Chapter 4
Initial Litter Chemical Composition

4.1 Introduction

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

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

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

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

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

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

The new analytical approach using ^{13}C NMR rather shows the frequency of type of bonds between carbon and carbon as well as carbon to other atoms. This means that the approach so far is not directly compatible with the more traditional ones and we have presented it as a separate methodological approach. See also Appendix III.
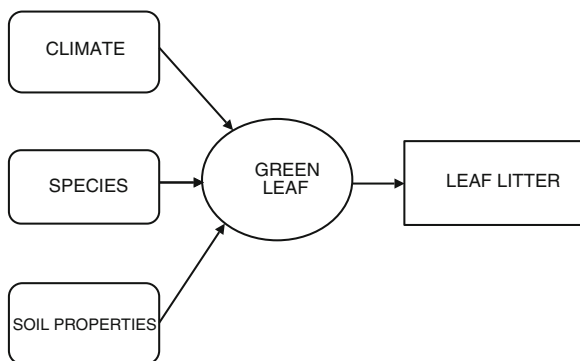
Fig. 4.1 Today, it appears that three main factors determine the chemical composition of foliar litter, namely species, climate, and soil properties. For a given species/genus, this means that climate and nutrient availability in soil have a dominant influence on (1) concentrations of nutrients and heavy metals in the live leaf (2) in the formed litter. Empirical findings indicate that the magnitude of the influences varies among litter species/genera

4.2 Organic-Chemical Components of Plant Litter and Fiber Structure

4.2.1 Organic-Chemical Components

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

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

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

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

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

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

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

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

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

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

The analytical approach using ^{13}C NMR presents frequencies of different bonds (Appendix III; Table 4.2), some specific for a certain compound and some in common for different ones.
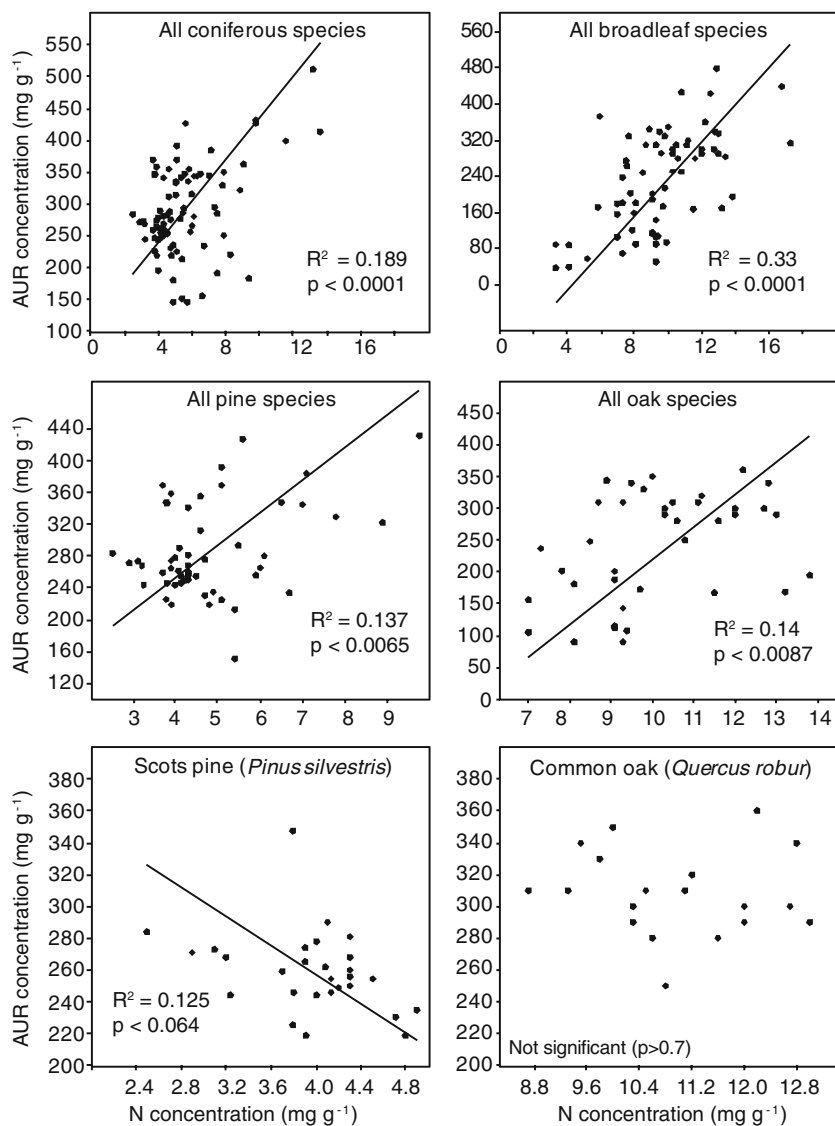
Fig. 4.2 Comparison of relationships between N and AUR concentrations in broadleaf ($p < 0.0001$) and coniferous ($p < 0.0001$) litter as well as in pine species ($p = 0.0065$) and Scots pine ($p = 0.064$) litter. Leaves of all oak species gave a significant relationship ($p < 0.0087$), whereas those of common oak did not (ns). From Berg et al. (2013)

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

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

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

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

4.2.2 Fiber Structure

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

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

Fig. 4.3 Overview of a plant fiber. **a** Tracheids. **b** Cell wall layers. **c** Arrangements of polymer carbohydrates and lignin in the secondary wall. Middle lamella (*ML*), primary wall (*P*), layers of the secondary wall (*S1, S2, and S3*). The microfibrillar orientation and the thickness are different among the layers, and some species have an additional warty layer over the inner (*S3*) layer. The model demonstrates the distribution of the lignin–hemicellulose matrix (*black*) hemicellulose (*white*) and cellulose fibrils (*dotted*). (From Eriksson et al. 1990)
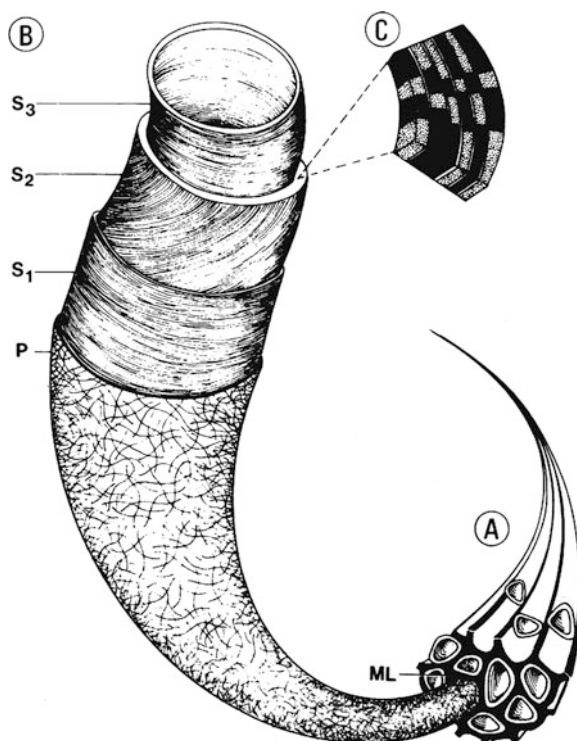
orientations. A model describing the arrangement of lignin, hemicellulose, and cellulose within the cell wall was proposed (Kerr and Goring 1975, Fig. 4.3). The model shows how a matrix of lignin and hemicellulose encrusts the cellulose fibrils. There is a tremendous diversity in wood structure among the hundreds of hardwood species that grow throughout the world (Panshin and de Zeeuw 1980). Still, the drawing in Fig. 4.3 may serve as a model for our discussion.

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

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

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

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

4.3 Nutrient and Heavy Metals' Concentrations in Newly Shed Litter

4.3.1 General Features

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

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

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

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

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

4.3.2 Nutrient Resorption and Withdrawal Efficiency

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

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

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

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

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

4.3.3 Nutrient Concentration Change; Green Foliage versus Brown Litter

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

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

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

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

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

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

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

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

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

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

4.4 Factors Influencing Litter Chemical Composition

4.4.1 General Factors

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

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

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

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

a Species	Concentration of nutrient (mg g^{-1})						
	N	P	S	K	Ca	Mg	Mn
S. pine (br)	3.6	0.20	0.44	0.5	5.6	0.34	1.19
S. pine (gr)	12.1	1.36	0.81	5.9	3.9	0.79	0.53
% concn change[a]	30	15	55	8	143	43	224
LP. pine (br)	3.1	0.29	0.44	0.5	8.7	1.06	2.03
LP. pine (gr)	10.5	0.82	1.17	3.8	4.0	0.93	0.82
% concn change	30	35	38	13	220	113	250
N. spruce (br)	4.2	0.41	–	1.0	13.1	0.89	1.32
N. spruce (gr)	8.5	1.32	–	4.0	11.3	1.22	1.07
% concn change	49.0	31	–	24	115	73	123
S. birch (br)	7.7	1.05	0.80	4.7	11.8	3.30	1.23
S. birch (gr)	24.3	1.96	1.54	9.0	9.5	3.37	0.76
% concn change	32	53	52	52	124	98	158
T. aspen (br)	6.8	0.63	1.37	6.3	17.1	2.13	0.15
T. aspen (gr)	24.2	2.12	1.87	14.2	8.4	2.29	0.10
% concn change	28	30	73	44	204	92	150
C. beech (br)	9.1	0.63	1.21	2.7	10.0	1.70	–
C. beech (gr)	22.6	1.44	1.18	5.4	7.7	1.67	–
% concn change	40	44	103	50	130	102	–
b Species	Concentration (µg g^{-1})						
	Pb	Cu	Fe	Al	Zn	Cd	Ba	Sr
S. pine (br)	2.5	1.4	57	280	51	0.2	7	4.6
S. pine (gr)	1	2.8	50	510	43	0.3	3.5	3.0
% concn change	250	50	114	55	119	67	200	153
S. birch (br)	2.6	3.4	61	130	340	0.8	13	31
S. birch (gr)	nd	6.4	53	46	140	0.2	54	16
% concn change	–	53	115	283	243	400	24	194
T. aspen (br)	0	8.6	46.4	nd	126	0.5	nd	nd
T. aspen (gr)	0	8.8	44.0	nd	107	0.3	nd	nd
% concn change	–	98	103	–	118	167	–	–

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

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

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

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

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

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

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

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

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

4.4.2.1 The Genus Pinus

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[1] 7 pine species were included

[2] 8 pine species were included

[b] Exponential relationship

[c] Linear relationship

ns not significant, *nd* no data

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

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

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

Fig. 4.4 Negative exponential relationship between litter Mn concentration and mean annual temperature (MAT) using data from 62 sites with a range from 70°N (northern Finland) to the Mediterranean area (northern Libya) and the American Midwest. Data from Berg et al. (2010)
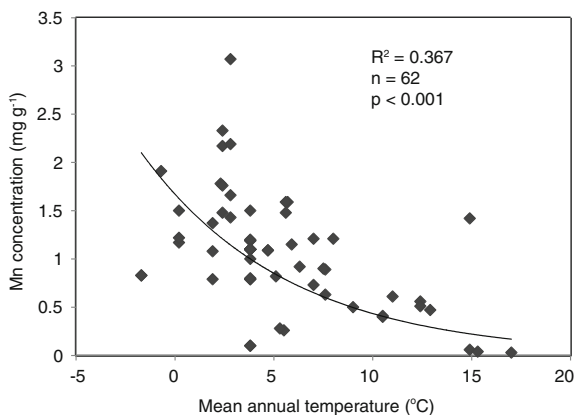
positive relationships to MAT and a negative one to MAP. We may note that the single genus *Pinus* investigated by Liu et al. (2006) behaved in different ways as compared to the larger group of different coniferous species as well as to the groups of broadleaf and coniferous litter, and we cannot exclude that single species and genera with their defined ecological niches have different behavioral patterns, for example as regards response to temperature as compared to continuously changing species along a continental gradient.

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

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

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

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

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

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

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

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

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

BrdCon Broadleaf plus coniferous

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

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

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

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

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

4.4.2.2 The Genus Picea

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

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

Fig. 4.5 Pattern for nitrogen concentration in needle litter of Norway spruce and Glehn's spruce, when related to site annual average temperature (MAT). The encircled points represent litter collected at sites subject to strong N pollution
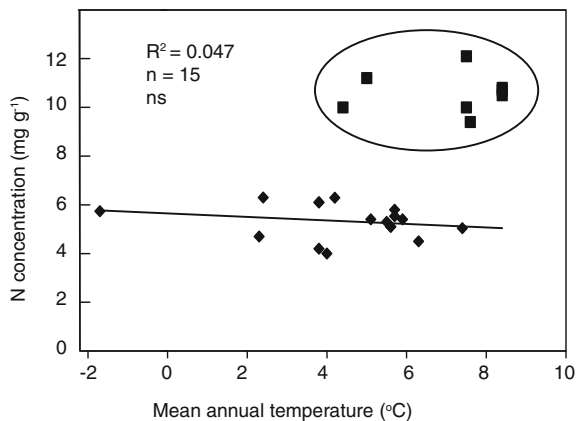
Table 4.9 Regression coefficients (r) for relationships between main nutrients and AUR in spruce needle litter and the climatic parameters annual average temperature (MAT) and annual precipitation (MAP)

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

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

4.4.3 Influence of Soil Properties

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

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

The influence of soil pH is also well illustrated by a study on leaf litter of common beech in 24 stands in a climatically homogeneous area. Ten plots with mull soils had significantly higher average humus pH, and the litter had higher concentrations of Ca (12.0 vs. 8.5 mg g^{-1}, $p < 0.002$) and Mg (1.97 vs. 1.56 mg g^{-1}, $p < 0.0001$) than those with a mor soil, whereas the concentration of N, P, S, and K were not affected. In the same study on Ca in common beech leaves, Staaf (1982) found a clear relationship between the humus (A$_0$) pH and Ca concentrations in the leaf litter.

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

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

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

4.5 Several Deciduous and Coniferous Leaf Litter Species

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

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

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

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

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

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

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

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

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

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

Lignin/AUR is a component that appears to have higher concentrations in coniferous than broadleaf litter. Using 152 datasets, Berg et al. (2013) found significantly different average values for the two groups. Thus, the average AUR
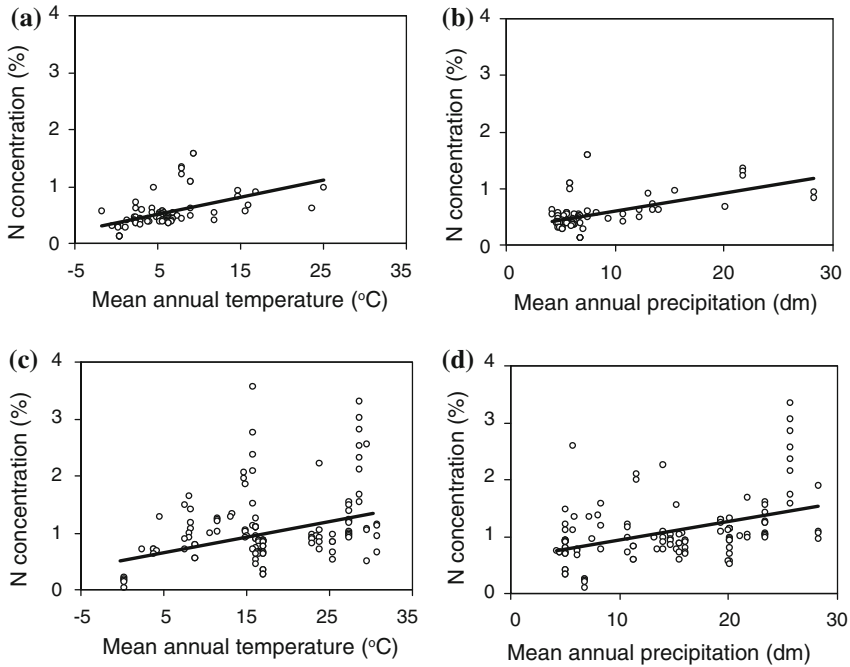
Fig. 4.6 Foliar litter N concentration related to MAT and MAP. Available data of both coniferous **a, b** and broadleaf **c, d** foliar litter with origin from Asia and Europe. The relationships are significant at $p < 0.001$. Cf Table 4.7. From Liu et al. (2006)

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

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

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

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

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

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

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

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

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

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

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

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

4.5.3 General (Global) Relationships

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

4.6 Wood and Fine Root Litter

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

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

4.7 Anthropogenic Influences on Initial Litter Composition

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

4.7.1 N-fertilized Scots Pine and Norway Spruce Monocultures

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

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

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

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

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

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

Fig. 4.7 Relationships
between dosage of N
fertilizer (ammonium nitrate)
and concentrations of N in
needle litter of Scots pine and
Norway spruce. (B. Berg
unpubl.)
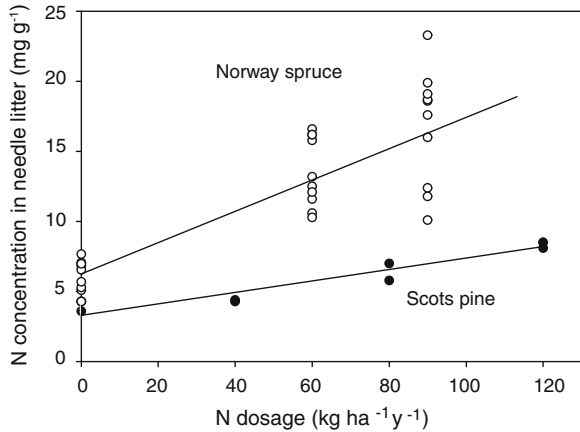
relationships to the N concentration, whereas Ca showed a negative relationship,
and there was no significant relationship found for Mg.

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

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

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

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

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

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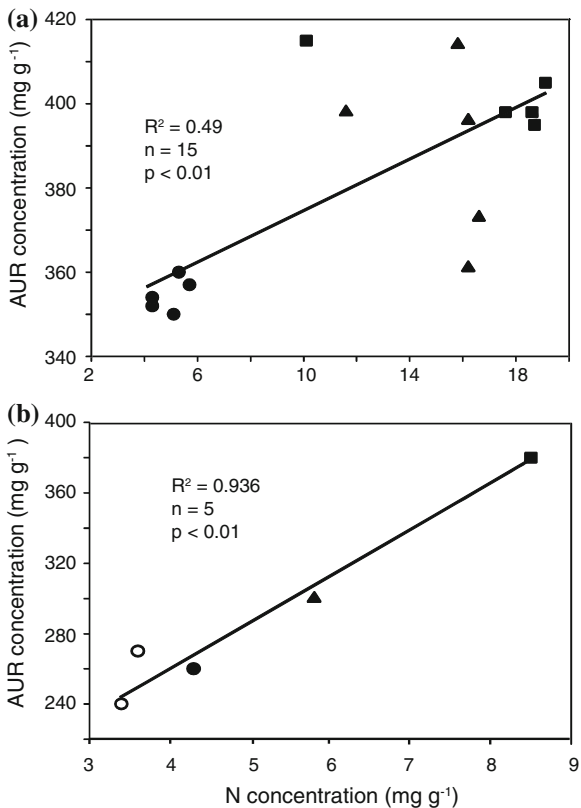

Table 4.11). This effect on lignin concentration seems to vary with the kind of system and appears to be indirect.

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

4.7.2 Heavy Metal Pollution and Initial Litter Chemical Composition

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

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

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

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

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