for example, during the drying process. The printed numbers are still readable after drying at 85°C.

Another approach is to assign a separate number typed on plastic tape to each litter-bag or to simply put the tape inside the bag together with the litter. Due to the numbering, in addition to the exact weight of a bag, other, even extensive, information can be recorded for each bag, such as, say, the tree species from which the litter originates, site names if litters from different ecosystems are incubated at one stand, placement of the litter-bag in a forest, or different litter treatments if such are used.

When brought to a laboratory, each bag is opened and its contents carefully cleaned from any ingrown material, such as roots, grass, moss, or mineral contamination and invertebrates. The cleaned litter is oven-dried until constant mass. Usually 24 hours of drying is sufficient. In a final step,

the mass loss for the incubation time is calculated. It should be noted, however, that cleaning from finer mineral particles cannot always be done using just a visual inspection. Contamination of litter with, for example, clay particles may result in serious underestimation of the decomposition rate because of the higher measured weight of the incubated litter than the actual weight of remaining organic material. Thus, analysis for ash content may be necessary (see the following text).

The number of replicate bags is important for the accuracy of the estimated mass-loss value. Under most circumstances, around 20 replicate bags give a standard error of less than 1.0 of the average at 50% mass loss, and 100 replicates do not improve the accuracy. One of the most common mistakes seen in decomposition studies is too low a number of replicates: numbers lower than 15 replicates should be avoided.

The incubation time and sampling schedule will differ, depending on the aim of the study and the precision required. For a comparison of two or more different ecosystems as regards initial litter decomposition rates (the early stage), a few samplings may suffice. How these are distributed in time must be related to the site's climate and the litter type. As an example: in a subarctic Scots pine forest with an annual mass loss of approximately 10%, two or three years may be needed to obtain a mass loss covering the early decomposition stage, which may encompass 25 to 30% accumulated mass loss. In a temperate climate where the first-year mass loss is maybe 40 to 50%, such a comparison may take just a few months. The litter species and its chemical composition may be important, too. At a given forest stand in temperate and boreal zones, the mass loss may range from 10 to 50% in a year, depending on litter species and its chemical composition. We have given some comparative values for first-year decomposition of Scots pine needle litter over a climatic transect ranging from a subarctic to a subtropical pine forest (Table 1). The incubated pine needles were a standardized preparation from one stand and chemically very similar. The mass-loss values are given, together with annual average temperature and precipitation. As litter mass loss varies a great deal among litter types and with specific local conditions, a table like this may be used as a planning guide for decomposition studies of a limited number of litter types, preferably pine species.

For more detailed studies, several litter samplings per year and longer incubation times may be necessary. This allows for better description of decomposition patterns as well as a more precise calculation of kinetic parameters. Furthermore, it allows the inclusion of climatic events in the model, such as differences in decomposition rates between seasons or effects of extreme weather conditions. A high number of samplings also makes it possible to follow the chemical changes during decomposition (Chapter 4 and the following text). Also, the dynamics of microbial or microinvertebrate succession during the decomposition can be studied that way. The

Table 1 List of sites with pine forest where unified Scots pine needle litter has been incubated[a]

Site name	Site no.	Lat/long	Altitude (m)	Ann. mean precip. (mm)	Ann. mean temp. (°C)	AET (mm)	1st year m.l. (%)	Pine species
Climates with a maritime influence								
Subarctic and boreal climate								
Kevo	1	69°45′N 27°01′E	90	443	−1.7	350	12.9	Scots pine
Harads	2	66°08′N 20°53′E	58	470	0.6	387	16.1	Scots pine
Manjärv	3:1	65°47′N 20°37′E	135	516	0.2	385	17.9	Scots pine
Kajaani	318	64°23′N 28°09′E	180	564	1.9	422	25.7	Scots pine
Norrliden	4:23	64°21′N 19°46′E	260	595	1.2	407	24.7	Scots pine
Granö	26	64°19′N 19°02′E	300	527	1.5	412	27.6	Scots pine
Ilomantsi	320	62°47′N 30°58′E	145	600	2.0	440	25.8	Scots pine
Jädraås	6:51	60°49′N 16°01′E	185	609	3.8	472	27.5	Scots pine
Brattforsheden	7	59°38′N 14°58′E	178	850	5.2	493	25.0	Scots pine
Temperate climate								
Nennesmo	8	58°16′N 13°35′E	155	930	6.2	509	34.5	Scots pine
Målilla	9	57°25′N 15°40′E	105	670	6.2	495	33.4	Scots pine
Mästocka	10:1	56°36′N 13°15′E	135	1070	6.8	519	37.1	Scots pine
Vomb	12	55°39′N 13°19′E	46	770	7.0	525	39.9	Scots pine

(*continued*)

Table 1 (*continued*)

Site name	Site no.	Lat/long	Altitude (m)	Ann. mean precip. (mm)	Ann. mean temp. (°C)	AET (mm)	1st year m.l. (%)	Pine species
Roggebotzand	300	52°34′N 05°47′E	−3	826	10.3	624	49.2	Austrian pine
Ehrhorn	13	53°00′N 09°57′E	81	730	9.0	559	36.3	Scots pine
Ede	14	52°02′N 05°42′E	45	765	9.3	616	45.7	Scots pine
La Gileppe	302	50°34′N 05°59′E	370	1200	6.9	566	37.3	Scots pine
Bois de la Commanderie	303	48°17′N 02°41′E	83	677	11.0	610	43.0	Scots pine
Capelada	305	43°40′N 07°58′W	500	1062	12.9	654	47.9	Monterey pine
Aguas Santas	306	42°44′N 08°45′W	450	1500	12.5	645	42.8	Maritime pine
Furadouro	308:1	43°58′N 09°15′W	80	607	15.2	596	41.9	Maritime pine
Furadouro	308:2	43°58′N 09°15′W	80	607	15.2	596	43.9	Mixed pine forest[b]
Inland climates and climate with long, dry summers								
Temperate climate								
Czerlonka	23	52°41′N 23°47′E	165	594	5.7	545	28.6	Scots pine
Mierzwice	24	52°20′N 22°59′E	142	569	7.2	538	25.6	Scots pine
Pińczów	25	50°31′N 20°38′E	191	689	7.6	585	25.8	Scots pine
Ołobok	28	52°22′N 14°36′E	60	604	8.1	549	27.3	Scots pine

Wilków	22	52°24′N 20°33′E	74	500	7.8	529	25.0	Scots pine
Mohican	401	40°36′N 82°17′W	390	970	10.3	645	39.3	Red pine
Blue Rock	402	39°36′N 81°51′W	275	990	11.9	686	36.3	Red pine
Ball's	403	40°41′N 81°18′W	300	960	9.7	633	22.5	Red pine
Mediterranean climate								
La Viale	304	44°11′N 03°24′E	920	793	8.2	565	23.8	Scots pine
Alberese	309	42°40′N 11°10′E	4	650	15.0	588	20.4	Stone pine
El Raso	307:1	41°47′N 05°26′W	760	402	12.4	396	19.8	Maritime pine
El Raso	307:2	41°47′N 05°26′W	760	402	12.4	396	19.0	Stone pine
Terzigno	310	40°49′N 14°28′E	250	960	13.2	635	27.5	Stone pine
Golia Forest	311	39°24′N 16°34′E	1210	1225	9.0	484	21.0	Corsican pine
Doñana	29	37°07′N 06°12′W	2	557	16.6	554	19.3	Stone pine
Subtropical climate								
Athens	16	33°53′N 83°22′W	207	1049	16.5	827	36.3	Loblolly pine
Tifton	15:2	31°28′N 83°32′W	101	1540	19.3	958	56.1	Loblolly pine

[a]The sites are divided into those with climate with maritime influence and those with dry and warm summers. Within each group, sites are listed according to latitude. The aim is to give approximate mass-losses for the first year of incubation and the information may be used to plan sampling schedules. Please note that almost all stands here were growing on granite sand. Calcium-rich ground may change the decomposition rates completely. The composition of the litter corresponds to the average value given in Table 10, Chapter 2. Data are, in part, unpublished and, in part, taken from Berg *et al.* (1993).

[b]50% Monterey pine, 50% Maritime pine.

sampling interval will differ depending on site climate, the decomposing material, for example, leaves of different species, bark, or cones, ecosystem type, and research problem. In general, more frequent samplings are necessary in wet and warm climates and for litter species that have a fast decomposition in the early stage. It is difficult to give more exact advice on sampling schedules for different litter species. Some deciduous leaf litter, such as alder, aspen, and birch leaves, have high early-stage mass loss rates that require more frequent samplings. We avoid general recommendations since it has been shown that leaves of a single species, say, beech leaves, may decompose at very different rates and with different patterns due to factors that still are not well explained. A typical sampling schedule in, for example, temperate pine forests would be ended within three years since the litter normally would be decomposed far enough in that period to allow fragments to fall out of the litter bag, which often takes place at a decomposition of above about 60% accumulated mass loss. The total number of samplings also depends on the information that is needed. Often, the chemical changes in decomposing organic materials are faster at the beginning of the process and become slower as the decomposition proceeds—which may lead to a higher sampling frequency in the first year. This normally allows for estimation of the dynamics of most chemical elements and organic compounds. If the decomposition pattern of a litter species not studied earlier is to be determined, at least 12 to 15 samplings will be necessary, with some more intense samplings to cover the early stage. If temporal climatic effects are to be included, more evenly scattered sampling would be better, for example, every one to three months.

Depending on the problem studied, litter-bags may contain either leaves of a single species or a mixture of different dead litter materials. The first type would be used, for example, in studies where decomposition of different materials, such as foliar litter of different plant species, is investigated. Single-species bags are also used sometimes for "standard" litter material for comparing decomposition rates or patterns in two or more ecosystems. They may be used also in experimental studies aiming at studying effects of different soil or ecosystem-level manipulations on the decomposition. Single-species bags usually offer less variable data than mixed-species bags because at least one source of variability—the composition of litter itself—is greatly reduced. Thus, one litter species is often preferred, especially for studies where only minor differences between ecosystems or treatments are expected. Also for making basic, descriptive studies of the kinetics or chemical changes of a given litter type during decomposition, bags with a single litter species are preferred. Despite these advantages, litter-bags with single litter species do not always represent the decomposition process of a particular ecosystem as well as is desirable. In monocultural forests or monocultural plant communities, this may be less of a problem. However,

in most ecosystems, the natural litter composition is by far more complicated and variable, and these circumstances have to be taken into account when the aim of the study is to assess the real decomposition rate or pattern for a particular ecosystem. In such studies, mixed litters are often used.

3. The First-Order Kinetics Function as Applied to Litter Decomposition

The mass loss can be evaluated using a set of different models and before using a specific model, it is necessary to assure that the decomposition pattern for the litter type in the particular ecosystem can be described adequately by the selected model. Most commonly used is the one-compartment exponential model, first used for describing litter decomposition by Jenny *et al.* (1949) but often ascribed to Olson (1963). Assuming the exponential decomposition model (see Chapter 4, Eqs. 1 and 2), having just one sampling date after t years of incubation allows us to calculate a decomposition constant k from the formula:

$$k = \frac{\ln \frac{W_t}{W_0}}{t} \tag{1}$$

where W_t is dry litter mass remaining after time t, (years) and W_0 is the initial dry mass of litter at the onset of the incubation. For a one-year incubation ($t = 1$), this simplifies to $k = \ln(W_t / W_0)$. In fact, only a few litter types have been found for which decomposition is well described by this model. Especially when litter decomposition is followed until high accumulated mass losses, this function normally does not describe the process well (see the critique in the following text and Chapter 4, Eq. 3). Although widely used due to its simplicity and description of the general trend, the model is a serious oversimplification of the complicated decomposition process. It is no more than the simplest empirical equation, which can be fitted to most data describing any simple degradation process.

4. The Double Exponential Model as Applied to Litter Decomposition

The decay of radioactive elements or decomposition of a number of organic molecules, such as sugars and pesticides, can be described precisely with the one-compartment model. However, applying it to litter decomposition neglects the fact that natural dead organic matter is an extremely complicated mixture of substrates, differing vastly in their degradability and, consequently, in decomposition rates. As we have described in earlier chapters, litter

contains such easily degradable substrates as simple sugars and other water-soluble organic compounds as well as chemical compounds that are very resistant to decomposition, the prime example being lignin in foliar litter. These two groups of compounds decompose at very different rates and the actual litter decomposition rate depends on the current proportions between such groups. Thus, the decomposition of each group should be described with a different equation, and the final outcome will depend not only on the initial proportions among the main substrate groups in the decomposing organic matter but also on changes in these proportions in the course of decomposition.

We assume, for the sake of simplicity, that litter consists of two major groups of substrates: those easily degradable and those resistant to decomposition. To describe the decay of such a mixture, we should not use a simple one-compartment exponential function but rather a two-compartment model, in which each compartment describes the decay rate of a different substrate group:

$$W_t = W_{0,1}e^{k1t} + W_{0,2}e^{k2t} \tag{2}$$

where $k1$ and $k2$ are the rate constants for easily degradable and resistant substrates, respectively, and $W_{0,1}$ and $W_{0,2}$ are initial amounts of these two groups of substrates in litter at $t = 0$. Thus, instead of one decomposition rate constant, we have two, each describing the decay of a different part of the organic matter. As we showed in earlier chapters, this is exactly what happens during decomposition: the easily degradable chemical compounds are quickly decomposed in the initial phase and the degradation of more resistant substrates starts to dominate the decay process when a substantial mass loss of easily degradable substrates has taken place. The more significant the distinction between the easily degradable and resistant substrates in a particular litter is, the more the process deviates more from simple first-order kinetics.

We know that, for example, a high nitrogen concentration promotes the development of more resistant organic matter, and may thus expect that the Olson model (Eqs. 1 and 2, Chapter 4) may fit relatively well to nitrogen-poor litter species, while for nitrogen-rich ones, the two-compartment model should be generally better. We will illustrate this with an example from studies on the effect of nitrogen fertilization on decomposition of Scots pine needles. The experiment covered several fertilization regimens, resulting in needle litter of different N concentrations, with the extreme litter type being green N-rich needles, and we will show data from the most N-poor and the most N-rich needles with 4 and 15.1 mg N per gram, respectively. As can be seen from Fig. 1, for the most N-poor needles from a control plot, the simple one-compartment exponential equation describes the litter

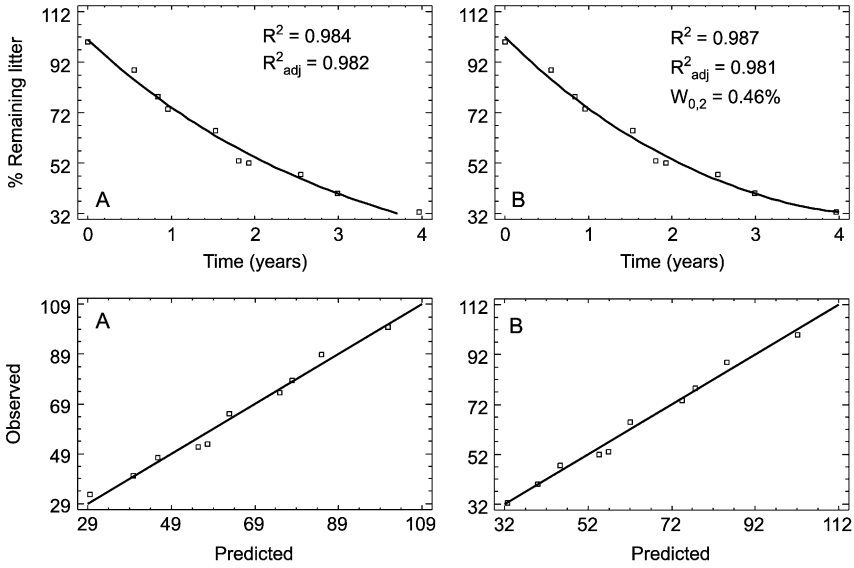

Figure 1 Comparison of the simple one-compartment (Olson's) model (A) and two-compartment model (B) for decomposition of a litter with low initial nitrogen concentration. Note the negligible difference between the models' fit and very low estimated content of the resistant compartment ($W_{0,2}$). See text for more details.

decomposition satisfactorily: the model fits the actual data well ($R^2 = 0.984$, Fig. 1A), and an additional compartment does not improve the fit significantly ($R^2 = 0.987$, Fig. 1A). In fact, the R^2 adjusted for the degrees of freedom, which is more appropriate for comparisons between models with different numbers of parameters, decreases from 0.982 to 0.981 after adding the second compartment (Fig. 1B). Thus, almost exactly the same proportion of the total variance is explained by both the one-compartment and the two-compartment models. At the same time, the model-estimated proportion of resistant materials ($W_{0,2}$) was as low as 0.46% (not significantly different from 0) so it is not surprising that the second compartment did not have any major effect on the decomposition process.

Although the one-compartment model still describes the general decomposition trend for nitrogen-rich litter pretty well (Fig. 2A) ($R^2_{adj} = 0.95$), there are clear deviations from a perfect fit in this case. In the early decomposition stage, the model-predicted values are consistently lower than the observed ones, while in later stages, the opposite occurs (Fig. 2A). Adding a second compartment significantly improves the fit: the R^2_{adj} increases to 0.994 and the plot of observed versus predicted values shows a perfect fit throughout the decomposition period covered by the studies (Fig. 2B). In

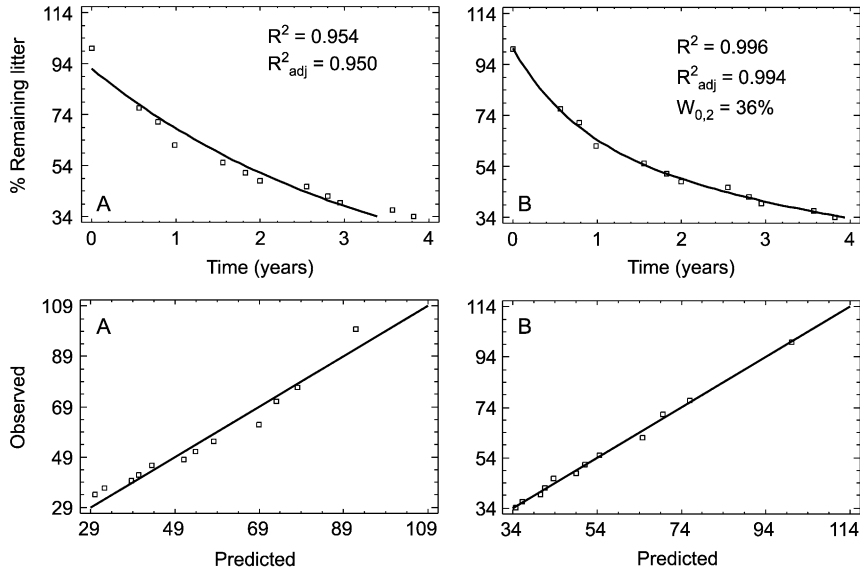

Figure 2 Comparison of the simple one-compartment (Olson's) model (A) and the two-compartment model (B) for decomposition of a litter with high initial nitrogen concentration. Note that including the second compartment improves the fit significantly (compare the R^2 values and the "predicted versus observed" plots, where a clear trend in residuals is visible for the one-compartment model) and that the estimated content of resistant compartment ($W_{0,2}$) is as high as 36%.

contrast to the nitrogen-poor litter, in this case, the estimated proportion of resistant material is significant and amounts to 36%.

An important advantage of the two-compartment model over the simple exponential equation is not just the fact that it fits to the data better, but that it offers more in-depth insight into the decomposition process. Thus, it has a deeper meaning and a better theoretical background since it recognizes different pools of substrates in decomposing litter and it even allows us to estimate the proportion of these two groups if that information is not available from chemical analyses. If necessary, the model can be modified to include more than two different groups of substrates, as was done by Couteaux *et al.* (1998), who used a three-compartment model. Also, a compartment with an asymptote, as described in chapter 4, can be added to test if decomposition reaches 100%.

5. Microcosms

The term "microcosm" is generally used in ecology for any small enclosure containing a small "sample of the real world," such as, a bottle of pond water with algae or—as in our case—a sample of litter with bacteria, fungi,

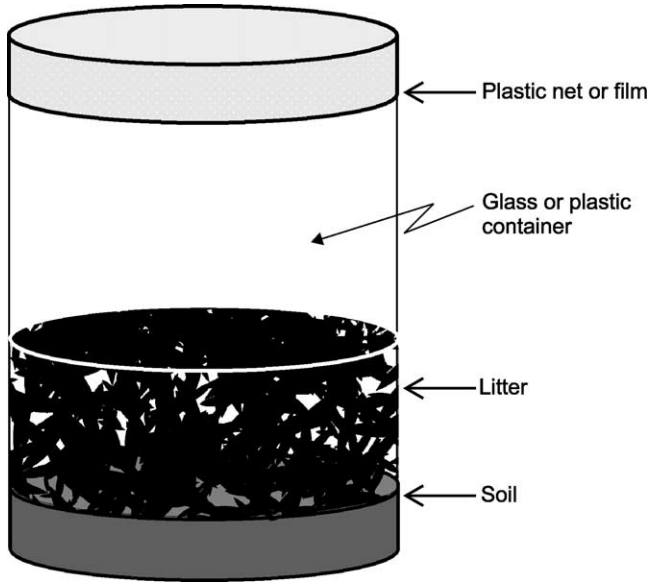

Figure 3 A type of microcosm used in litter decomposition studies. Microcosms may be filled with soil and/or plant litter and used for, say, studies on the effect of soil fauna on decomposition.

and invertebrates naturally inhabiting the soil/litter system. In practice, litter-bags are also microcosms since they contain whole microbial communities together with their environment. Still, the term microcosm in decomposition studies usually refers to a larger container with litter, sometimes with one or two intact layers of the soil profile, covered with a polyester or nylon net from two sides (Fig. 3). Thus, it is rather a matter of design, creating a larger space than in a litter-bag. By varying the mesh size of the net closing the microcosm, different groups of soil invertebrates can be excluded from entering it. When local litter is used in microcosms, they can be used—similarly as with litter-bags—for estimating actual decomposition rates and decomposition patterns.

Microcosms are preferred to litter-bags mostly by soil biologists interested in more detailed studies on effects of soil/litter fauna on decomposition. In such studies, they are used as small enclosures in which specific sets of soil/litter invertebrates are assembled, while immigration from outside is restricted by a dense net. Because the microcosms may contain a section of the whole soil profile, not just litter, they are also used in studies combining litter decomposition with other process studies, such as leaching of chemical elements from decomposing litter to lower layers of the soil profile.

Similarly to litter-bags, microcosms may be sampled at certain time intervals during the decomposition process, and the incubated material can by analyzed for its decomposition rate, chemical changes, and biological colonization.

6. *Methods Based on CO_2 Evolution*

Although the methods described above satisfy a broad range of needs for decomposition research, they are all based on mass loss from litter, without considering the form of mass loss. Both the release of CO_2 due to organic matter mineralization and the leaching of substances account for mass loss. However, the substances leached from a litter do not necessarily decompose completely at the same time as they are leached, and this fact may lead to a difference in rates of decomposition (measured as mass loss) and mineralization (CO_2 release). Further, litter incubated in litterbags or microcosms becomes contaminated with faeces of soil invertebrates, ingrown fine plant roots and mineral particles that are transported into bags or microcosms by animals and rain water. This, can lead to underestimation of the decomposition rate. We thus know that decomposition rate measurements based on litter-bags or microcosms incubation are not precise but, unfortunately, we are not able to estimate the error or even assess whether the decomposition is under or overestimated.

The precise amount of organic matter that has been indeed mineralized can be measured as CO_2 released from decomposing litter, since CO_2 is the ultimate product of mineralization of any organic compound and can be measured specifically. We may describe the difference between mass loss of plant litter and CO_2 release from the same litter so that whereas CO_2 release is a specific process giving a mineralized product, the measured mass loss is the sum of processes resulting in transformation of the litter to CO_2 and leachates. Irrespective of measurement method a recalcitrant fraction ultimately forms humus (see Chapter 6).

From the point of view of ecosystem mass balance, carbon mineralization is of prime importance as a major process for the transformation of C compounds. A prime example are the studies on global change, for which the carbon balance is a major source of concern and uncertainty. In such cases, methods other than those already described have to be used, the most important being measurement of CO_2 release from litter/soil. By measuring microbial respiration we measure the actual amount of carbon that is mineralized per time unit.

There is a range of techniques for measuring CO_2 evolution and all of them can be used both in the field and in the laboratory. In fact, most

of the methods are derived from laboratory studies, but can easily be adopted for field purposes. Traditionally, they are collectively called "respirometry" since the process of interest is respiration by organisms. Although in studies on the respiration rates of animals, usually both CO_2 production and O_2 consumption are measured, in litter decomposition studies, the latter is of less importance and rarely used.

Generally, respirometric techniques can be classified as either "closed" (static) or "flow-through" (dynamic). The first group encompasses all methods in which a sample is closed in an airtight container and the concentrations of CO_2 and/or O_2 is measured in the air sampled from the containers after a certain incubation time or by measuring CO_2 accumulated in KOH or NaOH solutions or in soda-lime. In flow-through methods, the air is pumped through the incubation chamber at a constant rate and analyzed at both the inlet and outlet. With the air flow rate known, CO_2 production is calculated from the difference in its concentration before and after the incubation chamber. Both techniques can be used in field studies, although for practical purposes, closed methods have been used much more frequently in the past. Nowadays, with miniaturization of automatic flow-through respirometers, these methods are more frequently used in field studies.

While for the closed-chamber technique only some soda-lime or KOH/NaOH and a box or a jar that can be inserted into the soil is needed, the flow-through methods require more equipment, such as air pumps, mass-flow controllers, on-line gas analyzers, and a power supply. Such portable flow-through respirometers are available on the market; however, their price is still prohibitive for studies where simultaneous, long-term measurements of many samples are necessary. In such situations, closed respirometry may be preferred.

In closed respirometry, metal or plastic cylinders are pressed into the soil, so that a small surface area is well separated from the atmosphere and the surrounding litter. In practice, this means that the cylinder must reach at least a few centimeters deep into the mineral soil. The cylinder size should be selected to fit the expected respiration rate and incubation time since too small chambers may result in too high concentrations of CO_2 and too low concentrations of O_2, which may affect the respiration of soil organisms, while too large cylinders (or too short incubation time) can make measurements difficult due to the sensitivity limits of the equipment and the method used. The CO_2 evolved can be trapped chemically (see following text) and its amount determined later in a laboratory, or the air from the cylinder can be sampled with airtight syringes and analyzed either directly in the field with a portable infrared gas analyzer (IRGA) or transported in tightly closed syringes to a laboratory for analysis with standard equipment, such as a gas chromatograph or a stationary IRGA.

The chemical absorption methods rely on the fact that CO_2 is readily absorbed by alkaline solutions and that the amount of the absorbed CO_2 can be measured gravimetrically or by titration. The most commonly used absorbents are NaOH or KOH solutions. An open beaker with hydroxide solution is placed on a small rack inside the incubation cylinder and after the selected incubation time, the beaker is transported to the laboratory. Usually, the incubation time should be at least 24 h in order to cover diurnal variation in respiration rate due to, say, variation in temperature and thus in the activity of soil organisms. In the absorption process, the CO_2 evolved by soil organisms reacts with NaOH (or, similarly, with KOH) to form Na_2CO_3:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Addition of $BaCl_2$ after finishing the incubation precipitates the absorbed CO_2 as $BaCO_3$:

$$Na_2CO_3 + BaCl_2 \rightarrow \downarrow BaCO_3 + 2NaCl$$

Finally, the excess of hydroxide (that is, the part that did not react with CO_2) is titrated with a diluted acid (usually HCl) in the presence of an indicator (e.g. phenophtalein):

$$NaOH + HCl \rightarrow NaCl + H_2O$$

Thus, the amount of CO_2 absorbed is calculated as the difference between NaOH (KOH) remaining in solution from a cylinder with soil/litter and that from an empty cylinder (blank sample). The concentration of NaOH used as a CO_2 trap should not be too high (usually about 0.1 to 1M) since at high concentrations, the rate and efficiency of CO_2 absorption decreases. The concentration of HCl should be adjusted accordingly to stoichiometry, while $BaCl_2$ should be used in excess. The amount of hydroxide should be adjusted to ensure that no more than maximum 50% is neutralized by CO_2 absorbed because above this limit the absorption efficiency decreases significantly. Also, too large amounts of NaOH (KOH) should be avoided because at very low proportion of hydroxide neutralized, differences between blank and litter samples may appear negligible. Thus, as a rule of thumb, approximately 10 to 50% neutralization can be accepted.

7. Problems with Measurements of the CO_2 Evolution in the Field

Although measurements of the CO_2 evolution from soil offer certain advantages over mass loss studies, especially for carbon budget studies, they are

not free from problems. One of the most important is the fact that CO_2 released from the soil surface is the sum of respiration by decomposers and by plant roots with mycorrhiza. While CO_2 produced by decomposer organisms can be regarded equivalent to organic matter mineralization, the part produced by live roots has nothing in common with decomposition of litter and soil organic matter and has to be subtracted from the total CO_2 evolution measured per unit area. This is a surprisingly difficult task because the actual root respiration rate is difficult to measure. A method used by scientists to estimate this part of soil CO_2 evolution comprises transferring plants with roots to a laboratory to measure the respiration of roots and remaining part of the plant separately. For obvious reasons, this methods can be used only with small plants, such as grasses or seedlings. Another method used to estimate rootfree respiration of the forest soil is to cut off all the roots beneath the respiration chamber. This method eliminates the respiration by live plants but decomposition of additional dead organic material (the cut roots) increases the heterotrophic respiration. Thus, to obtain rootfree respiration, the roots are sorted out from soil after the respiration samples have been taken, and their respiration is measured separately and subtracted from the total soil respiration.

A new approach, introduced a few years ago, is based on girdling the trees (Högberg *et al.*, 2001). Tree-girdling is done by stripping the stem bark to the depth of current xylem at breast height, which interrupts the flow of photosynthetate to the roots, and the root respiration ceases. Thus, the remaining respiration is presumably of only heterotrophic origin. Still, it is not clear how much the heterotrophic respiration is affected by the dying fine roots that start to decompose.

B. Decomposition Rate—Laboratory Methods

For specific studies, such as those on effects of selected environmental conditions on respiration rate (temperature, acidification, heavy metals, etc.), it is often convenient and efficient to perform laboratory experiments. Environmental conditions may be manipulated to some extent in field experiments, say, by soil warming and irrigation, and we can make recordings of the actual temperature and moisture. In a laboratory, however, we can control the incubation temperature and moisture, program the temperature amplitude, apply strictly controlled amount of precipitation, and manipulate its chemical composition. If we are investigating small effects of a particular environmental factor, such as moderate temperature changes or pollution, only full control over other variables can let us detect a significant influence. Under field conditions, natural environmental factors (frequently variable

during a day, a season, or a year) can mask minor effects and influences, effects which still may be significant in the long run.

Among laboratory methods, microcosms are particularly useful (Fig. 3). These consist of small containers with a sample of decomposing litter or humus, and even ordinary airtight twist-off jars can serve for this purpose. The respiration rate can be measured with the techniques described for CO_2 measurement in the field, that is, absorption in hydroxide solution, gas chromatography, or IRGA. Automated systems are available that allow for simultaneous measurements in a large number of microcosms. For example, the Micro-Oxymax respirometer (Fig. 4) by Columbus Instruments, Ohio, USA, allows for simultaneous automatic measurement of up to 80 chambers at intervals of a few hours. In the simplest configuration, the system measures CO_2 production rate but O_2 and CH_4 sensors can be added when required. For maximum sensitivity and versatility, this system utilizes a combination of the closed chamber and flow-through methods. The sample is closed in an airtight jar and a sample of air from its headspace is pumped through the sensors at preset time intervals. Because of this design, at low respiration rates, CO_2 accumulates and O_2 concentration decreases continuously during the incubation and even very low respiration rates can be measured. If the CO_2 concentration rises above or that of O_2 drops below a threshold value defined by the user, the system will refresh the air in a chamber. This allows for long-term, continuous respiration measurements.

Another example is a flow-through, single- or multiple-channel CO_2/O_2 recording system from Sable Systems International, USA. In this respirometer, the air is constantly pumped through the microcosm (incubation chamber) and analyzed by high-sensitivity CO_2 and/or O_2 sensors in real time.

The Respicond IV has been designed especially for measuring soil respiration. This is a computerized automatic respirometer made by Nordgren Innovations AB, Sweden. It works by combining KOH absorption and electrochemical methods in which the conductivity (of the KOH solutions) is measured and recalculated to give the respiration rate. The method makes use of the fact that KOH solution conductivity decreases as CO_2 is absorbed and this change, after calibration with KOH solutions with known additions of CO_3^- ions, is recalculated obtain to the amount of CO_2 absorbed. It allows for continuous measurements in up to 96 chambers. A set of sample data from Respicond IV is shown in Fig. 5.

In litter decomposition studies, real-time measurements are required only rarely (for example, in research where lag-time after substrate addition is measured) and, in all cases in which the *basal respiration rate* (see following text) is to be measured, the average daily respiration rate is quite sufficient. This can be done at almost negligible cost, using basic laboratory gear. The

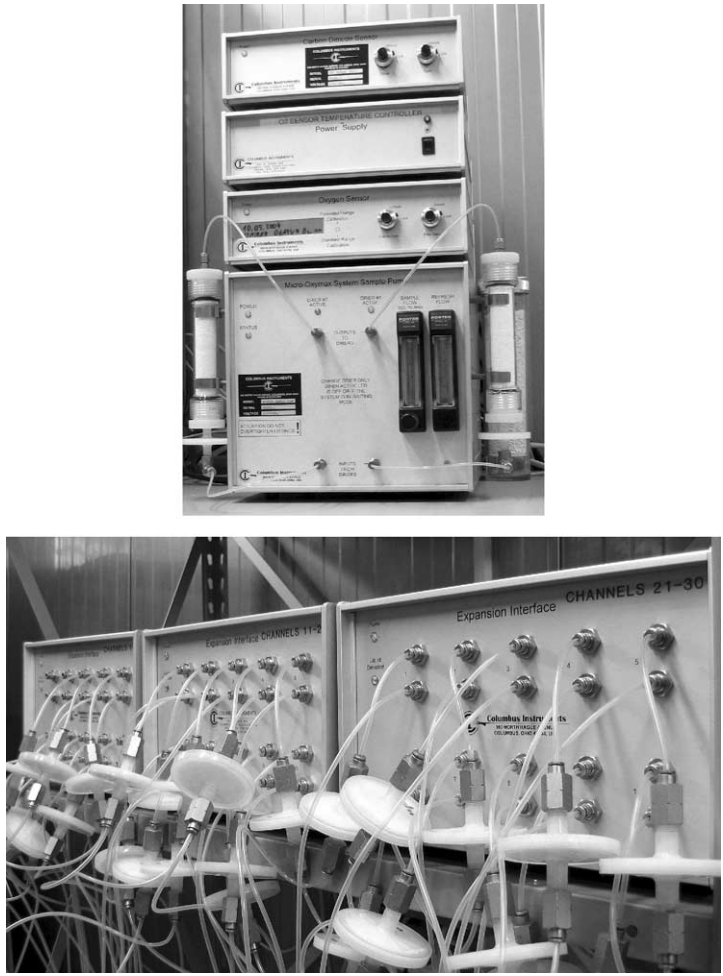

Figure 4 The Micro-Oxymax® respirometer by Columbus Instruments allows for simultaneous measurement of microbial respiration rates in up to 80 chambers.

litter is incubated in glass or plastic airtight jars together with a few ml of a hydroxide solution (Fig. 6). After the time interval required, the jars are opened and the hydroxide is titrated, as described earlier. With electronic burettes and magnetic stirrers, this can be a very accurate, efficient, and reasonably fast method, allowing for measuring of up to approximately 200 samples in one day by a single person.

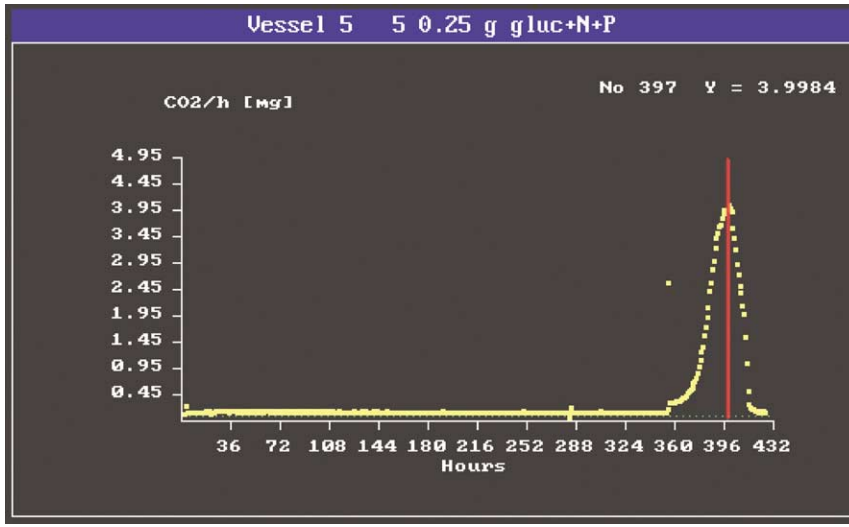

Figure 5 A sample screen shot from soil respiration measurement using the Respicond IV (Nordgren Innovations AB). The vertical line at approximately 396 hours indicates the maximal respiration rate reached after substrate + fertilizer addition (0.25 g glucose + N + P, as shown above the plot). Short intervals between consecutive measurements allow for precise determination of the maximum respiration rate (the peak) as well as the lag-time (in this case, the delay before respiration rate reached its maximum value after addition of glucose and fertilizer).

The so-called basal respiration rate is usually understood as the normal level of microbial activity, characteristic for a particular ecosystem and a specific fraction of organic matter. For example, basal respiration can be measured for the whole soil profile, the humic layer, or the leaf litter only. It measures the amount of organic carbon that is mineralized per unit time in a certain compartment of organic matter. In contrast, the *substrate-induced respiration* (SIR) which is the respiration is measured after addition of an easily degradable organic material (usually glucose), does not provide information about the normal rate of carbon mineralization but allows us to calculate the microbial biomass. The substrate-induced respiration rate can be measured with the same techniques as the basal respiration rate, for example, the CO_2 absorption in KOH or NaOH. In the Anderson and Domsch (1978) method, 100 g of field-moist soil or humus is mixed with 400 mg of glucose (preferably in solution but solid glucose is also used sometimes) and the samples are incubated in airtight jars in the same way

Figure 6 A simple closed respirometer—an airtight glass or plastic container with an organic matter sample and NaOH absorbing CO_2 evolved due to microbial respiration.

as for the basal respiration. After incubation of the glucose-amended samples for 4 hours at 22°C, the KOH (NaOH) is titrated and the microbial biomass, C_{mic}, is calculated from the empirical equation: $C_{mic} = 40.04 \times CO_2 + 0.037$, where C_{mic} is given in mg/g soil dry mass, and CO_2 evolution is measured in ml/g dry soil per hour. The SIR method assumes that the immediate increase in the respiration rate observed after adding glucose is proportional to the microbial biomass originally present in soil (humus) and accounts for active (nonsporulated) microorganisms only.

For answering specific questions, isotopes such as ^{13}C or ^{15}N can be used. The ^{13}C or ^{15}N-labeled material, for example, ground litter of plants grown in a $^{13}CO_2$-enriched atmosphere or soil with a ^{15}N-labeled N source, is allowed to decompose and the amount of ^{13}C evolved or ^{13}C or ^{15}N remaining in the samples is measured. This is a very precise method, with ^{13}C allowing for measuring general decomposition rate, and ^{15}N being very

useful in studies on nitrogen cycling in ecosystems. Both isotopes can be used in studies on effects of various natural and anthropogenic factors (such as pollution or climate change) on C and N mineralization or on storage of remaining or recalcitrant material. If the material used is the original organic matter of the ecosystem, this method can be used for calculating real rates of mineralization and C and N dynamics. For comparative studies, it is always a very powerful and accurate technique.

III. STUDYING CHEMICAL CHANGES DURING DECOMPOSITION

A. Introductory Comments

During plant litter decomposition, significant changes in the litter's chemical composition take place. As we already have discussed, part of the water-soluble organic compounds are leached out from the litter, and others are decomposed rapidly during the first weeks or months after the litter has fallen to the ground. On the other hand, resistant compounds slowing down the mineralization process of the litter and allowing visible parts of the litter to stay undecomposed for several years, and even millennia, have been recorded. Some chemical elements, such as potassium, are usually quickly leached out from litter, while others, such as nitrogen, often accumulate, at least during the earlier decomposition stages, and generally increase in concentration (Chapter 5). These chemical changes are of prime importance to ecosystem function since they determine, to a large extent, how quickly particular elements can cycle in an ecosystem, which ones are retained in soil organic matter for a prolonged time, and which ones that are lost with water percolating to deeper soil layers and finally leave the ecosystem in stream water. Like the decomposition pattern and rate, the patterns of chemical changes for a particular litter species can be affected by external factors such as climate or anthropogenic pollution.

The principal method for studying dynamics of chemical components during decomposition is the litter-bag technique. The only difference from the techniques already described is that the litter, after drying and weighing, is analyzed for concentrations of organic compounds or chemical elements of interest. As chemical changes often are particularly rapid in the initial decomposition stage, it is advantageous to design the experiment with more frequent samplings during this stage. In fact, a large part of the water-soluble components, such as simple molecules or elements such as potassium, may be leached out of the litter during the first weeks of decomposition, provided that the area is subject to enough precipitation.

B. Preparation of Samples for Chemical Analysis and Some Analytical Techniques

In this chapter, we aim to provide the reader with a brief overview of the most commonly used methods of chemical analyses, pointing to some specific problems and pitfalls when necessary. We do not intend to provide detailed descriptions of a whole range of analytical methodology for all chemical compounds and elements present in litter; for that, the reader will need to consult specialized handbooks.

The preparation of litter samples for analysis depends on what is being analyzed. A completely different sample preparation is required for the analysis of organic compounds than for analysis of mineral nutrients. Among the elements, nitrogen analysis requires a different sample preparation than do metals such as K, Ca, Mg, Zn, and Cu. Furthermore, there is no universal method that would allow us to measure concentrations of all chemical compounds or elements in the litter or SOM. As a consequence, any comprehensive research on chemical composition of decomposing litter requires good analytical knowledge and a range of laboratory equipment.

Since nitrogen is probably the most frequently studied nutrient in decomposition research, we start with analytical methodology for this chemical element. There are several methods for determining N concentration in a sample, and the most commonly used are those relying heavily on automated elemental analysis. Various analyses may work on slightly different principles but, for the end user, this is not of much importance as long as they give reliable results. For virtually all modern analyzers, sample preparation is the same. The nitrogen analyzers, frequently called CHN or CHNOS analyzers for the elements they are able to analyze, require a small sample of very finely ground material. The more finely ground the matter, the more reliable and replicable the results. In practice, high-precision planetary grinders are used for preparing samples for CHN analyzers. Small subsamples (usually in the range of 50–500 mg) of the finely ground material are enclosed in silver or aluminium cups, fed to the analyzer by automatic sampler, and burned at around 1000°C in oxygen. The resulting gas is carried through a set of absorption columns and analyzed for heat conductivity, which is strictly related to the composition of the gas obtained from the burned samples. The results are compared against calibration curves obtained with a standard material of precisely known concentrations of C, H, and N (plus O and S for CHNOS analyzers) and recalculated to concentrations of elements in the sample.

For other chemical elements, a number of techniques are used, most commonly the atomic absorption spectrometry (AAS) and inductively coupled plasma spectrometry (ICP). These two techniques may analyze most of the chemical elements of interest, such as P, S, K, Ca, Mg, Mn, Fe, Al, Pb,

Cu, Zn, and Cd. For some elements (mostly K, Na, and Ca), atomic emission spectrometry (AES) is useful, while for some trace elements, the anodic stripping voltametry (ASV) is sometimes used. In common for these methods is the sample preparation as, in contrast to CHN analyzers, all of them require liquid samples (there is a special case of AAS technique that allows analyzing solid samples but it is not very useful in litter decomposition studies). Samples for analysis are prepared by digestion in concentrated acid(s), and different digestion mixtures are used. The simplest is digestion in boiling concentrated HNO_3; however, for the most resistant organic compounds, this method can be prohibitively time-consuming (see following text). A sample of ground litter is placed in a quartz-glass tube or beaker, digested for approximately 24 to 48 h, or even longer at room temperature, followed by a slow rise to the boiling point. At this temperature, the sample is digested until complete mineralization, when the solution is clear and the fumes are white. Although the method works perfectly for simpler organic materials such as animal or fresh plant tissues, it sometimes appears not powerful enough to digest such resistant matter as humic substances. In the latter case, the digestion may take several days if performed at ambient pressure. For such samples, a very fast high-pressure microwave digestion may be used. The drawback of this latter method is the number of samples that can be digested simultaneously, which rarely is higher than 6 or 8. As a consequence, what is gained in speed is lost in the apparatus capacity. Still, an important advantage is that samples are not exposed to air for a prolonged period of time, which is always of concern as a possible source of contamination, especially in trace element analysis, such as that for Zn, Pb, or Cd. Some laboratories use other, more aggressive digestion methods, which may be considered a balance between high speed and high capacity. These methods include digestion in a mixture of nitric (HNO_3) and perchloric ($HClO_4$) acids, usually used in proportions 4:1 or 7:1. Although highly effective, the mixture is explosive and much care should be taken when digesting samples with this method.

In all these methods, the amount of acid(s) used for digestion should be sufficient to digest the sample completely. On the other hand, using too large volumes of acid(s) is not advisable because even the best quality acids contain some contaminants, which may become significant in trace element analysis. A good starting point is a proportion around 20 ml of acid per 1 g organic matter. Depending on the elements studied and their expected concentrations, the obtained solution is diluted with deionized water before analysis. As a rule of thumb, a dilution to 100 ml can be useful for 1 g sample digested in 20 ml acid.

In another digestion method, dry mineralization in a furnace at 450 to 550°C is followed by dissolution of the ashes in a mixture of diluted hydrochloric acid and hydrogen peroxide. This is a fast and effective method;

unfortunately, part of the more volatile metals may evaporate at high furnace temperatures.

After digesting, it is advisable to filter the solution before analysis because small inorganic particles may clog thin pipes in the analyzer. Practically, this means a necessity to filter all litter samples since they often are contaminated with mineral soil. Finally, when the samples are digested, diluted, and filtered, one may start the chemical analyses. Modern analytical equipment can analyze a broad range of elements. AAS and ICP techniques are impressively powerful, each offering the possibility of analyzing almost half of the periodic table, even at trace concentrations.

Atomic absorption spectrometry (AAS) relies on the fact that in the process of excitation (transfer of an atom from its ground state to excited state after absorption of external energy), every atom absorbs a specific spectrum of wavelengths, which is characteristic for the chemical element. For many elements, it is possible to identify at least one absorption peak, the wavelength of which does not overlap with absorption spectra of other elements. Thanks to this fact, the presence of an element in a sample can be easily identified by measuring the absorption of light at specific wavelengths during its passage through a cloud of atoms. The cloud is obtained by delivering an appropriate amount of energy to a sample. In AAS, this is done in basically two ways: injecting a liquid sample into a flame or into a high-temperature graphite furnace. In both cases, free atoms are generated, which are able to absorb energy from the light. Because every single atom absorbs a specific amount of energy at a given wavelength, the total amount of energy absorbed by a sample can be recalculated to indicate the amount of the element in the sample. The amount of an element is reported as its concentration in dry material, for example, in mg kg^{-1}.

With automated equipment, the AAS technique is relatively simple to use and very effective, offering possibilities of analyzing trace elements at concentrations in the range of parts per billion (μg kg^{-1}). One must keep in mind that such trace element analysis requires extreme care at all steps of the analytical procedure in order to avoid sample contamination. Only glassware of highest quality should be used (preferably made of quartz, lead-free glass), and before each run of digestion and analysis, all glassware should be thoroughly cleaned. The cleaning procedure usually encompasses a number of steps, starting with soaking in strong laboratory surfactant (washing fluid) for about 24 h, followed by at least double washings in distilled water, soaking in 2 to 5% high-grade HNO_3, triplicate washing in deionized water, and drying in a clean, closed oven. At all stages requiring handling, the glassware should remain covered with a parafilm or plastic foil and high-quality laboratory gloves should be used. (Use only nonpowdered ones since the powder may contain zinc!)

Another technique based on similar principles is atomic emission spectrometry (AES), in which the opposite process is measured—light emission by atoms during their transfer from an excited to a ground state. Atoms are excited by flame energy or by a plasma and the following light emission is measured. As in AAS, the emission spectra measured must be characteristic for a particular element, so the emitted light passes through filters, which select the wavelengths to be used. The flame AES equipment is much cheaper than AAS but allows only a few elements to be determined and the detection limits are much higher than in AAS. Nevertheless, for such metals as K, Na, and Ca, it gives very good results.

Yet another method based on measuring the emission spectra is inductively coupled plasma atomic emission spectrometry (ICP-AES). In this method, the digested sample solution is injected into a high-temperature argon plasma where the atoms are excited and the amount of emitted light is recorded at a broad spectrum of wavelengths. The main advantage over previously described techniques is a possibility of multi-elemental analysis. In ICP-AES, there is no need for a wavelength-specific light source (in contrast to AAS) and many more elements can be analyzed than in traditional AES. Analysis is considerably faster and, after a single run of a sample through the ICP-AES, a whole range of elements can be determined in one sample. Unfortunately, there are also some significant disadvantages. First of all, the technique is less sensitive to most elements than the graphite furnace AAS (but comparable to flame AAS). Second, the spectra recorded during the analysis are highly complicated and spectral interferences are common. Thus, high-resolution monochromators and software must be used to correct for these interferences efficiently and data analysis is more troublesome.

A further technique, which combines the sensitivity of graphite furnace AAS and the efficiency of ICP-AES, is the ICP-MS (inductively coupled plasma mass spectrometry). It belongs a group of so-called *hyphenated techniques* combining two different methods. In ICP-MS, the ions generated in plasma are transported to a mass spectrometer, where they are separated according to their mass and charge. The method has sensitivity comparable to graphite furnace AAS, allowing simultaneous fast multi-elemental analysis. Additionally, it allows us to detect and measure the contents of different isotopes of an element.

Other methods of elemental analysis, such as polarography or anodic stripping voltametry (ASV), are much less frequently used, especially in litter decomposition studies. Although ASV is an attractive method due its extremely high sensitivity (for some elements, higher than the graphite furnace AAS) and low cost of equipment, it is more useful for analyses of water or soil solution. Complex matrices and high concentrations of many

elements in digested organic samples are not suitable for ASV, and time required for sample preparation and analysis can be prohibitively long if no extremely high sensitivity is necessary. Still, it can be useful for analysis of, for example, chemical elements leached from decomposing litter with soil solution.

In common to all techniques of elemental analysis is the need for accuracy and precision. Accuracy can be defined as how close to the real concentrations we get with our analytical method, while precision is the measure of between-replicate variability in analytical results. Thus, high precision does not necessarily mean good accuracy, and good accuracy can be obtained even if precision is poor but large number of replicates are analyzed. Ideally, however, one would like to analyze as few replicates as possible and still be sure that the results well represent real concentrations of elements. Analytical precision can be measured relatively easily by simply repeating the analysis of the same sample a number of times. If all results are well concentrated around average, the precision is good; if they are highly scattered, we should think about improving our technique somehow. For example, dosage of an analyte to the graphite furnace can be imprecise or a pipe injecting a sample to the flame or plasma may be partly clogged. All modern spectrometers offer the option of replicated analyses and usually automatically calculate the precision. It is a good custom to run replicate analyses at all times because only then one can be sure that the samples were analyzed correctly.

With analytical accuracy, the situation is worse: unfortunately, we do not know the actual concentration of an element in a sample so we are not able to estimate how far the average of our measurements is from the real concentration. The only solution to this problem is to use special certified reference materials with known concentrations of the analyzed elements. Such materials are sold by some companies, which may be easily found over Internet. If precision is good and we obtain good accuracy for a reference material, we can trust the analytical results.

Even in the highest quality work, some contamination is unavoidable, and it should be a custom to run a set of at least three ''blank'' samples with every batch of samples. This routine allows one to detect possible contamination sources and to estimate real detection limits for particular elements under specific circumstances. The ''detection limit'' for an element is defined as the lowest concentration that can be detected with assumed probability (usually 95%). In practice, this value is frequently determined as higher than two or three standard deviations of the blank sample readings determined with at least 10 replicates. For graphite furnace AAS, a concentration giving the absorbance of 0.0044 units is sometimes reported as a detection limit for a particular element.

IV. DATA ANALYSIS

As in other experimental sciences, in litter decomposition studies a very important step in data analysis is the proper use of statistics. There is a plethora of statistical methods that are useful in litter decomposition research and their detailed presentation exceeds the scope of this book. However, when searching for a useful handbook (Textbox 1) and computer software, we need to know at least what kinds of methods we need to apply because many simpler or more specialized books and computer packages may not offer all necessary methods. The intention of our short overview is, thus, not to teach the proper use of statistics but rather to describe briefly those methods that are most frequently used in litter decomposition studies in order to help the reader choose adequate books and software. We deliberately do not give mathematical formulas for calculating particular statistics but rather concentrate on indicating which methods can be used for particular tasks and help to understand statistics and avoid pitfalls.

A. Regression Analysis

Regression analysis is by far the most frequently used method of statistical analysis in litter decomposition studies. It allows for the very basic, yet very important, analysis of decomposition rates as well as for more detailed studies of chemical changes during decomposition. In general terms, regression

TEXTBOX 1 Handbooks on Statistics

There is a huge choice of handbooks on statistics on the market, and we give just a small selection of those that we found particularly useful in our studies. This by no means indicates that one cannot find other books that are equally good. The examples presented here are, however, particularly suited for biological and ecological studies.

Fitzmaurice, G., Laird, N. and Ware, J. (2004) "Applied Longitudinal Analysis," p. 536. Wiley-Interscience

Montgomery, D.C., Peck, E.A. and Vining, G.G. (2001) "Introduction to Linear Regression Analysis," p. 672. Wiley-Interscience.

Rohlf, F.J. and Sokal, R.R. (1994) "Biometry," p. 880. W. H. Freeman.

Tabachnick, B.G. Fidell, L.S. Tabachnick, B. and Fidell, L. (2000) "Using Multivariate Statistics," p. 932. Allyn and Bacon.

Zar, J.H. (1998) Biostatistical Analysis, p. 929. Prentice Hall.

analysis tests the hypothesis that the behavior of one variable depends on changes in another, independent variable. The simplest case is the linear relationship in which the dependent variable y changes in direct proportion to changes in the independent variable x:

$$y = a + bx \tag{3}$$

where a and b are regression parameters, a indicating the intercept point that is the y value at which $x = 0$ and b is the slope of the relationship. A positive b value indicates a positive relationship (y increases with the increase of x), while a negative b means decrease of y with increasing x.

This very basic relationship can be easily developed to a more general one, a multiple regression relationship, in which y depends on several independent variables:

$$y = a + bx_1 + cx_2 + dx_3 + \ldots + nx_n \tag{4}$$

where $x_1, x_2, x_3, \ldots, x_n$ are different independent variables, and $a, b, c, d, \ldots, n$ are respective regression parameters.

Both regression types described belong to a general class of linear regression analyses. It is actually a rare case in litter decomposition studies that linear relationships are observed between the variables studied. As shown before, even the most basic process—the decay of organic matter—cannot be described properly with a linear regression. The simplest mathematical expression describing organic matter decay in time, the so-called *one-compartment exponential model* (the "Olson's model") is an equation where the amount of remaining organic matter asymptotically approaches zero with time (see previous text and Chapter 4). When the asymptote is different from zero, as discussed earlier, the equation describing the relationship between amount of organic matter amount and time is more complicated. For some other purposes, such as studies on chemical changes during decomposition or on dependence of decomposition rate on environmental factors, some other nonlinear models are useful. For example, the concentrations of some elements increase during the early decomposition stage and decrease later after reaching a maximum value. In such cases, a quadratic regression my describe the relation properly:

$$y = a + bx + cx^2 \tag{5}$$

In most cases, the shape of the relationship between variables studied in litter decomposition research is unknown and sometimes a number of different models should be investigated to find the one describing the relationship best. Familiarity with mathematical functions will certainly facilitate choice of the proper model.

Whatever regression model we use, calculating regression coefficients is not sufficient to answer the most basic question of whether the variable y

really does depend on the variable x (or on more variables x_1, x_2, x_3,. . ., x_n). In fact, there is unfortunately no possibility to be completely sure that a particular variable depends on the factor(s) chosen. Statistics helps us only to find out whether there is any relationship between the variables studied at all, and if so, how much of the variability in y that can be explained by the variability of x (x_1, x_2, x_3,. . ., x_n). Statistics itself cannot tell us whether the relationship observed includes the causal relationship between the variables y and x. The correlation may be just coincidental and determined by some other, not measured ("hidden") variable. Although there are some more advanced statistical methods that help us to sort out such intercorrelated variables (partial correlation analysis; see following text), it is the researcher's personal responsibility to interpret results of statistical tests with the greatest care.

When a regression analysis has been performed, a number of statistics are calculated, which help the researcher make the proper decision. The most important one is the so-called "significance level", p, indicating whether there is any relationship between the variables at all. To be more precise, the significance level does not indicate directly whether there is or is not any relationship, but it reports the probability of an erroneous assumption that there is a relationship between the variables if, in fact, there is none. In statistical language, such an error is called the *type I* or α error and means erroneous rejection of the null hypothesis, which always assumes *no relationship* between variables or *no difference* between treatments, ecosystems, etc. Thus, a "high significance level" means, somewhat counterintuitively, a low p value. To memorize it more easily: a low p value means low probability of the α error, which, in turn, means a *high* probability that the relationship is true, hence, *high significance* of the relationship. In ecological and biological sciences, it is customary to recognize a relationship (or the difference) as significant if $p \leq 0.05$, that is, if the probability of getting wrong when assuming the "real" relation is not greater than 0.05. Note that, at that significance level, one can still be wrong; in fact, in 5 cases out of 100, our assumption of an existing relationship between variables y and x may be incorrect. Although it is a commonly accepted practice, agreed among scientists, to take $p \leq 0.05$ as a borderline between significance and nonsignificance, one has to remember that this is nothing more than a common convention. It is up to a researcher to decide whether lower or higher probability should be used. For example, if, for some reason, one cares especially about erroneous assumption of significant differences if there is none (which is frequently the case in social sciences), a higher significance level (that is, lower p value) should be used, 0.01 or even 0.001. In contrast, if there are good reasons to be more afraid of not finding a significant difference when one really does exist (for example, in toxicological studies), a lower significance level can be chosen, for example, 0.1. However, p values higher than 0.1 are usually not accepted.

The significance level depends on a number of factors. First of all, it obviously depends on the strength of the relationship between the variables: when the relationship is strong, the significance level is high. Second, the significance level depends on the sample size: the larger the sample size, the higher the significance level for a particular relationship between variables. This leads to the important conclusion that when we are searching for relationships that presumably are not very strong, increasing the sample size may allow us to detect them more easily. However, increasing sample size above 20 to 30 only rarely improves the accuracy significantly. In the specific case of litter decomposition, this relates not so much to the very basic relationship between decomposition time and mass loss, which is always strong, and a significant regression can be obtained even with a few data points. However, in some more detailed studies, for example, on relationships between decomposition rates and concentrations of chemical components in the organic matter, sample size can be crucial. Thus, when planning decomposition studies, it has to be decided in advance what types of analyses will be performed and the sampling schedule should be adjusted accordingly. As a rule of thumb, one can say that while as few as three samplings may be sufficient for a reasonable estimation of the decomposition constant from a simple exponential Olson's model, at least five would be required to find a limit value for decomposition from an asymptotic exponential model, and still more samplings will be necessary when investigating dynamics of chemical components in decomposing matter. Of course, samplings should be distributed properly in time to cover a significant range of changes in the variable studied. The shortest period would be necessary to estimate a decomposition constant k from the single exponential model, while using the two-compartment model, finding a limit value or changes in chemical composition, requires longer incubation times. The time necessary for the studies depends, in turn, on climate and litter type. If decomposition is fast, as in warm, humid climate, a few weeks may suffice for determining the initial decomposition rate, and more detailed studies may be carried out in a few months. However, in more harsh climates (cold or dry) and with organic matter resistant to decay, usually a longer litter incubation time is required for even the most basic studies, and as long as 5 to 10 years' incubation may be necessary to estimate an asymptote, the k_1 and k_2 parameters for a two-compartment model, or to describe the dynamics of chemical changes.

When the general pattern of litter decomposition or the dynamics of chemical components is described using an appropriate regression equation, a further step frequently involves a comparison of different ecosystems and/or substrates during decomposition. Thus, we want to know if the regression equations obtained for those different systems/substrates are more or less the same or whether they differ enough to allow us to conclude that their

dynamics are different. There are several methods for comparing regression equations and the most useful and frequently used one relies on use of so-called "indicator" or "dummy" variables. Without going into detail, the method requires yet another step in data preparation. We need to add an indicator variable(s) that consists of only zeros (0) and ones (1), the sole purpose of which is to distinguish between the ecosystems/substrates compared and between any other factors. For example, while comparing two ecosystems as regards decomposition rates of a given litter type, we create an indicator variable containing zeros for the first ecosystem and ones for the other. For the sake of simplicity, we will use the linear model as an example. With an indicator variable (I) created, the simple linear regression model extends to

$$y = a + bx + Ia_1 + Ib_1x \tag{6}$$

where a, b, a_1, and b_1 are the regression parameters. In the particular case of decomposition studies, the Ia_1 term may be omitted since the decay starts from 100% remaining mass in all ecosystems, and thus the intercept is the same. Such an equation becomes a simple regression when $I = 0$, but for $I = 1$ (and recall that this is the case for the second ecosystem only), it turns into a combination of two equations describing two ecosystems. If the ecosystems differ significantly, then adding information on decomposition rate in the second ecosystem (the second part of the equation for $I = 1$ will add a significant b_1 value. Turning this reasoning around, the significance of b_1 means that the decomposition rates in the ecosystems studied are significantly different. Of course, the same method and reasoning can be used for comparing more than two ecosystems. Although it can also be used for nonlinear models, the interpretation of the results gets quite complicated for more complex models. Thus, it is strongly advisable to linearize a model or to use as simple nonlinear equations as possible (regular exponential and asymptotic exponential models are still interpretable).

B. Analysis of Variance (ANOVA)

Analysis of variance is probably the most commonly used technique in the natural sciences. However, in litter decomposition studies, it is not as useful as the regression analysis. ANOVA lets us find significant differences between populations, treatments, ecosystems, etc., in the variables measured. In decomposition studies, it may be useful to check whether the ecosystems studied differ, for example, in concentrations of some chemical elements (such as nutrients or pollutants) so that a researcher knows if results obtained for decomposition rate can be pooled for all ecosystems used in the study or whether they should be treated separately. ANOVA is even more useful in

experimental treatments, for example, in laboratory experiments on effects of pollution or soil fertilization on organic matter respiration rate.

Analysis of variance relies on the assumption that two or more treatments do differ significantly if the variance between groups (that is, between treatments, populations, etc.) is larger than the variance within the groups (treatment, populations, etc.)—hence, the name of the technique. In practice, the test statistics are calculated as the ratio of the average between-group sum of squares to the average within-group sum of squares and the value obtained is compared to the so-called F distribution to check the probability of obtaining that particular F value or larger if the groups do not differ. As in the regression analysis described previously and in many other statistical tests, we assume that the difference is *significant* if that probability is equal or less than 0.05. Thus, $p \leq 0.05$ indicates that the groups studied, for example, treatments or ecosystems, do differ.

If more than two groups are compared, ANOVA is only the first step in data analysis. Usually, a researcher is not satisfied with the information that there are significant differences between the groups studied and wants to know precisely which groups that differ from the others. This may be accomplished with the ''post-hoc'' tests, also called the ''a posteriori tests'' or ''multiple range tests,'' which compare the groups (treatments) against each other. There is a range of post-hoc tests differing in their power, that is, the probability of detecting between-group differences as significant. To describe them is beyond the scope of this book, but a researcher should be aware of these differences because, depending on the selected test, one may or may not detect a difference between two particular treatments or ecosystems as significant. Among a number of available post-hoc tests, the Scheffe's test belongs to the least powerful (most conservative), protecting a researcher against erroneously accepting a difference as significant. In contrast, the LSD (*lowest significant difference*) test is the most powerful, and the Tukey's HSD (*honest significant difference*) test is a good balance between the two.

Analysis of variance allows a researcher to investigate for the significance of an effect of one factor (one-way ANOVA) or a number of factors (multifactor ANOVA). The idea behind the two methods is the same, only the calculations are somewhat more complicated for multifactor ANOVA. With still more calculations, one can use ANOVA for finding a significant effect of a number of factors on more than one dependent variable (multivariate ANOVA or MANOVA). In that case, a significant p value for a particular factor indicates that it has a significant overall effect on the dependent variables measured.

The *general linear models* (GLM) may be considered an extension of both regression analysis and analysis of variance since they allow for simultaneous testing of linear relationships among variables as well as differences

among groups (treatments). More complicated layouts, such as multifactor ANOVA and multivariate ANOVA, can be used and interactions between quantitative and qualitative factors can be studied.

C. Multivariate Methods

If a number of variables are studied and we are not sure about the relationships among them (that is, in contrast to the regression analysis or ANOVA, we are not able to separate dependent variables from independent variables/factors), then multivariate methods may appear useful. The simplest one, very often used as an initial step in data analysis, is the *correlation analysis*. The "simple" or "Pearson product moment" correlations measure the strength of linear relationships between each pair of variables entered into the analysis. The correlation coefficients range between –1 and 1, the first indicating a perfect negative correlation, the latter a perfect positive correlation. A correlation coefficient equal to 0 means no correlation. As in regression analysis, the correlations are tested for statistical significance, and similar to all other tests, $p \leq 0.05$ indicates a significant correlation between two particular variables. Simple correlations have their weaknesses: they are sensitive to outliers (exceptionally high or low values) and do not account for possible effects of other variables on correlations between any pair of variables. The first problem can be solved by computing the correlations from the ranks of the data values rather than from the original values themselves—these are known as the "Spearman rank correlations." Interpretation of results is similar to simple correlations. The problem of separating the effect of other variables on correlation between any two variables is more difficult to solve and, in fact, there is no possibility to sort out what variable influences another one unless we do not have reasons for some a priori assumptions. The only information that one can obtain mathematically is an estimate of the effect of a variable on a particular correlation, given that the information from all other variables has been taken into account. This is done with a technique known as "partial correlations analysis." Partial correlation analysis calculates correlations between each pair of variables, having first adjusted for their relationship to other variables in the data set. Interpretation of this table is a bit more difficult than simple or rank correlations and makes sense only in comparison to one of the latter two.

More advanced multivariate techniques include *principal components analysis* (PCA) and *factor analysis* (FA). The first is used to obtain a small number of linear combinations of variables used in the study which account for most of the variability in the data. Each principal component represents a linear combination of all variables in the data set. Thus, for each data point a "combined value" can be calculated that summarizes effects of all

variables considered. Usually, a few principal components can summarize a sufficiently large proportion of the variability in the data. The number of principal components for further analysis can be extracted using one of the three criteria: percentage of variability explained, eigenvalue, and the so-called scree plot. The first criterion is used if we want to have at least a specified proportion of the variability explained by principal components selected. One may, for example, assume that at least 80% of the variability in the data has to be explained, and consequently extracts as many principal components as is enough to reach this limit. Depending on the data, this can be usually reached with three to four first principal components. A more ''objective'' criterion is based on calculated eigenvalues for particular principal components. Both the percentage of variance explained and the eigenvalues are the largest for the first component and then decrease. The rule of thumb is to use only those components with eigenvalues greater than 1.0, since these are supposed to add significant explanatory power to the model. The last method, a scree plot, is graphical: eigenvalues are plotted against their numbers and the cutoff line is drawn below the last component where the plot is still steep. After this point, the line levels out, indicating that the following components add only minor explanatory power. Whatever method is used, usually two to four components are extracted, so the number of variables can be substantially reduced if original data set includes lots of different measures (such as concentration of a number of chemical elements and environmental variables in decomposition studies). Looking more closely at the principal components structure (the values assigned to particular variables) and their relation to, say, decomposition rate, one may judge the relative importance of combined chemical litter structure against combined environmental factors for the decomposition.

The *factor analysis* (FA) can be considered an extension of principal components analysis, as the first step and the goal are similar to those of PCA. However, in FA, the principal components extracted for further analysis (the extraction methods are the same as described previously) are rotated in space to obtain the best separation between them. There are some rotation methods, but the general goal is the same: the rotated components should be as dissimilar to each other as possible: if, for example, the equation parameter for one variable reaches high value in the first component, the components are rotated in such a way that this particular variable has as low a value as possible in the next component. In that way, we obtain a set of (ideally) highly distinct linear combinations of all variables in the data set, which makes their interpretation easier. The idea behind factor analysis is that there are some hidden factors (hence, the name of the method) controlling the variability of the data. We are not able to measure those hidden factors directly, but they may be uncovered by measuring some specific variables. Again, using an example from litter decomposition

studies, it is reasonable to assume that decomposition rate is controlled by a "climatic factor" (combined effect of average temperature, temperature amplitude, soil moisture, yearly rainfall and its distribution over the year, etc.), a "nutrient factor" (concentration of a number of nutrients, pollutants, soil pH), and a "substrate factor" (contents of lignin, sugars, tannins, resins, etc.). If one would like to estimate how much variability in litter decomposition rate can be attributed to each of these three complex factors, using raw variables is very useful. On the other hand, there is no one measure of a climatic factor, a nutrient factor, or a substrate factor. Here, the factor analysis appears helpful since it allows the researcher to separate the real variables into the complex factors. As we do not assign particular variables to particular factors a priori, the method is quite objective since the real nature of each factor is deduced a posteriori—after initial PCA and the rotation of the selected components. The method is not yet widely used in decomposition studies, but we can see a potential in identifying general rules in organic matter decomposition.

V. PRESENTATION OF THE RESULTS

Whatever statistical method is used, and even if none is used at all, the research results should be presented in a way that is easy to understand. In the following text, we discuss briefly some general rules of presenting results in scientific papers, posters, and illustrated talks.

A general rule says that a well-prepared report from a study should be comprehensible from figures alone. This requires a careful design of graphs, not necessarily simply following the options automatically generated by the software used. A graph does not completely replace numerical test results, but it is a good habit to show the results as statistical plots, possibly supplemented with a table with more detailed information. Professional statistical software packages usually offer a range of graphs for presenting results. In fact, the choice may be overwhelming, especially for a student working on his or her first paper or report.

When choosing graphs to illustrate a study, one should follow two basic principles. First, a good graph should be understandable without reading the text; a short figure caption should explain what can be read from the graph. Second, the graph should be easy to understand, and unnecessary extra layouts should be avoided since they only make graphs more difficult to read. A common example of such superfluous "ornaments," unfortunately used quite frequently even in papers published in high-quality journals, are "three-dimensional" bar plots, histograms, and pie plots. While three-dimensional graphs may be justified when showing relationships among three variables, using them in any other case is simply an error.

Each type of statistical analysis requires a different type of plot and we give some general rules of presenting research results in a professional and easy-to-understand manner for the most commonly used statistical techniques.

In regression analysis, a plot showing original data points and the regression line, possibly with confidence intervals, is probably the best solution (Fig. 7A). It allows a reader to see not only the estimated regression line itself

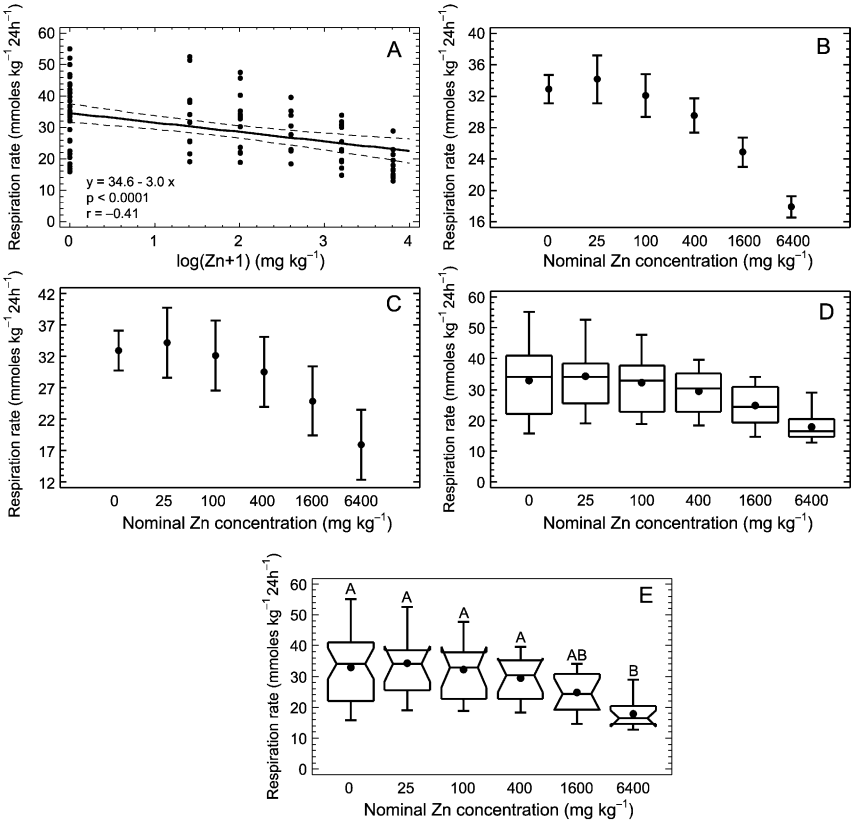

Figure 7 Different ways of presenting the same data on litter respiration rates: regression line with original data points and 95% confidence intervals (A); averages with 95% confidence intervals (B); averages with 95% Tukey HSD intervals (C); box-and-whisker plot with medians (horizontal lines in the boxes), averages (dots), interquartile ranges (boxes), and minimum and maximum values (whiskers) (D); notched box-and-whisker plot, same as D but with notches indicating approximate 95% confidence intervals for medians (E). See text for more comments. Data from Niklińska *et al.* (1998).

but also how scattered the data points are and to judge how well the model fits the data. A more detailed description should be added in tabular form, in text, or pasted directly into the graph. In original research papers, the crucial information is the significance level of the regression (p), the correlation coefficient (r), or the determination coefficient (r^2) and the regression equation itself. Such information allows the reader to interpret the results him- or herself for example, whether the p level obtained justifies considering the regression significant. Further, the reader can use the regression equation for his/her purposes (such as comparing with his/her own studies or predicting unknown y values for known x values. Without all this information, a report cannot be regarded complete.

ANOVA results can be presented in a number of ways. Many statistical packages automatically generate average value $\pm$ standard deviation (SD) or average $\pm$ standard error (SE) plots. Some offer also plots of averages $\pm$ confidence intervals (CI) (Fig. 7B, C). If the latter option is used, one has to remember to present exactly the same confidence intervals as used in post-hoc comparisons. It does not make sense to use, say, Scheffe's post-hoc test and show LSD intervals on the plot. Similarly, if ANOVA is performed on log-transformed data, usually to meet the assumption of normal distribution, either the data should also be plotted as logarithms or, if showing original values is preferred, the confidence intervals should be back-transformed from logarithms. The latter approach results in nonsymmetrical confidence intervals around means.

All options described here are correct if properly used; however, most of them, with the exception of regression analysis plots with original data points included, significantly reduce the amount of information available in original data. Probably the best method of summarizing and presenting results of studies in which data can be combined into separate groups (such as different treatments, ecosystems, or substrates in decomposition studies) are the so-called "median box-and-whisker plots" (Fig. 7D). Box-and-whisker plots are also sometimes used for presenting simply an average $\pm$ SD/SE but this does not add any information in comparison to regular average $\pm$ SD/SE plots. Median box-and-whisker plots are constructed by plotting median, 25th, and 75th percentiles (that is, lower and upper quartiles) of each group as short horizontal lines that are joined to form a rectangular box. Then, the box is supplemented with "whiskers" extending to the maximum and minimum values in each sample, except for any outliers and far outliers, that is, points that lay 1.5 and 3 times interquartile range (the range between 25th and 75th percentile) below or above the box, respectively. Each outlier and far outlier is plotted as a separate point, usually distinguishing between the two groups. For yet more information, sample average can be indicated inside the box (Fig. 7D).

A modification of median box-and-whisker plots are notched median box-and-whisker plots, in which the notch indicates approximate 95% confidence interval for the median. The plot can be used for direct graphical judgment of the significance of between-group differences. One has to remember, however, that this is not as formal a test as, for example, analysis of variance (Fig. 7E).

Median box-and-whisker plots summarize as much information about the data as is possible to present lucidly on a single graph. With a glimpse, one may learn from the graph not only what is the group average and how large is the variance (the only information provided by the average $\pm$ SD plots), but also whether the data are approximately normally distributed and, if not, in which direction the distribution is skewed, whether there are many outliers in the data, and how far the median is from the average. With the addition of confidence interval notches, even a first judgment of significant differences among the groups can be made.

Consequently, in most cases, when data for different groups (treatments, etc.) are collected in an experiment, median box-and-whisker plots are the best way of presenting the results. When formal statistical tests are performed (such as ANOVA), their results can be reported in tabular form or added to the plot to condense information on a single graph even more. A common way of presenting ANOVA results on a plot is adding letters above the boxes to indicate which groups differ significantly according to the post-hoc test performed. Groups not differing from each other are assigned the same letter, while statistically different groups receive different letters (Fig. 7E).

We do not discuss here some more obvious rules of good graph design, such as a reasonable use of the plot space or proper line thickness and lettering. Still, together with what has been described, they all determine eventually whether the results are presented in a professional manner.

Appendix I

ENGLISH AND LATIN NAMES OF VASCULAR PLANTS MENTIONED IN THE BOOK

We have listed the names of the vascular plant species mentioned in the text in alphabetical order. The English names are given as they appeared in quoted papers, followed by their Latin names. Our purpose has been merely to identify the litter species used by giving the Latin name, being aware of that not only American and English names sometimes differ but also that different dictionaries give different names. This means that some species are listed twice, since our intention has been to use the name given in the original publication.

Austrian pine (*Pinus nigra* Arnold)
Annual ryegrass (*Lolium multiflorum* Lam.) (= *L. perenne* L. ssp. *multiflorum* (Lam.) Husnot)
Aleppo pine (*Pinus halepensis* Mill.)
American beech (*Fagus grandifolia* Ehrh.)

Basket oak (*Quercus prinus* L.)
Black cherry (*Prunus serotina* Ehrh.)
Bilberry (*Vaccinium myrtillus* L.)
Black birch, sweet birch (*Betula lenta* L.)
Black alder, common alder (*Alnus glutinosa* (L.) Gaertn.)
Black oak (*Quercus velutina* Lam.)
Bigtooth aspen (*Populus grandidenta* Michx.)
Blueberry (*Vaccinium myrtillus* L.)

Chestnut oak (*Quercus prinus* L.)
Cloudberry (*Rubus chamaemorus* L.)
Common ash (*Fraxinus excelsior* L.)
Common oak (*Quercus robur* L.)
Common alder (*Alnus glutinosa* (L.) Gaertn.)
Common hazel (*Corylus avellana* L.)
Common beech (*Fagus silvatica* L.)
Common oak (*Quercus robur* L.)
Corsican pine (*Pinus nigra* var. *maritima* (Ait.) Melv.)

ADVANCES IN ECOLOGICAL RESEARCH VOL. 38 0065-2504/06 $35.00

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Cowberry (*Vaccinium vitis-idea* L.)
Candle tree (*Parmenteria cereifera* Seem.)
Chinese cork oak (*Quercus variabilis* Bl.)
Chinese fir (*Cuninghamia lanceolata* (Lamb.) Hook.)
Chinese pine (*Pinus tabulaeformis*)
Coulter pine (*Pinus coulteri*)

Douglas-fir (*Pseudotsuga menziesii* Mirb. Franco.) (= *Pseudotsuga douglasii*)
Downy birch (*Betula pubescens* Ehrh.)
Downy oak (*Quercus pubescens* Willd.)
Durmast oak (*Quercus petraea* Lieb.)

Eastern hemlock (*Tsuga canadensis* (L.) Carr.)
Elm sp. (*Ulmus* sp.)
English ryegrass (*Lolium perenne* L.)
European beech (*Fagus silvatica* L.)
European maple (*Acer platanoides L.*)
Eastern hemlock (*Tsuga canadensis* L. Carr.)
European beech (*Fagus sylvatica* L.)
European oak (*Quercus robur* L.)

Flowering dogwood (*Cornus florida* L.)

Grand fir (*Abies grandis*)
Grey alder (*Alnus incana* (L.) Moench)
Grand fir (*Abies grandis* Lindl.)

Heather (*Calluna vulgaris* (L.) Hull)

Italian ryegrass (*Lolium multiflorum* Lam.) (= *L. perenne* L. ssp. *multiflorum* (Lam.) Husnot)

Jack pine (*Pinus banksiana* Lamb.)
Japanese beech (*Fagus crenata* Bl.)

Limber pine (*Pinus flexilis* James)
Lingonberry (*Vaccinium vitis-idea* L.)
Loblolly pine (*Pinus taeda* L.)
Lodgepole pine (*Pinus contorta* var. *latifolia* Engelm.) (*Pinus contorta* var. *contorta*)
Locust sp. (*Robinia* sp)

Maritime pine (*Pinus pinaster* Ait.)
Mountain ash (*Sorbus aucuparia* L.)
Mountain palm (*Prestoea montana* (R. Graham) Nichols.)
Manzanita (*Manzanita sp.*)
Mountain birch (*Betula pubescens* ssp *czerepanovi*)

Norway spruce (*Picea abies* (L.) Karst.) (= *Picea excelsa* Link.)
Nepalese alder (*Alnus nepalensis* D. Don)

Pacific silver fir (*Abies amabilis* Douglas ex J. Forbes)
Pendulate oak (*Quercus robur* L.)
Perennial ryegrass (*Lolium perenne* L.)
Ponderosa pine (*Pinus ponderosa* Laws.)
Pyrenean oak (*Quercus pyrenaeica* Willd.) (= Q. toza D.C.)
Pinyon pine (*Pinus edulis* Engelmann 1848)

Red spruce (*Picea rubens* Sarg.) (= *P. rubra* [DuRoi] Link)
Red alder (*Alnus rubra* Bong.) (= *A. oregona* Nutt.)
Red pine (*Pinus resinosa* Ait.)
Red oak (*Quercus rubra* L.) (*Q. rubra* du Roi) (*Q. borealis* Michx. f.)
Red maple (*Acer rubrum* L.)

Scots pine (*Pinus sylvestris* L)
Scrub oak (*Quercus berberidifolia and Quercus dumosa*)
Sierra palm (*Prestoea montana* (R. Graham) Nichols.)
Silver fir (*Abies alba* L.)
Silver fir (*Abies alba* L.) (= *Abies pechinata* D.C.)
Silver birch (*Betula pendula* Roth.) (= *B. verrucosa* Ehrh.)
Sitka spruce (*Picea sitchensis* (Bong.) Carr)
Small six-weeks grass (*Vulpia microstachys* (Nutt.) Munro).
Soft chess, soft brome (*Bromus hordaceus* L.) (= *B. mollis* L.)
Stone pine (*Pinus pinea* L.)
Subalpine fir (*Abies lasiocarpa* (Hook.) Nutt.)
Sugar maple (*Acer saccharum* Marsh.)
Scrub oak (*Quercus petraea* Liebe.)
Sessile oak (*Quercus petraea* Liebe.)

Tabonuco (*Dacryodes excelsa* Vahl)
Trembling aspen (*Populus tremuloides* Michx.)
Tulip poplar (*Liriodendron tulipfera* L.)

Western hemlock (*Tsuga heterophylla* (Raf.) Sarg.)
White oak (Quercus alba L.)
White pine (*Pinus strobus* L.)
White spruce (*Picea glauca* (Moench.) Voss)
Wild oats (*Avena fatua* L.)
Willow sp. (*Salix* sp.)
White fir (*Abies concolor*)

Yellow birch (*Betula alleghaniensis* Britt.) (= *B. lutea* (Michx.))
Yellow poplar (*Liriodendron tulipfera* L.)
Yellow birch (*Betula alleghaniensis* Britt.)

Appendix II: Exercises

In this section, we present a set of problems to solve, using real data. Appendix II contains a few simple exercises that can be solved with basic calculations as well as some more advanced problems for which some knowledge in statistics is necessary. The section consists of two parts, the first one presenting the problems and the data sets and the second giving the solutions. In those cases where some statistics has been used, we have included printouts from a statistical package with additional comments (in italics) helping to understand the results of tests performed.

The number of problems offered here is limited and an additional and increasing number is found on the web page http://www.eko.uj.edu.pl/deco. Some of the exercises are clearly related to a specific chapter and some integrate information from several chapters. Please note that Chapter 9 contains some general information about selected statistical methods. Comments on the exercises are welcome, as are suggestions and new data sets for additional exercises which you would like to appear on the web site. Should you have such comments or suggestions, please send them to r.laskowski@eko.uj.edu.pl.

SECTION I: PRESENTATION OF TASKS

Exercise I: Foliar Litter Fall

Presentation of the Problem

You measure foliar litter fall in a mature Austrian pine forest. The canopy is not really closed and you have placed 15 litter traps with 0.25 m^2 surface randomly over an area of ca 50 $\times$ 50 m. The litter traps are placed in the field on August 15. You decide to empty the traps three times in the first year, the first time after the litter fall peak in late October, the 2nd time in late May, and the 3rd time on August 15. As you will note, two litter traps were found disturbed, one in the 2nd and one in the 3rd sampling.

ADVANCES IN ECOLOGICAL RESEARCH VOL. 38
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After samplings, the foliar litter is sorted out from other litter, dried at 85°C, weighed, and approximately one month after the last sampling, you have the following table, with foliar litter mass given as grams per trap.

The task is to calculate the annual foliar litter fall and give the results as kg/ha.

Table I.1 Amount of litter (g dry mass) recorded in particular traps, 1 through 15, on the three sampling occasions

Litter trap No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sampling 1	45	61	42	21	55	59	75	52	48	19	38	43	62	59	44
Sampling 2	18	15	19	9	11	9	16	14	13	5	22	–	13	14	12
Sampling 3	10	14	15	8	7	5	7	11	17	2	12	8	5	–	14

Exercise II: Comparing Foliar Litter Fall of Different Tree Species

Presentation of the Problem

The stand described in the Exercise I was, in fact, one of the stands in a block experiment. You have four stands of Austrian pine and four stands of Sitka spruce, each stand measuring 50 × 50 m. All stands, which are paired, are located within a limited area that is less than 1000 × 1000 m. The climate is the same and the soil conditions are similar throughout this area. You have measured foliar litter fall for one year, using 15 replicate litter traps in each stand as in the Exercise I.

The task is to determine whether there is any significant difference in litter fall between the two tree species.

Table II.1 Litter fall measured at the eight stands used in the experiment. The results are given in kg dry matter per hectare with standard deviation in parentheses

	Stand pair 1	Stand pair 2	Stand pair 3	Stand pair 4
Austrian pine	2843 (514)	3063 (634)	2438 (386)	2987 (624)
Sitka spruce	2207 (563)	2577 (483)	1989 (351)	2416 (462)

Exercise III: Foliar Litter Fall in a Climatic Transect after Climate Change

Presentation of the Problem

We have seen (Chapter 2) that the foliar litter fall of mature Norway spruce stands is well related to the climate index actual evapotranspiration (*AET*) ($R^2 = 0.787$) for a boreal to temperate area ranging from about 66°30′N to about 55°45′N, corresponding to an AET interval from 370 to 626 mm. The equation relating litter fall to AET is:

$$Litter\ fall = 12.1 \times AET - 3650.4$$

In a given forest stand with the AET value of 405 mm, the annual foliar litter fall today is 724 kg/ha^{-1}. A new climate prediction suggests that there will be a full climate change in approximately year 2050. This boreal system (in Fennoscandia) is energy limited (Berg and Meentemeyer, 2002) and we can estimate that a climate change will give an increase in AET of ca 27%, corresponding to an increase in annual average temperature of ca 4°C and an increase in precipitation of ca 40%.

The task is to estimate foliar litter fall at that stand in the year 2050 for a mature Norway spruce forest. We make the assumption that nutrient availability does not become limiting for tree growth in the new climate.

Exercise IV: Calculating Litter Mass Loss

Problem Presentation

You have prepared a set of litter bags, incubated them, made a sampling, and want to determine litter mass loss. When you prepared the litter bags, you dried them in the air at room temperature for 4 weeks. To make an exact determination of the moisture content, you took 20 samples of the air-dried litter and dried them at 85°C for 24 hours. That determination gave a moisture level of 6.04% and a standard error of 0.17. Thus, the litterbags were prepared with litter containing 6.04% water and the registered litter weight thus also includes that moisture.

The litterbags were then incubated in the field, and you have made a first sampling of 20 bags, cleaned their contents, dried the leaves at 85°C, and weighed them. Finally, when ready to calculate the mass loss, you have the following data listed (Table IV.1).

The task to calculate litter mass loss for all samples as well as the average mass loss.

Table IV.1 Litter mass in litter bags before and after incubation (air-dried mass)

Original weight (grams per litter bag)	The same litter after 1 yr incubation (grams per litterbag)
0.613	0.2783
0.611	0.2802
0.611	0.1798
0.613	0.1098
0.614	0.2733
0.616	0.2944
0.613	0.1923
0.619	0.1717
0.615	0.2449
0.617	0.1650
0.612	0.1880
0.610	0.1612
0.618	0.2551
0.614	0.3031
0.617	0.2049
0.618	0.2443
0.619	0.2533
0.615	0.3037
0.613	0.1422
0.615	0.2605

Exercise V: Calculating Annual Litter Mass Loss during Decomposition

Presentation of the Problem

The data used for this example originate from a study on decomposition of Scots pine needle litter. The litter bags were incubated for 5 years and collected a few times a year with 20 replicates (Table V.1).

The task is to calculate annual mass loss rates for consecutive years of decomposition.

Exercise VI: Describing Accumulated Litter Mass Loss Dynamics by Functions

Problem Presentation

A decomposition experiment has been made using two different litter species, one being lodgepole pine needle litter and the other, grey alder leaf litter. The litterbags of the two litter species were incubated in parallel in the

Table V.1 Average accumulated mass loss and the remaining mass for consecutive samplings for decomposing Scots pine needle litter

Date (yy-mm-dd)	Incubation time (days)	Accumulated mass loss (%)	Remaining mass (%)
74-05-02	0	0	100
74-09-02	123	10.4	89.6
74-11-03	185	17.8	82.2
75-04-11	344	24.4	75.6
75-05-13	376	27.3	72.7
75-09-04	490	35.7	64.3
75-10-29	545	43.2	56.8
76-04-28	734	44.4	55.6
76-08-25	846	51.2	48.8
76-11-10	923	55.8	44.2
77-06-01	1126	58.8	41.2
77-09-12	1229	63	37
77-10-27	1274	63.8	36.2
78-05-22	1481	66.5	33.5
78-08-31	1582	70.8	29.2
78-10-16	1628	71.4	28.6
79-05-14	1838	75	25
79-10-02	1979	77.1	22.9

same stand and samplings were made at the same time and with the same intervals, with 25 replicate bags in each sampling. Table VI.1 reports average accumulated mass loss for each time interval with accompanying standard errors (SE), and Table VI.2 gives initial chemical composition of both litters, which may be helpful in interpreting the results of the exercise.

The task is to determine which function describes the accumulated mass loss best and to determine whether the decomposition patterns differ among the litter species studied. You should compare the three functions you find in the book, namely the one-compartment exponential, the two-compartment exponential and the asymptotic function.

Exercise VII: Regulating Factors for Litter Decomposition Rates

Problem Presentation

The data given in Table VII.1 present results of an experiment with litter decomposition rates in one Scots pine stand using needle litter with five

Table VI.1 Accumulated mass loss (%) with standard errors (SE) for the two species being compared

	Grey alder leaves		Lodgepole pine (%)	
Incubation time (days)	(%)	(SE)	(%)	(SE)
0	0	–	0	–
204	40.3	0.7	10.5	1.6
286	42.1	1.2	15.6	3.0
359	44.0	1.0	23.5	2.8
567	48.3	1.0	30.3	4.3
665	48.3	0.7	39.4	6.1
728	48.4	0.8	45.4	5.5
931	49.4	0.7	51.6	6.9
1021	49.2	0.8	55.9	8.5
1077	50.1	0.9	58.7	10.1
1302	51.3	0.7	61.0	7.3
1393	53.1	1.2	65.9	12.1
1448	55.5	1.6	63.1	12.7

Table VI.2 The initial chemical composition (mg/g) of nutrients in the two litter species

	N	P	S	K	Ca	Mg	Mn
Grey alder leaves	30.7	1.37	6.12	15.6	12.3	2.32	0.10
Lodgepole pine needles	3.9	0.34	0.62	0.56	6.35	0.95	1.79

different nutrient levels. Ih needles originate from a very nutrient-poor Scots pine forest, N0 from a Scots pine forest on relatively rich soil— although N is still limiting for the microorganisms. N1, N2, and N3 are denominations for litter originating from stands fertilized with 40, 80, and 120 kg N as ammonium nitrate per hectare and year. The litter bags were incubated in parallel with all five litter types in the same design in the same stand for 4 years and sampled at the same dates. Besides litter mass loss, the litter was also analyzed for concentrations of N, P, and lignin.

The task: to determine possible regulating factors for the decomposition rate of Scots pine needle litter, using needles from trees fertilized with different concentrations of N.

Table VII.1

Incubation time (days)	Accumulated mass loss (%)	N (mg g^{-1})	P (mg g^{-1})	lignin (mg g^{-1})
Ih litter				
0	0	4	0.21	267
202	11.1	4.4	n.d.	n.d.
305	21.6	4.6	0.22	308
350	26.5	5.3	0.24	323
557	35	6	0.25	370
658	47	7.2	0.29	419
704	48.1	8.3	0.41	415
930	52.6	8.6	0.52	439
1091	59.9	9.7	0.59	442
1286	n.d.	n.d.	n.d.	n.d.
1448	67.5	10.9	0.67	482
N0 litter				
0	0	4.4	0.32	256
202	13.8	4.9	0.33	327
305	26.2	5.6	0.35	338
350	32.7	5.8	0.37	364
557	n.d.	n.d.	n.d.	n.d.
658	47.4	8.4	0.48	418
704	51.2	8.2	0.45	438
930	56.3	8.9	0.61	437
1091	62	11.1	0.7	456
1286	62.2	10.8	0.6	467
1448	68.8	11.6	0.71	486
N1 litter				
0	0	4.4	0.3	251
202	14	4.9	0.31	310
305	26.7	5.9	0.34	340
350	31.3	5.9	0.32	367
557	n.d.	n.d.	n.d.	n.d.
658	47.6	8.3	0.44	431
704	49.3	8.7	0.43	437
930	53.4	9.6	0.53	456
1091	59.4	10.9	0.66	463
1286	63.2	10.9	0.67	466
1448	67.7	11.6	0.67	480
N2 litter				
0	0	7	0.34	269
202	15.5	7.2	0.39	344
305	28.5	7.6	0.37	369

(*continued*)

Table VII.1 (*continued*)

Incubation time (days)	Accumulated mass loss (%)	N (mg g^{-1})	P (mg g^{-1})	lignin (mg g^{-1})
350	32.2	7.7	0.38	
557	n.d.	n.d.	n.d.	n.d.
658	50	11.3	0.57	442
704	51.1	11.8	0.53	453
930	53.6	11.9	0.58	453
1091	60	12.8	0.68	466
1286	64.8	13.8	0.68	467
1448	70.4	13.4	0.69	490
N3 litter				
0	0	8.1	0.42	268
202	18.3	8.8	0.4	353
305	30.3	9.1	0.39	388
350	36.3	11.2	0.44	401
557	n.d.	n.d.	n.d.	n.d.
658	50.7	13.8	0.63	452
704	53	13.9	0.59	464
930	58	14.4	0.68	469
1091	60.4	14.3	0.72	458
1286	64.9	15.2	0.71	481
1448	67.6	14.9	0.72	480

Exercise VIII. Nitrogen Dynamics—Concentrations and Amounts

Problem Presentation

The data set below originates from decomposing local Scots pine needle litter in a boreal Scots pine monoculture stand, covering approximately 3 ha. Bags were incubated on 20 spots, distributed randomly all over the stand. At each sampling, 20 replicate litter bags were collected. Litter mass loss was determined and nitrogen concentration was measured on combined samples from each sampling (Table VIII.1).

The task in this exercise is to calculate and plot the changes in absolute amount and in concentrations of N with time for decomposing Scots pine needle litter using the following data set.

Table VIII.1 Litter mass loss and N concentration during decomposition of Scots pine needle litter

Time (days)	Litter mass loss (%)	N concentration (mg g^{-1})
0	0	4.8
204	15.6	5.1
286	22.4	5.4
358	29.9	5.4
567	38.4	8.3
665	45.6	9.2
728	47.5	8.8
931	54.1	9.8
1021	58.4	11.1
1077	62.5	11.5
1302	66.0	12.2
1393	67.4	12.5

Exercise IX: Increase Rate in Litter N Concentration

Problem Presentation

The data set to be used in this exercise is that in Table VIII.1, which originates from decomposing local Scots pine needle litter in a boreal Scots pine monoculture stand, covering approximately 3 ha. Bags were incubated on 20 spots, distributed randomly all over the stand. At each sampling, 20 replicate litter bags were collected. Litter mass loss was determined and nitrogen concentration was measured on combined samples from each sampling.

The task in this excercise is to calculate the increase rate in litter N concentration.

Exercise X: Differences in Increase Rates for Nitrogen Concentrations

Problem Presentation

Two litter types have been incubated in the same stand during the same time period and using the same incubation and sampling design. The data originate from decomposing green and brown local Scots pine needle litter incubated in a boreal Scots pine monoculture (Table X.1). Twenty replicate litter bags were taken of each litter type at each sampling.

The task in this exercise is to calculate the increase rate in litter N concentration in the two litter types and to determine whether the slopes (NCIR) are significantly different.

Table X.1 Accumulated mass loss and corresponding N concentration in decomposing green and brown Scots pine needles

Green needle litter		Brown needle litter	
Mass loss (%)	N (mg g^{-1})	Mass loss (%)	N (mg g^{-1})
0	15.1	0	4.8
23.3	19.0	15.6	5.1
28.8	20.8	22.4	5.4
38.0	23.8	29.9	5.4
44.9	27.3	38.4	8.3
48.8	30.4	45.6	9.2
52.1	30.8	47.5	8.8
54.2	30.7	54.1	9.8
58.0	31.7	58.4	11.1
60.5	29.5	62.5	11.5
63.4	31.6	66.0	12.2
65.9	31.6	67.4	12.5

Exercise XI: Calculating the Sequestered Fraction of Litter N

Problem Presentation

During a 4-year experiment, you have collected the following data (Table XI.1) for the decomposition of Scots pine needle litter. The experiment was performed in a Scots pine monoculture covering 3 hectares and there were 20 litter bag replicates in each sampling. For each sampling date, you have the accumulated litter mass loss and N concentration in the litter.

The task is to calculate the fraction of the original amount of N that will be stored in the recalcitrant part of the litter.

Table XI.1 Accumulated mass loss and N concentrations in decomposing Scots pine needle litter

Days	Accumulated mass loss (%)	N conc (mg g^{-1})
0	0	4.8
204	15.6	5.1
286	22.4	5.4
358	29.9	5.4
567	38.5	8.3
665	45.6	9.2
728	47.5	8.8
932	54.1	9.8
1024	58.4	11.1
1078	62.5	11.5
1304	66.0	12.2
1393	67.4	12.5

Exercise XII: Nitrogen Stored in Litter at the Limit Value

Problem Presentation

This exercise is related to exercise XI, in which you calculated the fraction of remaining nitrogen in a foliar litter that had reached the limit value or the humus stage. In that exercise, you started with accumulated mass-loss values and N concentrations. In the present case, we have simplified the task somewhat since we give the calculated limit values and N concentrations at the limit value for seven litter types. See Table XII.1.

The task is to calculate (i) the amount of N that is stored in the remains of what initially was 1.0 gram litter, and (ii) the fraction of initial litter N that is stored in the recalcitrant remains.

Table XII.1 Initial N concentrations in seven different litter species and related estimated asymptotic decomposition limit values and N concentrations at the limit value

Litter type	Initial N conc. (mg g^{-1})	Limit value (%)	N conc. at limit value (mg g^{-1})
Lodgepole pine	4.0	94.9	13.6
Scots pine	4.2	81.3	12.76
Scots pine	4.8	89.0	14.7
Norway spruce	5.44	74.1	14.46
Silver birch	9.55	77.7	22.71
Common beech	11.9	59.1	24.05
Silver fir	12.85	51.5	21.93

SECTION II: SOLUTIONS TO EXERCISES

Exercise I: Foliar Litter Fall

There are several ways to solve the problem and we will give two slightly different ones. One is to simply add the amounts collected in each litter trap that is not disturbed, which is 13, calculate an average value per litter trap, which also is the average litter fall per 0.25 m^2. We obtain a value of 71.08 grams (SD = 18.4), which means 284.32 grams per square meter or 2843.2 kg per hectare.

An alternative is to calculate an average value per sampling using n = 15 in sampling 1, and n = 14 in samplings 2 and 3. The values we obtain for the separate samplings Nos. 1, 2, and 3 are thus the average values for 0.25 m^2, and, in this case, 71.4 grams per trap or 2856 kg per hectare. An advantage is that in this latter case we use all values:

Litter trap No.	Sampling 1	Sampling 2	Sampling 3	
1	45	18	10	73
2	61	15	14	90
3	42	19	15	76
4	21	9	8	38
5	55	11	7	73
6	59	9	5	73
7	75	16	7	98
8	52	14	11	77
9	48	13	17	78
10	19	5	2	26
11	38	22	12	72
12	43	–	8	
13	62	13	5	80
14	59	14	-	
15	44	12	14	70
Average[b]	48.2	13.6	9.6	71.1[a]/71.4[b]

[a]Average using the 13 litter traps.
[b]Average value per sampling including intact traps only.

Exercise II: Comparing Foliar Litter Fall of Different Tree Species

The way to set up a study with measurements on litter fall such as the present one is to arrange the stands in blocks. A not uncommon situation is that you may obtain values from experiments for which the design is less clear or not well described and the results of statistical tests may then become less clear. In the present case, the stands were actually arranged in a block design with four blocks, each block having one stand of Sitka spruce and one stand of Austrian pine. Thus, we have four paired stands, each pair consisting of the two species.

This is a typical "comparison problem," one of the most widely met problems in natural sciences. Not surprisingly, a broad range of methods have been developed to compare populations (in statistics, the term *population* has a somewhat different meaning than in biology and means simply a group of objects that are studied). In this section, we present only a few examples of how the problem can be approached.

Solution I. One of the simplest methods that can be used to compare two populations, not necessarily blocked in pairs, is the Student's *t*-test. One can also use the simple analysis of variance (ANOVA), which with two groups being compared is equivalent to Student's *t*-test. This method can be used any time, even if stands were not paired. Remember, however, that without blocking (for example, with stands distributed randomly over larger areas), differences that you would detect between species might be actually caused by differences in local climate or soil rather than by species-specific

characteristics. In each case, care must be also taken of the assumptions of the method (normal distribution and homoscedascity, that is, constant residual variances across treatments).

Below, we give a printout from such an analysis:

One-Way ANOVA - II_Litter fall by II_Species

Analysis Summary

Dependent variable: II_Litter fall
Factor: II_Species

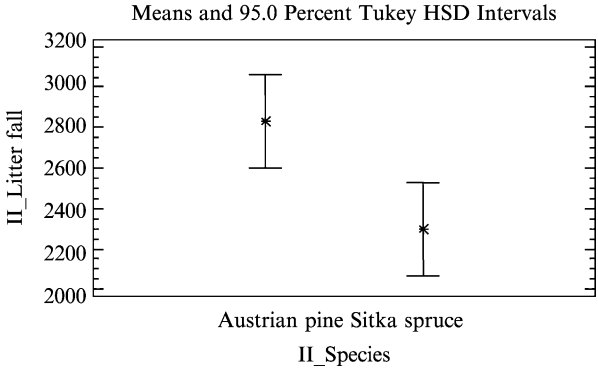
Number of observations: 8
Number of levels: 2

ANOVA Table for II_Litter fall by II_Species

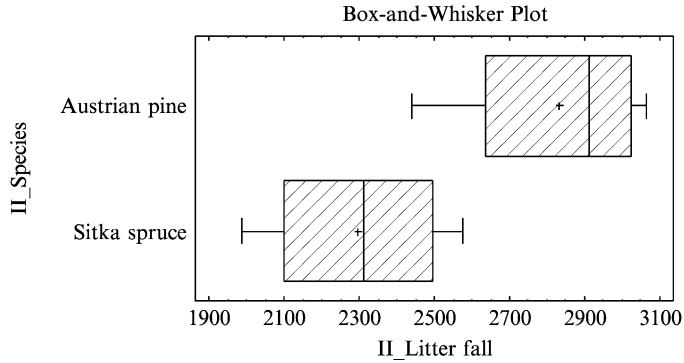
Analysis of Variance

Source	Sum of squares	Df	Mean square	F-ratio	P-value
Between groups	568711.0	1	5687110	7.97	0.0302
Within groups	428142.0	6	71357.0		
Total (Corr.)	996853.0	7			

Comment: *The analysis of variance divides the variance of the variable studied (in this case, litter fall) into two components: a between-group component and a within-group component. The F-ratio is a ratio of the between-group estimate to the within-group estimate. The p value indicates the probability of type I error and is called the significance level. In this particular case, the significance level is ca. 0.03, meaning that the difference observed between the average litter fall values for the two species may result from pure chance rather than representing the real difference between the species only in 3 cases of 100. In natural and social studies, it is commonly accepted that the difference is assumed to be true if p is lower or equal to 0.05.*



Comment: *There is a number of methods to calculate confidence intervals around mean values when comparing populations. In this case, we used the so-called "Tukey Honestly Significant Difference" (HSD) intervals. This method offers a good balance in protection against type I and type II errors.*



Comment: *As mentioned in Chapter 9, Box-and-Whisker plot gives very rich information about a data set. Here, you can see medians (the central vertical lines inside the boxes), lower and upper quartiles (the boxes to the left and to the right of the median, respectively), means (small crosses inside the boxes), and minima and maxima (whiskers to the left and to the right of the boxes, respectively). The asymmetry of a box around the median value also gives some information about data distribution, i.e., if the data approximately follow the normal distribution or are heavily skewed to the right or to the left.*

Solution II. Although the method presented in the preceding text is correct and very general, we did not make any use of the fact that the experiment was designed in paired stands. This actually may be an important advantage since we know that, in each pair, the two species grew in exactly the same climate and on similar soil. Some of the variance unexplained in ANOVA, and thus adding to the error, may be explained by the variance between the stands which, however, should not affect differences between the species in litter fall. So, we make use of the differences in annual litter fall, namely 636, 486, 449, and 571 kg/ha^{-1}. Thus, we will use another comparison method–developed especially to compare paired samples:

Paired Samples - Ap litterfall & Sp litterfall

```
Analysis Summary

Data variable: Ap litterfall-Sp litterfall

4 values ranging from 449.0 to 636.0

Summary Statistics for Ap litterfall-Sp litterfall
```

Comment: *Note that this time all statistics are calculated not for each species separately but for the difference in litter fall between the species in paired stands. Thus, the hypothesis tested is not that mean litter fall of species 1 equals mean litter fall of species 2 but that the mean difference between the species equals 0.*

```
Count = 4
Average = 533.25
Median = 528.5
Variance = 6514.92
Standard deviation = 80.715
Minimum = 449.0
Maximum = 627.0
Range = 178.0
Stnd. skewness = 0.180395
Stnd. kurtosis = -1.19441

Hypothesis Tests for Ap litterfall-Sp litterfall

Sample mean = 533.25
Sample median = 528.5

t-test
-----------
Null hypothesis: mean = 0.0
Alternative: not equal

Computed t statistic = 13.2132
P-Value = 0.00093663
```

Comment: *Please note that when we used the information about paired stands, we obtained a much higher significance level (that is, smaller p value = 0.000937). Thus, with exactly the same data as before, by performing the analysis that makes use of additional information about pairing the stands, we obtained much stronger "confirmation" of the hypothesis that the species do differ in amount of litter fall.*

Exercise III: Foliar Litter Fall in a Climatic Transect after Climate Change

In the present problem, the equation basically gives us the answer. First, we calculate the new AET value, which was 27% higher than the old one, or 514 mm. This value is used in the relationship given on page 339 and yields the value of 2569 kg/ha^{-1}.

Exercise IV: Calculating Litter Mass Loss

The litter that you originally weighed, placed in litterbags, which then were incubated, later was air dried and contained 6.04% water. To obtain the real dry mass, you need to subtract the 6.04% of water. When you have done that (column 2 in table below), you will have a new set of values for litter mass dried at 85°C. Here, we have organized those values in a new column, giving that weight (original litter dry weight). To calculate litter mass loss, you now simply use the data in columns 2 and 3 and obtain the mass loss values in column 4. A comment: when using this method, the standard error normally is below 1.7 up to about 60% mass loss. The reason for the higher SE value here may be that the litter was incubated in four blocks of which one block deviated as regards moisture and the litter decomposed somewhat faster there (last five values).

Original litter "wet" weight (g per bag)[a]	Original litter dry weight (g per bag)[b]	The same litter after 366 days incubation (g per bag)[b]	Mass loss (%)
0.613	0.576	0.2783	51.7
0.615	0.578	0.2605	54.9
0.611	0.574	0.2802	51.2
0.611	0.574	0.1798	68.7
0.614	0.577	0.2733	52.6
0.616	0.579	0.2944	49.1
0.615	0.578	0.2449	57.6
0.612	0.575	0.1880	67.3
0.618	0.581	0.2551	56.0
0.614	0.577	0.3031	47.5
0.617	0.580	0.2049	64.7
0.610	0.573	0.1612	71.9
0.618	0.581	0.2443	58.0
0.619	0.582	0.2533	56.5
0.615	0.578	0.3037	47.5
0.613	0.576	0.1923	66.6
0.617	0.580	0.1650	71.5
0.619	0.582	0.1717	70.4
0.613	0.576	0.1422	75.3
0.613	0.576	0.1098	80.9
			Average 61.0 Standard dev. 9.8 Standard error 2.2

[a]Litter dried at room temperature.
[b]Litter dried at 85°C.

Exercise V: Calculating Annual Litter Mass Loss During Decomposition

As a first step, we suggest that you draw a graph showing accumulated mass loss against time, as shown on Fig. V.1. In the (approximately) first year, the mass loss was 27.3%, leaving 72.7% as remaining mass. For year 2, which is the period between day 376 and day 734, we simply consider the remaining substrate on day 376 and its chemical composition as a new starting point. Thus, the amount of substrate is the remaining mass, namely, 72.7% of the original material, which may be regarded as the initial substrate for the decomposition in the 2nd year.

We have noted that many of us prefer not to think in the unit % but rather in an imaginary specific amount of litter, so let us say that we initially had samples with 1.0 gram in each. With 27.7% mass loss in the first year, the remaining amount was $1.0 - 0.273$ g, or 0.727 g. After two years' decomposition, the accumulated mass loss was 45.8% and the remaining amount thus 0.542 g. The mass loss in the second year is the amount of the substrate at the beginning of the second year minus what remained after 2 years (0.727 – 0.542 g). To obtain the percentage decomposition, we divide by the initial amount at the start of the second year, which yields the fraction. By multiplying by 100, we recalculate the fraction to %. The expression thus becomes $100 \times (0.727 - 0.542)/0.727$, giving the mass loss of 25.4% of the amount still remaining after 1 year decomposition.

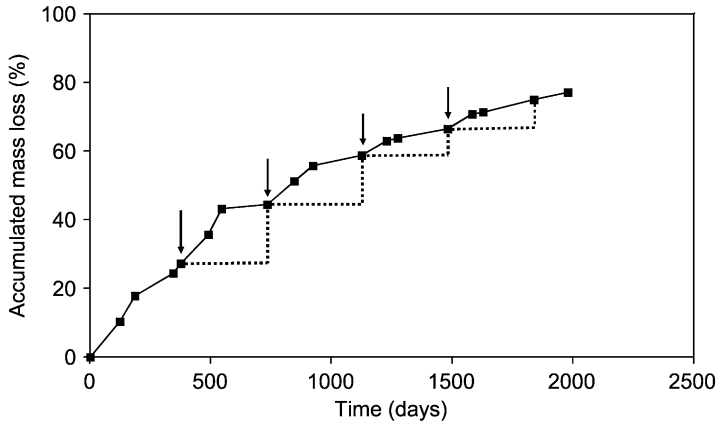


Figure V.1 Accumulated litter mass loss plotted versus time. Arrows indicate the samplings made at approximately 1-year intervals and the dotted horizontal and vertical lines show the period and the intervals for accumulated mass loss, respectively, that are used as basic units for calculating the annual mass loss.

When we perform the same operation for year 3, we obtain the expression $100 \times (0.542 - 0.412)/0.542$, which gives a mass loss of 24.0%. For year 4, the expression is $100 \times (0.412 - 0.335)/0.412$ which gives a mass loss of 18.7%, and for year 5 it is $100 \times (0.335 - 0.250)/0.335$, or a mass loss of 25.4%.

We can object about this kind of calculation that some sampling times deviate from a year, which, of course, is a weakness that has been illustrated in the present example. However, in an example such as this, the average decomposition per day would be approximately 0.07%, which means that a few days difference are not that important. As the reader probably has noted about the data, the three samplings per year are made in early summer, in September, and in late autumn. With a data set such as this one, it is, of course, possible to select any one-year period. We have chosen one-year periods starting with the original incubation date, which is not necessary. As the litter chemical composition and, in part, the weather is different among the samplings, we may use all possible one-year periods without risk of using the same information twice. In the present data set, there are about 14 periods encompassing about one year and how many days the chosen periods should be allowed to deviate from 365 days can be decided upon for each data set and the purpose of the calculation.

Exercise VI: Describing the Accumulated Litter Mass Loss Dynamics by Functions

The evident way of solving the problem is to fit the equations described earlier in the book, namely, the one-compartment exponential function (first-order kinetics model), the two-compartment model, and the asymptotic model. In the following text, you can see printouts from such analyses with some comments about the results obtained. Considering that different software packages offer slightly different sets of information, only the most important information from the report has been retained.

Please note that to meet the requirements of the different models fitted, the data were used either as given previously (accumulated mass loss in percent, AML) or recalculated to remaining mass (100-AML). Also, time has been expressed in years rather then in days since k values are usually reported per year, and when given per day, the values become very small and less convenient for reporting.

Nonlinear Regression–alder leaves, one-compartment (Olson's) model

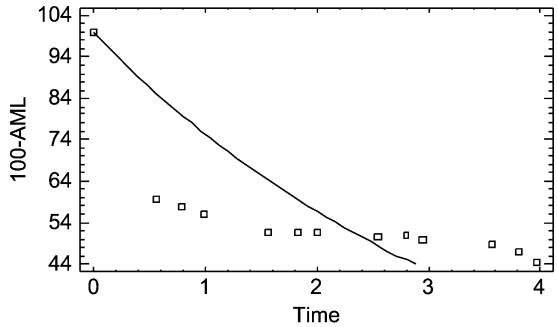
```
Dependent variable: 100-AML
Independent variables: time
Function to be estimated: 100*exp(k*time)
```

Estimation Results

Parameter	Estimate	Asymptotic standard error	Asymptotic 95.0% confidence interval Lower	Upper
k	−0.284802	0.0368065	−0.364997	−0.204607

R-Squared = 1.47508 percent
R-Squared (adjusted for d.f.) = 1.47508 percent

The output shows the results of fitting a nonlinear regression model to describe the relationship between 100-AML and 1 independent variable. The equation of the fitted model is 100*exp(−0.284802*time)



Comment: *Please note that although the estimated k value is significant (i.e., differs significantly from 0 at 95% confidence level as indicated by the estimated 95% confidence intervals reported in the table), the fit is actually very poor. The R^2 is less than 1.5%, ($R^2 = 0.015$) and the fitted line obviously does not describe the decomposition of alder leaves well. It can be clearly seen from the plot given above that at the early decomposition stage, the actual decomposition rate is substantially higher than predicted by the model, while at the late stage, the litter decomposes slower than the model would predict. Thus, we should conclude that the Olson's model, even if significant, is inadequate for describing decomposition of grey alder leaves.*

Nonlinear Regression–lodgepole pine needles, one-compartment (Olson's) model

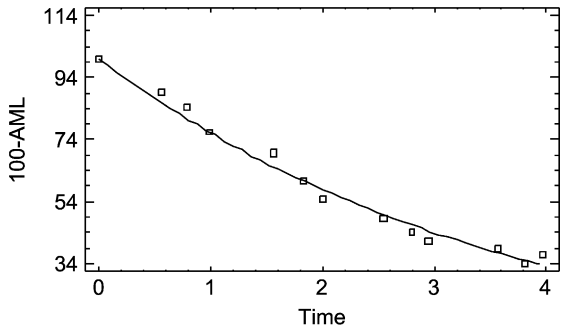
Dependent variable: 100-AML
Independent variables: time
Function to be estimated: 100*exp(k*time)

Estimation Results

Parameter	Estimate	Asymptotic standard error	Asymptotic 95.0% confidence interval Lower	Upper
k	−0.273737	0.00695995	−0.288902	−0.258573

R-Squared = 98.4866 percent
R-Squared (adjusted for d.f.) = 98.4866 percent

The output shows the results of fitting a nonlinear regression model to describe the relationship between 100-AML and 1 independent variable. The equation of the fitted model is 100*exp(−0.273737*time)



Comment: *In contrast to grey alder leaves, the decomposition of lodgepole pine needles seems to be described well by the Olson's model. Note that as much 98.5% of the variability in mass loss is described by the model. We could thus conclude that lodgepole pine needles decompose following the simple, one-compartment model at least within the investigated interval for accumulated mass loss. However, we should still check whether the other two models do not explain the decomposition of lodgepole pine needles even better.*

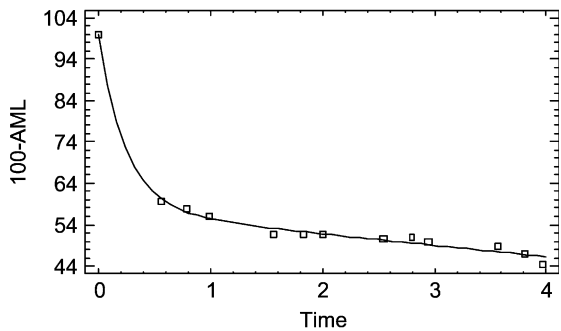
Nonlinear Regression–grey alder leaves, two-compartment model

Comment: *Note that in this model, we have two decomposition constants, k1 and k2. We also have two compartments, w1 and w2, which represent two different groups of organic matter, namely,'easy-decomposable' and 'resistant' parts of organic matter, expressed as percentages in the initial material.*

```
Dependent variable: 100-AML
Independent variables: time
Function to be estimated: w1*exp(k1*time) + w2*exp(k2*time)
Initial parameter estimates:
  w1 = 20.0
  k1 = -1.0
  w2 = 80.0
  k2 = -0.0001

Estimation Results
```

			Asymptotic 95.0% confidence interval	
Parameter	Estimate	Asymptotic standard error	Lower	Upper
w1	42.1254	1.73477	38.201	46.0497
k1	-4.15049	0.66995	-5.66603	-2.63496
w2	57.8601	1.33276	54.8451	60.875
k2	-0.0552087	0.00831569	-0.0740201	-0.0363973

```
R-Squared = 99.5194 percent
R-Squared (adjusted for d.f.) = 99.3592 percent

  The output shows the results of fitting a nonlinear regression
model to describe the relationship between 100-AML for alder and 1
independent variable. The equation of the fitted model is
42.1254*exp(-4.15049*time + 57.8601*exp(-0.0552087*time)
```



Comment: *Note how much better the two-compartment model fits the data for grey alder leaves, explaining almost 100% of the variability in mass loss. We would conclude that grey alder leaves apparently contain two very different compartments of organic matter: approximately 42% of easily decomposed*

matter with a k value of −4.2, and approximately 58% of resistant substrate decomposing at a k value as low as −0.055. The latter k value, although low, is still significantly different from 0, indicating that indeed this part of litter is not completely resistant to decomposition, although it decomposes at a very low rate as seen in the previous figure.

Nonlinear Regression—lodgepole pine needles, two-compartment model

Comment: *As we have mentioned, although the single exponential model fits well to the decomposition data for lodgepole pine litter, we will still use the two-compartment model to investigate for possible distinction between resistant and easily decomposable fractions in this litter.*

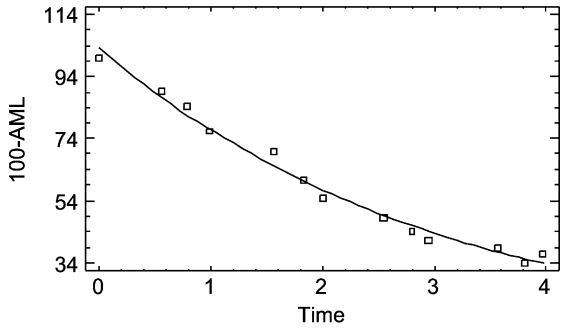
```
Dependent variable: 100-AML
Independent variables: time
Function to be estimated: w1*exp(k1*time) + w2*exp(k2*time)
Initial parameter estimates:
  w1 = 80.0
  k1 = -1.0
  w2 = 20.0
  k2 = -0.0001

Estimation Results
```

			Asymptotic 95.0% confidence interval	
Parameter	Estimate	Asymptotic standard error	Lower	Upper
w1	102.398	16.257	65.6223	139.174
k1	−0.303766	0.129616	−0.596979	−0.0105539
w2	0.768211	17.432	−38.6659	40.2023
k2	0.383385	4.13055	−8.96058	9.72736

```
R-Squared = 98.7407 percent
R-Squared (adjusted for d.f.) = 98.321 percent
```

The output shows the results of fitting a nonlinear regression model to describe the relationship between 100-AML for Lp and 1 independent variable. The equation of the fitted model is

```
102.398*exp(-0.303766*time) + 0.768211*exp(0.383385*time)
```



Comment: *The two-compartment model also seems to fit the data for lodgepole pine needles quite well with* $R^2_{adj} = 98.3\%$*, which is only marginally lower than the* R^2 *obtained with the single exponential model. To solve the question of whether there are one or two compartments in lodgepole needle litter, look closely at the results table. You will notice that the estimate for the first compartment is 102% and does not differ significantly from 100% and that both parameters describing the second compartment, k2 and w2, are not significant (i.e., their 95% confidence intervals cover 0). Thus, we may reject the hypothesis that the lodgepole pine needle litter consists of two compartments with different decomposition rates.*

Nonlinear Regression—alder leaves, asymptotic model

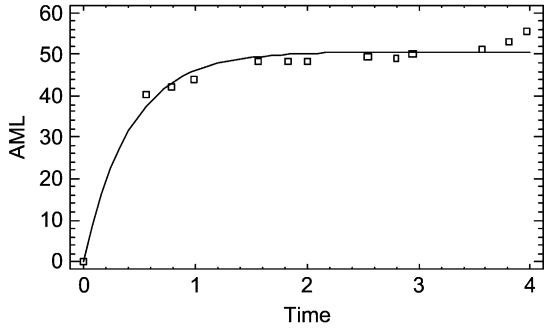
Comment: *Note that this is a two-parameter model: besides the k value (which is not equivalent to the k values from the single and the two-compartment models described earlier in the book), the asymptote m is also estimated.*

```
Dependent variable: AML
Independent variables: time
Function to be estimated: m*(1-exp((k*tyrs)/m))
Initial parameter estimates:
  m = 60.0
  k = -100.0

Estimation Results
```

			Asymptotic 95.0% confidence interval	
Parameter	Estimate	Asymptotic standard error	Lower	Upper
m	50.6259	0.786011	48.8959	52.3559
k	-122.466	11.4297	-147.623	-97.3095

```
R-Squared = 97.7356 percent
R-Squared (adjusted for d.f.) = 97.5298 percent
```

The output shows the results of fitting a nonlinear regression model to describe the relationship between Alder aml and 1 independent variable. The equation of the fitted model is 50.6259*(1−exp((−122.466*time)/50.6259))



Comment: *The asymptotic model fits well the decomposition dynamics of the grey alder leaves with both estimated parameters, k and m, significant. Thus, we cannot reject the hypothesis that the decomposition of alder leaves stops after approximately 2.5 years of decomposition. This undecomposable fraction has been estimated to 50.6%. Notice however, that the* R^2_{adj} *value is lower in this model than in two-compartment one (97.5% versus 99.4%). Thus, although both regressions are significant, the two-compartment model gives a better fit and explains the decomposition dynamics better.*

Nonlinear Regression—lodgepole pine needles, asymptotic model

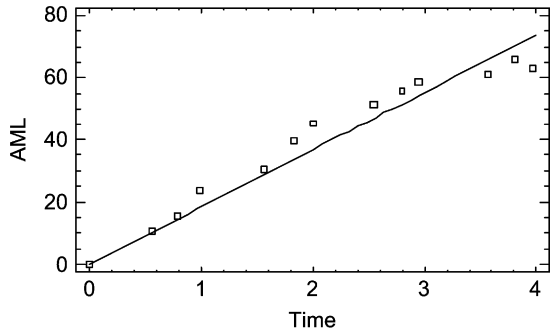
Dependent variable: AML
Independent variables: time
Function to be estimated: m*(1−exp((k*time)/m))
Initial parameter estimates:
m = 80.0
k = −10.0

Estimation Results

			Asymptotic 95.0% confidence interval	
Parameter	Estimate	Asymptotic standard error	Lower	Upper
m	5.10074E8	2.88789E8	−1.25548E8	1.1457E9
k	−18.4271	0.633325	−19.8211	−17.0332

R-Squared = 94.1361 percent
R-Squared (adjusted for d.f.) = 93.603 percent

```
The output shows the results of fitting a nonlinear regression
model to describe the relationship between Lp aml and 1 independent
variables. The equation of the fitted model is
5.10074E8*(1-exp((-18.4271*time)/5.10074E8))
```



Comment: *Although the asymptotic model explains as much as 93.6% of the variability in the decomposition dynamics of the lodgepole pine needles, the asymptote m is apparently not significant. Thus, we may reject the hypothesis that the lodgepole needles do not decompose completely.*

Final conclusion:

After analyzing the three different models of litter decomposition for the grey alder leaves and the lodgepole pine needles, we may conclude that the two litter types differ substantially in their decomposition patterns and rates. The lodgepole pine needles follow the one-compartment decay model described by one decomposition constant k, with the asymptote giving 0% remaining material (that is, asymptotically 100% decomposition). In contrast, the grey alder leaf litter consists of two markedly different fractions, one being easily decomposable and composing approximately 42% of the organic matter and the other decomposing very slowly and forming the remaining 58% of the matter, which alternatively may be called recalcitrant.

Exercise VII: Regulating Factors for Decomposition Rates

One way of determining the decomposition rate is to use the mass loss over a certain period, e.g., one year. We discussed in the Exercise V how to do this and that we may consider the remaining litter as a new substrate with a new chemical composition at the start of each such one-year period. As a first step in solving the problem we have calculated the one-year mass loss values and listed them in the following table. In principle, we can take any period

that covers 365 days, but since we want to determine the substrate quality factors that influence litter mass loss rate, we want to avoid the influence of climate and we do that by selecting and comparing periods for which the climate (or weather) is constant for all five litter types.

So, after some calculation, you will have a new data base with 20 numbers:

	Yearly mass loss			
Litter type	yr 1	yr 2	yr 3	yr 4
Ih	26.5	29.4	22.8	19.0
N0	32.7	27.4	22.1	18.0
N1	31.3	26.6	19.3	20.4
N2	32.2	27.9	17.3	26.7
N3	36.3	26.3	15.7	18.2

In this way, we may find which factors determine the decomposition rate during the consecutive years of decomposition and, thus, how they change in the course of decomposition.

Let us start with the first year mass loss to see what regulated the mass-loss rate during that period. In a linear regression between 1st year mass loss and concentrations of single nutrients, we obtained $R = 0.99$ for P, $R = 0.76$ for N and $R = 0.03$ for lignin ($n = 5$). Of these relationships, only that to P is significant at $p < 0.05$.

We continue with year 2. For N, we obtain $R = -0.580$; for P, R becomes $= -0.762$; and for lignin, R is $= -0.815$. Of these relationships, the best one is that to lignin, although not quite significant at $p < 0.1$.

For year 3, we obtain the following: for N, an R value of -0.926; $p < 0.05$; for P, an R value of -0.898; $p < 0.05$; and for lignin, an R value of -0.917; $p < 0.05$.

For year 4, we obtain for N an R value of 0.663, for P an R value of 0.000, and for lignin an R value of 0.338. None was significant at $p < 0.1$.

An overview of the R-values gives us the following table:

	N	P	Lignin
Year 1	+0.76	+0.99	+0.03
Year 2	−0.580	−0.762	−0.815
Year 3	−0.926	−0.898	−0.917
Year 4	0.663	0.000	0.338

The R values in the table may be interpreted as follows:

In the first year, the concentration of P has a stimulating effect on the decomposition process which is significant. Although no really significant effect of N is seen, the high R value gives some support to the hypothesis that

there is a stimulating effect of the main nutrients in the first year of decomposition. We have seen (chapter 4) that the components that are decomposed in the first year for Scots pine needles are mainly water solubles and hemicelluloses and, according to basic physiology, their degradation should be stimulated by higher levels of the main nutrients. It also appears that there is no effect of lignin. According to the existing information, lignin should be degraded slowly, at least in the presence of N at the levels found in foliar litter.

In the second year, the relationships to N and P are negative, suggesting a suppressing effect of the two main nutrients on decomposition. The concentrations of both of these nutrients increase during the decomposition process so, had there been a stimulating effect of one of them or of both, that should have been seen not only as positive R values but also as a generally higher rate in the second year. The mass loss data for year 2 show that the most N- and P-poor litter has the highest mass loss and the litter being the most nutrient-rich has the lowest rate. We may look at the relationship to lignin, which is negative. Although not really significant, we may say that $p < 0.1$ suggests some effect. Lignin has been suggested as a compound that is resistant to decomposition and we can see, for example, in Chapter 4, that its degradation starts late and that its concentration increases as decomposition of the whole litter proceeds, or expressed in another way–lignin has a slower decomposition than other litter components. A reasonable conclusion is that there may be a suppressing effect of lignin on the decomposition rate. Thus, in the second year, there may be a change in factors that regulate litter mass loss rate and judging from the R values, lignin concentration may have a strong negative influence. We have seen in Chapter 4 that litter N concentration may have a suppressing effect on lignin degradation rate but the R value is rather low to allow us to suggest such an effect. See also Fig. VII.1.

In the third year, the negative effect of lignin is statistically significant, as is a negative relationship to N. The negative relationship to P may not necessarily be interpreted biologically since there is no known such suppressing effect of P on, for example, lignin degradation. The high R value may simply be due to the fact that the concentrations of both N and P increase with accumulated mass loss. These relationships support what we found for year 2. See also Fig. VII.1.

The R values for the fourth year do not give any clear picture of regulating factors and we cannot exclude that lignin concentration as a regulating factor has been replaced by another one as the R value now is lower. See also Fig. VII.1.

Years 2 and 3 combined. We may combine the values for, say, years 2 and 3 and investigate a relationship with $n = 10$. We can see that the negative relationship between annual mass loss and lignin concentration was improved (Fig. VII.1). A combination of N and lignin in a multiple regression did not add any further explanation ($R^2 = 0.866$ for lignin and $R^2 = 0.868$ for

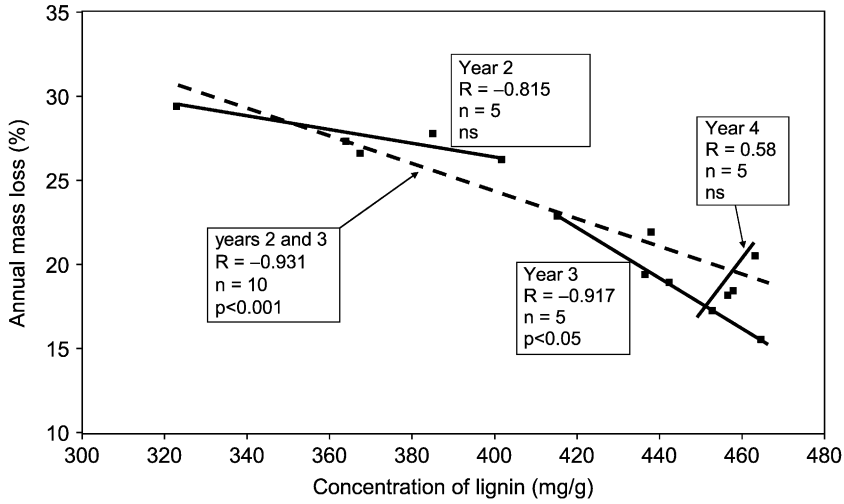


Figure VII.1 Linear relationships between concentration of lignin and annual mass loss. Full lines give mass losses for the single years 2, 3, and 4 and the dashed line gives the regression for years 2 and 3 combined.

lignin and N). We should be aware that we have now used two different years and that a difference in climate between years may influence the result.

A general conclusion of this investigation is that we may see an early stage illustrated by the mass loss in year 1. In years 2 and 3, the mass losses appear regulated by lignin degradation, which may constitute another (later) stage. Finally, in the last year, it appears that the regulating effect of lignin disappears. Still, we can only observe this, and hypothesize that a next stage appears but, in this investigation, we cannot distinguish any regulating factor.

Exercise VIII: Nitrogen Dynamics–Concentrations and Amounts

Solution I. To plot N concentration versus time is relatively simple since all information is already there. To plot the changes in absolute amount, you need to calculate the values for absolute amount. By absolute amount we mean, of course, the remaining amount as related to the initial amount. For example, in the initial litter, 1.0 g contains 4.8 mg N. After 15.6% decomposition, 0.844 grams remain with a concentration of 5.1 mg/g. By multiplying 0.844 by 5.1, we obtain the remaining amount of N, which is 4.3 mg. Performing these calculations, we obtain the following data set. As some

Time (days)	Litter mass loss (%)	Remaining amount of litter (g)	N concentration (mg/g)	N abs. amount (mg)
0	0	1.000	4.8	4.8
204	15.6	0.844	5.1	4.3
286	22.4	0.776	5.4	4.2
358	29.9	0.701	5.4	3.8
567	38.5	0.615	8.3	5.1
665	45.6	0.544	9.2	5.0
728	47.5	0.525	8.8	4.6
931	54.1	0.459	9.8	4.5
1021	58.4	0.416	11.1	4.6
1077	62.5	0.375	11.5	4.3
1302	66.0	0.340	12.2	4.1
1393	67.4	0.326	12.5	4.1

of us may find it easier to imagine remaining amounts of a certain given original mass, we have chosen to use the unit 1.0 gram as an imaginary initial amount.

With this data set, we may plot the data. As we can see (Fig. VIII.1), the concentration increases as far as the litter decomposition process was followed. We can also see that for this litter type, there are just small fluctuations in amount, and at the end of the measurements, most of the N is still bound to the litter structure.

Solution II. If we need to test formally whether the concentration or amount changes significantly with time (that is, can we really say that the concentration or amount increases/decreases or that the changes can be considered a random variance) we have to perform a slightly more complicated

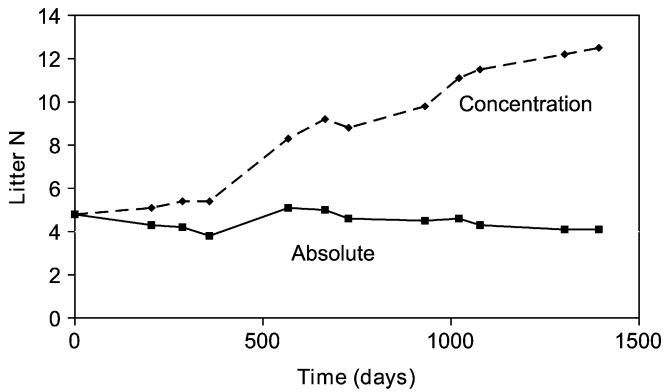


Fig. VIII.1 Plot of the dynamics in N concentration and N amounts in decomposing litter with time.

task, namely, the regression analysis. In this particular case, the increase in concentration seems approximately linear for the time span used in the investigation so we will apply the linear regression. As in earlier exercises, you will find below a printout from a statistical program with some comments.

Simple Regression - VIII_N conc vs. VIII_time

Regression Analysis - Linear model: Y = a + b*X

Dependent variable: VIII_N conc
Independent variable: VIII_time

Parameter	Estimate	Standard error	T statistic	P-value
Intercept	4.15835	0.34294	12.1256	0.0000
Slope	0.00635253	0.000413599	15.3592	0.0000

Analysis of Variance

Source	Sum of squares	Df	Mean square	F-ratio	P-value
Model	88.1268	1	88.1268	235.90	0.0000
Residual	3.73571	10	0.373571		
Total (Corr.)	91.8625	11			

Correlation Coefficient = 0.979456
R-squared = 95.9334 percent
R-squared (adjusted for d.f.) = 95.5267 percent

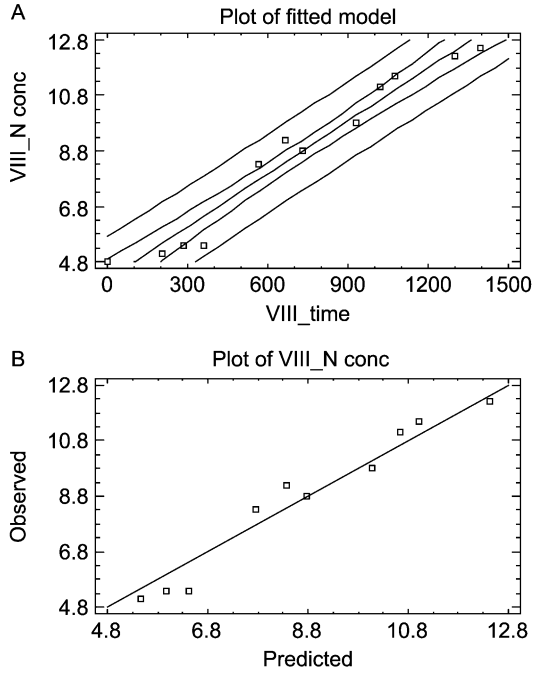
The output shows the results of fitting a linear model to describe the relationship between VIII_N conc and VIII_time. The equation of the fitted model is

VIII_N conc = 4.15835 + 0.00635253*VIII_time

Since the P-value in the ANOVA table is less than 0.01, there is a statistically significant relationship between VIII_N conc and VIII_time at the 99% confidence level.

Comment: *As could be expected from the simple X–Y plot (Fig. VIII.1), the relationship between time and N concentration appeared highly significant. The relationship itself can be seen in the following text as a plot of the fitted model, including the original data points as well as 95% confidence limits (inner bounds) and 95% prediction limits (outer bounds). The latter indicate the area around the regression line, where 95% of real observations should fall. Before we are satisfied with the regression, we should investigate whether we*

have selected a proper model. It may happen that although the model is significant, it is not really a good model for a particular data set. For example, a linear regression would be significant when used to describe the relationship between litter mass loss and time, but it is certainly not a good model when the relationship is nonlinear. Whether the model is proper can be checked simply by looking at the "observed versus predicted" plot (plot below). If the model fits the data set well, then the points should be randomly distributed around the 1:1 line. Any clear deviation from this random distribution (e.g., points drop down off the 1:1 line at the upper end) suggests that we should look for a better model. In this particular case, there are no indications of bad fit of the model so we may accept the hypothesis that N concentration increases approximately linearly in the litter studied throughout the whole incubation time. There is also a more formal test for the goodness of fit, but it requires that the data are replicated at least at some points. Thus, from that point of view, it would be better to use the original data points rather then averages.



Simple Regression - VIII_N amount vs. VIII_time

Regression Analysis - Linear model: Y = a + b*X

Dependent variable: VIII_N amount
Independent variable: VIII_time

Parameter	Estimate	Standard error	T statistic	P-value
Intercept	4.57906	0.224298	20.4151	0.0000
Slope	−0.000181518	0.000270513	−0.671015	0.5174

Analysis of Variance

Source	Sum of squares	Df	Mean square	F-ratio	P-value
Model	0.0719537	1	0.0719537	0.45	0.5174
Residual	1.59805	10	0.159805		
Total (Corr.)	1.67	11			

Correlation Coefficient = −0.207572
R-squared = 4.30861 percent

Comment: *As you can see from the ANOVA table, the regression is highly nonsignificant and therefore we do not show the regression plot. The nonsignificance of a regression means that the slope coefficient does not differ from zero. In this particular case, it means that the N amount was approximately constant during the 1400 days of incubation (there was no net release or accumulation of nitrogen). This also explains the increase in concentration during the decomposition because as much as 67% of organic matter has been mineralized.*

Exercise IX: Increase Rate in Litter N Concentration

Refer to the discussion in chapter 5 about N concentration increase rate (NCIR). We use the linearity in the relationship between the accumulated litter mass loss and N concentration. What this measure gives is the increase relative to the mass loss. See also Fig. IX.1.

We obtain a highly significant linear relationship:

$$\text{N concentration} = 3.219 + 0.1289 \times \text{Acc. ml.}$$

The standard error for the intercept is 0.839 and for the slope 0.0117.

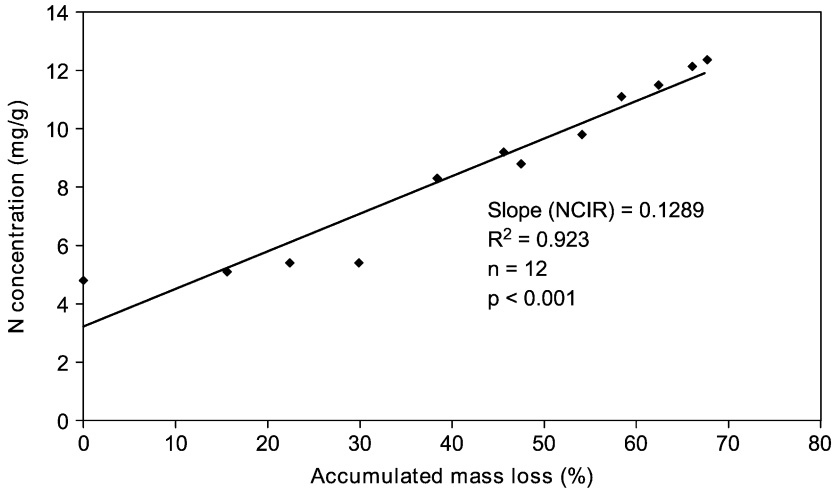


Fig. IX.1 The linear relationship between accumulated mass loss and litter N concentration.

Exercise X: Differences in Increase Rates for Nitrogen Concentration

This is a typical regression analysis problem, where two or more regression lines are to be compared. As described earlier in the book, the solution to this problem is a regression with "dummy" (or indicator) variables. Many statistical packages offer either an option of directly comparing regression lines or automatic creation of dummy variables. If this is not the case, one can still easily perform the analysis by adding a dummy variable. In our example, the analysis requires adding just one column consisting of zeros and ones, so that the data appear as shown in Table X.2:

As you can see, the only purpose of the dummy variable (D) is to distinguish between the two types of litter (see Table X.2). Now we can formulate the full model including the information about the litter type:

$$N = a1 + b1 \times MassLoss + a2 \times D + b2 \times D \times MassLoss$$

Analyze this model closely and you will see that, for brown needles, the models simplifies to

$$N = a1 + b1 \times MassLoss$$

because for brown needles $D = 0$ so both $a2 \times D$ and $b2 \times \mathrm{D} \times MassLoss$ also become 0. Thus, the regression coefficients for brown needles are $a1$ and

Table X.2 Accumulated mass loss and N concentration in two decomposing litter types with an additionally created dummy variable necessary to compare two calculated regressions

Mass loss (%)	N (mg g^{-1})	Litter type	Dummy variable (D)
0.0	15.1	green	1
23.3	19.0	green	1
28.8	20.8	green	1
38	23.8	green	1
44.9	27.3	green	1
48.8	30.4	green	1
52.1	30.8	green	1
54.2	30.7	green	1
58	31.7	green	1
60.5	29.5	green	1
63.4	31.6	green	1
65.9	31.6	green	1
0	4.8	brown	0
15.6	5.1	brown	0
22.4	5.4	brown	0
29.9	5.4	brown	0
38.4	8.3	brown	0
45.6	9.2	brown	0
47.5	8.8	brown	0
54.1	9.8	brown	0
58.4	11.1	brown	0
62.5	11.5	brown	0
66	12.2	brown	0
67.4	12.5	brown	0

$b1$. However, for green needles $D = 1$ so $a2 \times D$ and $b2 \times D \times MassLoss$ become meaningful (nonzero). If, say, the slope of the regressions for brown and green needles are the same, then almost all of the variability will be explained by the first part of the model ($N = a1 + b1 \times MassLoss$) anyway and adding the term $b2 \times D \times MassLoss$ will not change the fit significantly–the $b2$ term will be nonsignificant. Turning that reasoning around, if regression analysis results in significant $b2$, it means that the regressions do differ significantly in their slopes. By analogy, the significance of the $a2$ term means significant difference in intercepts. Now let us have a look at the computer printout from such an analysis:

Comparison of Regression Lines - X_N versus X_AML by X_type

```
Dependent variable: X_N
Independent variable: X_AML
Level codes: X_type
```

Comment: *The variable names stand for: X_N - N concentration; X_AML – accumulated mass loss; X_type - litter type (this variable is automatically recoded to dummy variable).*

Number of complete cases: 24
Number of regression lines: 2

Multiple Regression Analysis

Parameter	Estimate	Standard error	T statistic	P-value
CONSTANT	3.21945	0.830358	3.87718	0.0009
X_AML	0.128922	0.0176394	7.30877	0.0000
X_type = green	10.7991	1.26185	8.55816	0.0000
X_AML*X_type = green	0.157521	0.0263551	5.97686	0.0000

Analysis of Variance

Source	Sum of squares	Df	Mean square	F-ratio	P-value
Model	2408.4	3	802.799	505.58	0.0000
Residual	31.7574	20	1.58787		
Total (Corr.)	2440.15	23			

R-Squared = 98.6985 percent
R-Squared (adjusted for d.f.) = 98.5033 percent

The output shows the results of fitting a linear regression model to describe the relationship between X_N, X_AML and X_type. The equation of the fitted model is

X_N = 3.21945 + 0.128922*X_AML
+ 10.7991*(X_type = green)
+ 0.157521*X_AML*(X_type = green)

where the terms similar to X_type = green are indicator variables which take the value 1 if true and 0 if false. This corresponds to 2 separate lines, one for each value of X_type. For example, when X_type = brown, the model reduces to

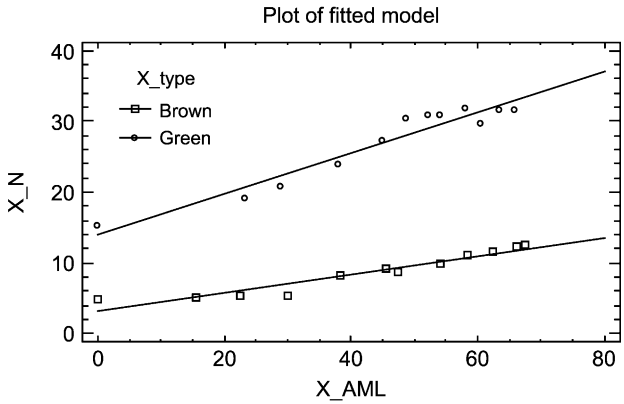
X_N = 3.21945 + 0.128922*X_AML

When X_type = green, the model reduces to

X_N = 14.0185 + 0.286443*X_AML

Because the P-value in the ANOVA table is less than 0.01, there is a statistically significant relationship between the variables at the 99% confidence level.

Comment: *As you can see, the regression is highly significant (cf. Analysis of Variance table), as are all the variables (Multiple Regression Analysis table). The latter table suggests also that both the intercepts and the slopes do differ significantly. However, we will still perform the formal test by checking the significance of the all variables (in the following text) in the order in which they are fitted. The plot shows the two regression lines fitted and, indeed, the two litter types appear quite different both in their initial N concentrations and in N increase rates.*



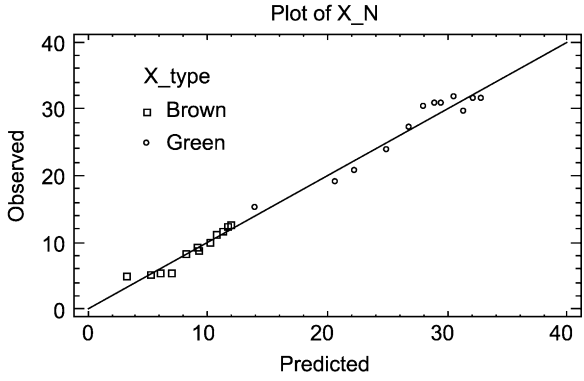
Further ANOVA for Variables in the Order Fitted

Source	Sum of squares	Df	Mean square	F-ratio	P-value
X_AML	483.181	1	483.181	304.29	0.0000
Intercepts	1868.49	1	1868.49	1176.73	0.0000
Slopes	56.7232	1	56.7232	35.72	0.0000
Model	2408.4	3			

This table allows you to test the statistical significance of the terms in the model. Because the P-value for the slopes is less than 0.01, there are statistically significant differences among the slopes for the various values of X_type at the 99% confidence level. Because the P-value for the intercepts is less than 0.01, there are statistically significant differences among the intercepts for the various values of X_type at the 99% confidence level.

Comment: *The analysis is finished and now we can tell that: (1) in both litter types, N concentration increases significantly with litter mass loss (model*

significant as indicated in the ANOVA table); (2) the litters differ in their initial N concentrations (significant difference in intercepts); (3) the litters differ in N concentration increase rates (significant difference in slopes); (4) the linear model fits the data well (no major trends in the "observed versus predicted" plot).



Exercise XI: Calculating the Sequestered Fraction of Litter N

The basic information necessary to solve this problem is given in chapters 4 and 5. The recalcitrant part of the litter we find as the remains when the litter has decomposed to the limit value. So, a first step would be to calculate the limit value and we obtained 88.5%. Please note that the estimated asymptote may vary slightly, depending on the estimation procedure used. Here, we used the Marquardt procedure (see the printout on the next page).

In a next step, we calculate the concentration of N at the limit value, as described in chapter 5. We obtain the equation $N = 0.1289 \times (\text{mass loss}) + 3.218$.

We substitute mass loss for 88.5 since the limit value also is a value for accumulated mass loss and we obtain an N concentration of 14.6 mg g^{-1}. That is the N concentration in the remaining amount, which is 11.5% of the original amount.

If we imagine an initial amount of 1.0 gram with N concentration of 4.8 mg g^{-1}, this means that in 1 g, there was 4.8 mg of N. The litter has now decomposed and only 11.5% remains, which means 0.115 grams. These 0.115 grams have an N concentration of 14.6 mg g^{-1}. Thus, 0.11×14.6 mg g^{-1}, or 1.68%, which is the amount of N that remains in the litter. The fraction that remains is 1.68/4.8 or 0.350, which also can be written as 35.0% of the N initially present.

Step 1–Estimating the Decomposition Limit Value (the Asymptote)

Nonlinear Regression - XI_AML

Dependent variable: XI_AML
Independent variables: XI_years
Function to be estimated: m*(1-exp((k*XI_years)/m))
Initial parameter estimates:
  m = 100.0
  k = -10.0
Estimation method: Marquardt
Estimation stopped due to convergence of residual sum of squares.
Number of iterations: 9
Number of function calls: 35

Estimation Results

			Asymptotic 95.0% confidence interval	
Parameter	Estimate	Asymptotic standard error	Lower	Upper
m	88.5262	3.67862	80.3297	96.7227
k	-34.1105	1.08391	-36.5256	-31.6953

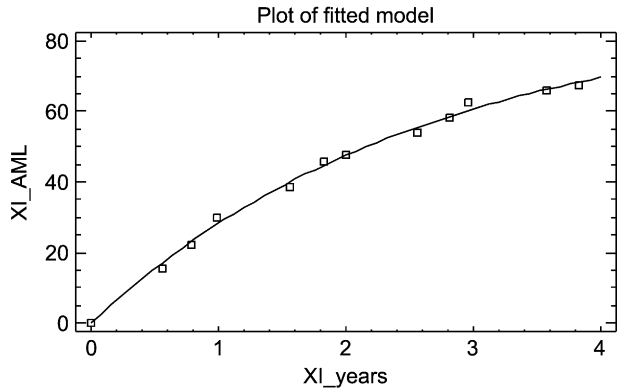
Analysis of Variance

Source	Sum of squares	Df	Mean square
Model	26581.7	2	13290.8
Residual	17.7024	10	1.77024
Total	26599.4	12	
Total (Corr.)	5102.5	11	

R-Squared = 99.6531 percent
R-Squared (adjusted for d.f.) = 99.6184 percent

The output shows the results of fitting a nonlinear regression model to describe the relationship between XI_AML and 1 independent variables. The equation of the fitted model is

88.5262*(1-exp((-34.1105*XI_years)/88.5262))



Exercise XII: Nitrogen Stored in Litter at the Limit Value

In the presentation of the problem, you obtained the information about the limit values and thus about how much recalcitrant remains there are from each litter species. You also know the N concentration in these remains. We can apply here the same method as we used in Exercise XI.

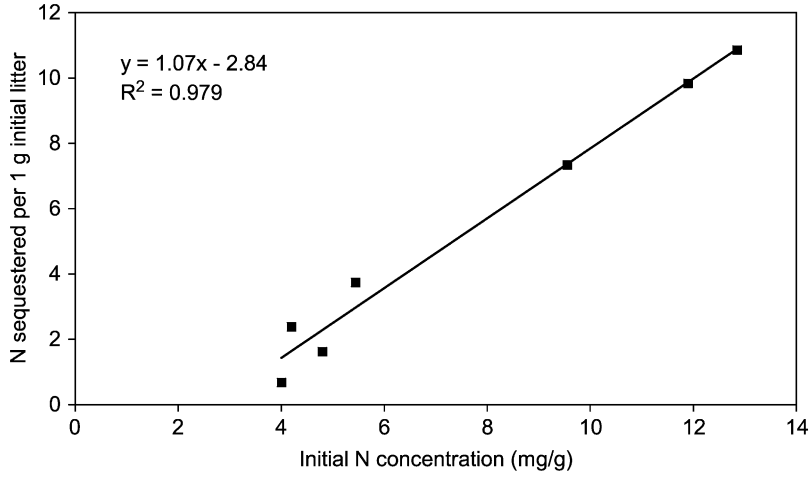
Table XII.2 The same data as in Table XII.2 supplemented with two columns giving the calculated capacities of litters to store N (N_{capac}) and the percentage of initial N sequestered

Litter type	Initial N conc. (mg g^{-1})	Limit value (%)	N conc. at limit value (mg g^{-1})	N_{capac} (mg g^{-1})	Sequestered part of the N (%)
Lodgepole pine	4.0	94.9	13.6	0.68	17
Scots pine	4.2	81.3	12.76	2.39	57
Scots pine	4.8	89.0	14.7	1.62	34
Norway spruce	5.44	74.1	14.46	3.74	69
Silver birch	9.55	77.7	22.71	7.34	77
Common beech	11.9	59.1	24.05	9.84	83
Silver fir	12.85	51.5	21.93	10.86	85

Our table (XII.2) has obtained two further columns, one giving N_{capac} as mg of N that is stored in the remains of originally 1.0 grams of litter. This is simply the amount of N given in milligrams per gram litter.

The last column gives the fraction as the remaining N/initial N, for example, 0.68/4.0. By multiplying by 100, we obtain the percentage of N remaining, in the given example 17%.

As a final step, why not plot the calculated data in the two last columns, for example, versus initial N concentration. What is your conclusion?



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Index

Advances in Ecological Research Volume 1–38

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