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Carbon Quality and Stocks in Organic Horizons in Boreal Forest Soils

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ABSTRACT

We investigated the mechanisms that determine the quality and quantity of organic carbon (C) stocks in boreal forest soils by analyzing both qualitative and quantitative changes in the organic fractions in the soil organic matter (OM) in a vertical gradient in the decomposition continuum of the organic horizon [litter layer (L), fermentation layer (F), and humus layer (H)] in forest soils using a sequential fractionation method at two forest types along a climatic gradient in Finland. We predicted that the concentrations of water-soluble (WSE) and non-polar (NPE) extractives should decrease and those of the acid-soluble (AS) fraction and acid-insoluble residue (AIR) should increase from the L to the F, and from the F to the H layers, but the C/N ratio of soil OM should stay constant after reaching the critical quotient. We also predicted that the AIR concentrations should be higher in the south than north boreal, and in sub-xeric than mesic forests. Consistent with our hypothesis, the concentrations of WSE and NPE fractions decreased and concentrations of AIR increased in the vertical soil gradient. The highest concentrations of the AS fraction were found in the F layer. The C/N ratio was lowest in the F layer, and the highest in the H layer, indicating that soil OM is depleted in N in relation to C along the vertical soil gradient. Concentrations of WSE and NPE were lower, and concentrations of AIR were higher in the south than in north boreal forests, which is in agreement with our hypothesis that higher soil temperatures may enhance accumulation of slowly decomposable OM in the soil. The concentrations of AIR were higher in the sub-xeric than mesic forests. Contrary to our expectations, however, the differences in the chemical quality in soil OM between the site types were amplified from the L to the H layer. The size of the C storage was significantly larger in south than north boreal sites, and larger in the mesic than in the sub-xeric sites.

Key words: boreal forests; decomposition; carbon storage; organic matter quality; AIR; litter.

INTRODUCTION

Forest soils in the boreal zone are an important reservoir for global carbon (C) (Goodale and others 2002). Understanding the mechanisms of C and nitrogen (N) sequestration in soil organic matter (OM) has attracted considerable attention in recent years, because of the important question of how organic C stocks will respond to a change in the global climate, which is expected to be the greatest in the northern boreal and sub-arctic and arctic regions (Vucetich and others 2000). For predicting responses to changes in the environment, it is imperative to understand the processes and mechanisms that determine the decomposition and accumulation rates of soil OM. The buildup of soil OM is a highly complex process that is determined

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by both the quantity and quality of the decomposing plant litter and the rate and completeness of its decomposition. Plant litter constitutes a wide range of C compounds that decompose at different rates (McTiernan and others 2003; Janzen 2005), and respond in different ways to ecological changes or changes in the abiotic environment (Vedrova and others 2002). The concentration of easily decomposable, water-soluble substances generally enhances litter decomposition rates, whereas the concentrations of slowly decomposable tannins and other polyphenols retard the decomposition rates.

Litter decomposition experiments in the boreal zone have demonstrated that the release of carbon from newly shed, fresh plant litter is very rapid, whereas in the stabilized part of litter and humus the decomposition rate reaches the asymptotic level of zero (Berg 2000; Girisha and others 2003; and elsewhere). As different chemical constituents decompose at different rates, the concentration of soluble compounds decreases and that of slowly decomposable compounds correspondingly increases during the course of decomposition (Berg 2000; Berg and others 1987; McTiernan and others 2003). At the same time, the C/N ratio of the decomposing material falls to a critical value, after which C and N are released from litter in approximately the same proportions and the C/N ratio remains unchanged. In the final phases of decomposition, the soil OM contains both plant and animal residues, microbial products and humified substances, and the decomposition of the most recalcitrant fraction regulates the overall decomposition rate (Berg 2000; Weintraub and Schimel 2003). According to the traditional view, lignin and other aromatic polymers form the most recalcitrant fraction of soil OM (Melillo and others 1989; Berg 2000), but recent studies have demonstrated that the recalcitrant fraction in soil OM is not predominantly aromatic but in fact consists of alkyl C and high proportions of O-alkyl compounds (Almendros and others 2000; Lorenz and others 2000; Kögel-Knabner 2002; Sjöberg and others 2004).

As the individual layers in the organic horizon of forest soils represent different phases in the decomposition process (Berg 2000), changes in the chemical fractions in a vertical direction down through the organic horizon can provide information about the factors regulating C and N sequestration in boreal ecosystems. We used the sequential fractionation method, also known as proximate analysis, for investigating factors that determine the quality and quantity of soil OM stocks down the decomposition continuum [litter layer (L), fermentation layer (F), and humus layer (H)] in forest soils. The fractionation method separates the soil OM into four fractions: non-polar extractives (NPE) (for example, waxes, fatty acids, and lipids), water-soluble extractives (WSE) (for example, sugars and phenolis), the acid-soluble (AS) fraction (for example, cellulose and hemicellulose), and the acid-insoluble fraction (AIR) which constitutes the most recalcitrant fraction of soil OM. We tested the following specific questions and hypotheses:

1. How does the chemical composition of OM change down the decomposition continuum in the organic layer? Due to differences in decomposition rates between different types of substrate, the concentration of soluble compounds generally decreases and that of slowly decomposable compounds correspondingly increases during the course of decomposition (Tian and others 2000). Consequently, decomposing plant litter of very different plant origins should gradually become similar, and the heterogeneous plant material be converted into relatively homogeneous humus material (Melillo and others 1989). We predicted that the concentration of more decomposable WSE should decrease, and that of AIR increase, down the profile in the organic layer. However, the C/N ratio should remain constant after reaching the critical value. Furthermore, we predicted that the chemical quality of the L layer on different forest site types and in different climatic zones should differ more than that in the F and H layer.
2. Do the chemical changes in the decomposition continuum differ between the south boreal and north boreal climatic zones? Soil OM that has developed under different climatic conditions may have a varying chemical quality, and consequently, resistance to decomposition (Berg and others 1993). Climatic transects in litter decomposition experiments have demonstrated that, in warm and moist conditions, soluble substrates are decomposed more rapidly than in cool conditions, and therefore the accumulation of recalcitrant substances is higher in a warm than in a cool climate (Berg and others 1993; Couteaux and others 1998; McTiernan and others 2003). Although the overall litter decomposition rates may be higher in warm climatic conditions, soil OM quality in cooler conditions may be less recalcitrant than that in warmer conditions. Therefore, we predicted that more AIR should accumulate in soil OM in proportion to other fractions in the

south boreal zone than in the north boreal zone.

3. Do the chemical changes in the decomposition continuum differ between nutrient-poor and nutrient-rich boreal forest sites? The understorey vegetation of nutrient-poor, sub-xeric boreal forests primarily consists of evergreen dwarf shrubs that form slowly decomposable litter, but in nutrient-rich, mesic forests, the decomposition rates are higher due to, for example, lower concentrations of phenolic compounds in the plant litter (Flanagan and Van Cleve 1983). However, it has not been investigated how the differences in the decomposability of dominant vegetation manifest themselves in the chemical quality of the lower layers in the organic horizons. We predicted that the decomposability of plant litter should be reflected in the chemical quality of the soil OM, and therefore soil OM should contain less WSE and more AIR in the nutrient-poor, sub-xeric forests than in the nutrient-rich, mesic forests.

MATERIAL AND METHODS

Study Sites and Sampling

The boreal coniferous forest belt, the taiga, is divided in Finland into four climatic zones: the hemiboreal, south boreal, middle boreal, and north boreal. We selected 12 forest stands for the study, 6 of which were located in the north boreal zone and 6 in the south boreal zone (Figure 1). Eleven of the sites investigated in this study are a part of the Finnish Forest Focus (EU)/ICP Forests (UN/ECE) Level II intensive monitoring plot network. The forest sites belong to two different types: herb-rich, mesic forests dominated by Norway spruce (*Picea abies* L.), and sub-xeric forests dominated by Scots pine (*Pinus sylvestris* L.). The two site types differ in ground vegetation, soil nutrient availability, and stand productivity. The growing conditions (climate and soil) in the south boreal zone are better than those in the north boreal zone (Meriluoto and Soininen 1998). In our approach to investigate vertical variations in OM quality and quantity, it is important to know that the ecosystem type has remained the same during the accumulation time of the present OM in soils. Even though the OM may contain plant residues from past vegetation from younger successional stages of the same sites, the vegetation components (that is, tree and needle residues, mosses, lichens, dwarf shrubs, herbs, and graminoids) have remained the same throughout the succession.

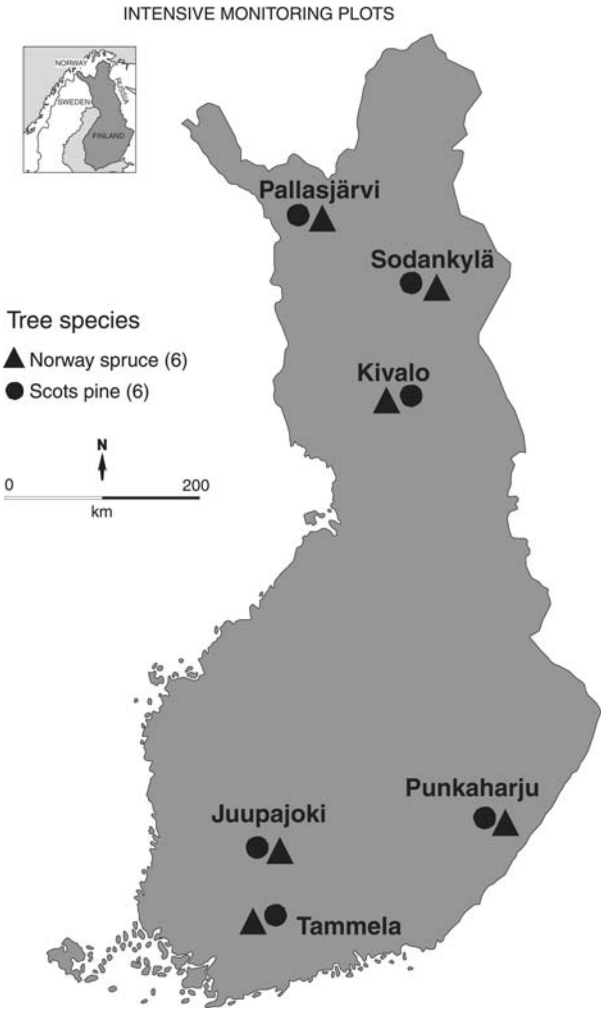

Figure 1. Map of the study sites.

There were some differences in the species composition and diversity index of the ground vegetation between the plots, but the most common species in the two groups of sites were the same. The coverage of different plant growth forms (dwarf shrubs, mosses, and herbs and grasses) is presented in Table 1. The Level II monitoring plots consist of a group of three plots (30 × 30 m), each surrounded by a buffer zone. The plot used for assessing ground vegetation (one of the three) was used in this study (Raito and Mäkinen 1999). The plot in the Sodankylä spruce stand was also 30 × 30 m square, and was the control plot of a fertilization experiment. At each site, a total of 28 small squares (30× 30 cm) were marked out immediately outside the four edges (seven along each edge) of the 30 × 30 m square plot during mid-July to mid-August in either 2002 or 2003. The coverage of plant species and litter was assessed visually on the squares, and a digital photograph

Table 1. Site Characteristics on the Mesic and Sub-Xeric Plots in the South and North Boreal Climatic Zones

Stand	Latitude	Elevation, m a.s.l.	Effective temperature sum, °C[1]	Precipit. mm bulk deposit.[2]	Stand age, years[3]	Site type[4]	Forest type	Site index (H_{100}), m	Basal area, $m^2\ ha^{-1}$	Cover%, Dwarf shrubs	Cover%, Mosses	Cover%, Herbs and grasses	pH, F + H	Growing season length d	Sampling date
Mesic															
Tammela	61°48′N	88	1602	526	70	Herb-rich	MT	34.69	28.5	38	63	17	4.4	189	9/7/2002
Punkaharju	61°48′N	88	1602	526	70	Herb-rich	OMT	34.69	28.5	2	90	8	3.9	176	26/7/2002
Juupajoki	61°51′N	177	1529	629	80	Herb-rich	OMT	27.95	33.2	15	89	20	3.9	160	23/7/2002
Kivalo	66°20′N	252	1074	585	70	Mesic	HMT	17.26	21.6	23	123	4	4.0	133	30/7/2002
Sodankylä	67°42′N	240	730	500[5]	96	Mesic	HMT	13.4	11.5	31	89	6	4.4	127[5]	12/8/2003
Pallasjärvi	67°60′N	300	683	545	140	Mesic	HMT	10	13	15	85	6	4.3	132	18/8/2003
Sub-xeric															
Tammela	60°37′N	120	1577	619	60	Sub-xeric	VT	25.52	21.9	23	73	19	4.0	189	9/7/2002
Punkaharju	61°46′N	99	1602	526	80	Sub-xeric	VT	25.98	29.4	24	92	2	4.1	176	25/7/2002
Juupajoki	61°52′N	154	1523	629	80	Sub-xeric	VT	23.61	17.9	31	112	14	3.8	160	22/7/2002
Kivalo	66°21′N	145	1009	587	55	Sub-xeric	EMT	17.85	21.3	38	99	0.2	4.0	133	29/7/2002
Sodankylä	67°20′N	201	730	500[5]	80	Sub-xeric	EMT	16.03	18.3	32	89	0	3.9	127[5]	11/8/2003
Pallasjärvi	67°57′N	321	886	550[5]	90	Sub-xeric	EMT	14.03	12.9	32	74	0.1	4.2	132	19/8/2003

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m a.s.l. = m above sea level.

[1] *The effective temperature sum is the sum of the differences between the daily mean temperature on each day during the growing season and the threshold value of +5°C.*

[2] *Mean 1996–2003.*

[3] *1999.*

[4] *Site type: Mesic = relatively moist and fertile; Sub-Xeric = dryish, relatively infertile; Herb rich = moist, fertile.*

[5] *Measurements of nearest weather station of Finnish Meteorological Institute.*

taken. The total area of the squares was 2.52 m^2 on each site. Each sample square was then carefully removed so as to include all the living ground vegetation and the organic layer (L, F, H), but none of the underlying mineral soil. The squares were placed in plastic bags and stored in a freezer (−18°C). After thawing in the laboratory, all the aboveground living (green) plant material was removed and reserved for further studies.

The organic layer was divided into the L, F, and H layers. The L layer consists of fresh litter intermixed with older litter, some of which presumably several years old. However, the samples were collected prior to the leaf senescence of that year. The L layer was sorted into the following litter fractions: needles, coarse tree litter (branches, bark, cones, seeds etc.), dwarf shrub leaves and stems, dead yellow/brown lower parts of mosses and lichens, herb and grasses, and other litter. Each fraction was dried (60°C) and weighed separately. A detailed study on the individual litter fractions will be published elsewhere, but for this study the total mass of the L layer was obtained by summing the mass of the individual litter fractions. The masses of herb and grass litter, lichen litter and other litter amounts were so small (only 1–2% of the total mass) that there was insufficient material for the chemical analyses. Separation of the F and H layers was based on visual differences between the layers. Identifiable roots and rhizomes were separated from the F and H layers to calculate C storage in the roots and rhizomes (data will be reported elsewhere). The F and H layers were dried (60°C) and weighed separately. The litter fractions and F and H material were milled to pass through a 1-mm sieve prior to chemical analyses.

Litter Decomposition Trials

Senescent leaves from bilberry (*Vaccinium myrtillus* L.), pine and spruce needles, and mosses were collected during the autumn of 2005, and fresh samples taken to laboratory. In the laboratory, yellowish and brown parts of the mosses were cut from the green and living ones, and used in a decomposition experiment. One composite sample from each litter type was immediately taken for moisture content measurement, which was used for calculating the initial dry weight of the litter decomposition samples. Remaining samples were kept in a refrigerator until weighed into polyester bags (6 × 6 cm, mesh 1 mm). Litter bags were then placed underneath the moss layer in the field. In sites with a sparse moss layer, the litter bags were placed under the L layer. Litter bags were collected from the field after 1 year, dried in the laboratory at 60°C, and weighed. The proportion of the substances decomposed in 1 year was calculated by subtracting the final weight from the initial weight and dividing the mass loss by the initial weight. The litter decomposition experiment will be continued and more long-term decomposition rates from the same sites will be available in the future.

Soil and Litter Analyses

The dry matter content was determined by drying sub-samples for 24 h in an oven at 105°C. The OM matter content was determined as the loss in weight on ignition in a muffle furnace at 550°C for 2 h. Total C and N concentrations were determined on an automatic CHN analyzer (Leco). The milled samples were analyzed using a sequential extraction technique according to Ryan and others (1990) into the following fractions: (1) NPE (waxes, fatty acids, and lipids), (2) WSE (for example, sugars and phenolics), (3) AS extractives (for example, cellulose and hemicellulose), and (4) relatively inert, acid-insoluble aromatic compounds (for example, large molecular weight compounds and humus substances).

Non-polar extractives (NPE). A total of 2 g (±0.010) of dry sample was weighed into glass fiber thimbles (Gerhardt SE33A) and 120 ml of chloroform added. The samples were boiled for half an hour at 62°C in an extraction device (Soxthern 2000). The thimbles were dried overnight at 50°C and weighed. The difference in weight before and after extraction was taken as NPE.

Water-soluble extractives (WSE). A total of 120 ml of distilled water was added to the residue, boiled at 100°C for 1 h, dried overnight at 105°C, and weighed. The difference in weight before and after extraction was taken as WSE. Detailed analyses were also performed on the water extractions and their results will be reported elsewhere.

Acid-soluble (AS) extractives and acid-insoluble residue (AIR). A total of 300 mg of the dry residue remaining after NPE and WSE determination was weighed out and 3 ml of 72% H_2SO_4 added. The mixture was left to stand for 1 h at 30°C. Eighty-four milliliters of distilled water were added and the mixture autoclaved (120°C) for 1 h. The hot samples were filtered through glass microfiber filters (Whatman GF/A), dried at 105°C, and weighed. The loss in weight during acid extraction was taken as AS, and the weight of the residue as AIR. The AIR/AS ratio was calculated as the proportion (%) of the acid-insoluble fraction divided by the proportion (%) of the AS fraction. All the results were calculated on an OM basis.

Table 2. ANOVA Table of the Effects of Soil Layer (L), Sub-Xeric and Mesic Site Type (S), Location (NS), Plot (P) and Interactions on the Concentrations of Chemical Fractions and Total C and N

Response	**Layer** *P*	**L × NS** *P*	**L × Plot (NS)** *P*	**L × Site type** *P*	**L × P × S (NS)** *P*	**L × NS × S** *P*	**NS** *P*	**Plot (NS)** *P*	**Site type** *P*	**P × S (NS)** *P*	**NS × S** *P*
Acid insoluble fraction	<0.001	<0.05	<0.001	<0.001	<0.001	>0.05	<0.001	<0.001	<0.05	<0.001	>0.05
Acid soluble fraction	<0.001	>0.05	<0.001	<0.001	<0.05	<0.05	>0.05	<0.001	<0.001	<0.001	>0.05
Nonpolar extract	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.05
Water soluble extract	<0.001	<0.001	<0.001	<0.001	<0.001	<0.05	<0.001	<0.001	>0.05	<0.001	>0.05
Total C	<0.001	<0.001	<0.001	<0.001	>0.05	<0.05	<0.001	<0.001	>0.05	>0.05	<0.05
Total N	<0.001	<0.001	<0.001	<0.001	<0.001	<0.05	<0.001	<0.001	<0.001	<0.05	<0.001

Layer × NS × Site type hypothesis df = 2, error df = 83, L × Plot (NS) and L × P × S (NS) hypothesis df = 168, error df = 8, NS, Site type and NS × S hypothesis df = 1, error df = 84, Site type (NS) and P × S × (NS) hypothesis df = 4 and error df = 84.

Data Analysis

The results are expressed in concentrations to investigate the differences in the composition of the OM between the sites, and in amounts (g/m^2) to investigate the stocks of soil C and individual organic fractions. The differences in concentrations and amounts of total N, C, and different organic fractions were tested statistically with repeated measures ANOVA with the soil layers (L, F, H) as within-subject factors, and location (north boreal or south boreal), site type (mesic or sub-xeric forest), and plot as between-subject factors. Plot was nested within the location in the north or south. The normality of the residuals was checked using normal-probability plots. The statistical significance of the effects was tested using Pillai's trace (Metsämuuronen 2005).

The interactions between total C and N, WSE, NPE, AS, AIR, and the C/N ratio and AIR/N ratio in the litter layer with the accumulation of total C in the F layer were tested using stepwise regression analysis. The total C storage in the H layers was explained on the basis of the total N, individual organic fractions, and the C/N and AIR/N ratio of the L and F layers. The normality of the residuals was tested with normal probability plots, and collinerity of the variables was tested with squared multiple correlation (Metsämuuronen 2005).

RESULTS

Organic Fractions along the Decomposition Continuum

The concentrations and amounts of organic fractions differed significantly between the soil layers, between the sub-xeric and mesic site types, and between the south and north boreal climatic zones (Tables 2 and 3). The concentrations of WSE and NPE extractives decreased significantly down the vertical profile, being highest in the L and the lowest in the H layer (Table 2, Figure 2A, B). In all organic layers, the NPE concentrations were higher on the sub-xeric sites than on the mesic sites. On the mesic sites, the NPE concentrations were higher in the north than in the south boreal zone, whereas on the sub-xeric sites it was lower in the south only in the H layer (Figure 2B). On both site types, the WSE concentrations were significantly higher in the north than in the south (Figure 2A). In the decomposition continuum, the concentration of AS increased from the L to the F layer and decreased from the F to the H layer. The AS concentrations were higher on the mesic than the sub-xeric sites,

Table 3. ANOVA Table for the Effects of Soil Layer (L), Sub-Xeric and Mesic Site Type (S), Location (NS), Plot (P) and Interactions on Soil Stocks

Response	**Layer** *P*	L × NS *P*	L × Plot(NS) *P*	L × Site type *P*	L × P × S (NS) *P*	L × NS × S *P*	**NS** *P*	**Plot (NS)** *P*	**Site type** *P*	P × S (NS) *P*	**NS** × S *P*
Acid insoluble fraction	<0.001	<0.001	<0.001	> 0.05	<0.001	<0.001	<0.001	<0.001	>0.05	<0.001	<0.001
Acid soluble fraction	<0.001	<0.001	<0.001	<0.001	<0.001	>0.05	<0.001	<0.001	<0.001	<0.001	<0.001
Nonpolar extract	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.05	<0.001	<0.001	<0.001	<0.001
Water soluble extract	<0.001	>0.05	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Total C	<0.001	<0.05	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Total N	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	>0.05
AIS:N	<0.001	>0.05	<0.001	<0.001	<0.001	<0.001	>0.05	<0.001	<0.001	<0.001	<0.001
C/N	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Layer, L × NS, L × Site type, L × NS × S hypothesis df = 2, error df = 322, L × Plot (NS) and L × P × S (NS) hypothesis df = 8, error df = 646, NS, Site type and NS × S hypothesis df = 1, error df = 323, S (NS) and P × S (NS) hypothesis df = 4 and error df = 323.

but did not differ between the climatic zones (Figure 2C). The AIR concentrations increased gradually from the L to the H layer on both site types, and were significantly higher in the south than in the north in the F and H layers. The AIR concentrations in the F and H layers were higher on the sub-xeric than on the mesic sites, but there was no difference in AIR concentrations in the L layer between the site types (Figure 2D).

When calculated on an areal basis, the NPE and WSE stocks were the highest in the H and the lowest in the L layer on both site types (Table 3, Figure 3A, B). The differences in NPE and WSE stocks on the site types varied between the climatic zones: on the mesic sites the stocks of NPE and WSE were larger in the north than in the south, whereas on the sub-xeric sites the same stocks were larger in the south (Figure 3A, B). The stocks of NPE in the L layer were lower on the mesic than on the sub-xeric sites. However, in the F and H layers, more NPE and WSE accumulated on the mesic than on the sub-xeric sites (Figure 3A, B).

The stock of AS increased from the L to the H layer. The AS stock in the L layer did not differ between the site types, but in the F and H layers there was significantly more AS on the mesic than on the sub-xeric sites (Figure 3C). On the sub-xeric sites the stock of AS was higher in the south than in the north in all layers, but on the mesic sites the difference was significant only in the H layer (Figure 3C). Of the total AIR stock, the L layer contained only a small proportion and the H layer clearly the largest proportion. Similar to the AS stock, the AIR stock in the L layer did not differ between the site types, but there was significantly more AIR in the F and H layers on the mesic than on the sub-xeric sites in the north (Figure 3D). On the sub-xeric sites the AIR stock was larger in the south than in the north boreal zone in all layers, but on the mesic sites there was no difference in the F layer between the south and the north (Figure 3D). The AIR/AS ratio increased gradually from the L to the H layer, and in the F and H layers it was higher on the sub-xeric sites than on the mesic sites (Table 4).

Total C and N and the C/N and AIR/N Ratios

The C concentration was at its highest in the L layer and at its lowest in the H layer (Figure 4A), and in the H layer of the mesic sites it was significantly higher in the north than in the south. The size of the total C stock increased from the L to the F layer, and from the F to the H layer (Figure 5A), and in

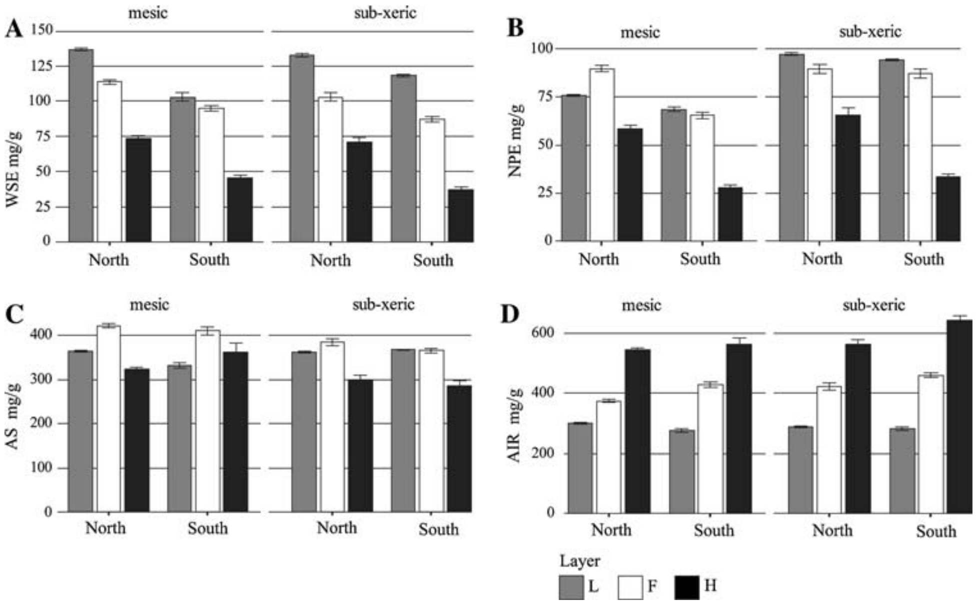

Figure 2. Concentrations of the organic fractions in L, F, and H layers in mesic and sub-xeric sites in north and south boreal forests.

the F and H layers it was higher on the mesic than on the sub-xeric sites especially in the north. On the sub-xeric sites the stock of C was significantly higher in the south than in the north, whereas on the mesic sites there was no difference between the climatic regions (Table 3, Figure 5A). The proportion of the C stock in the L layer was considerably higher on the sub-xeric than on the mesic sites.

The N concentration increased from the L to the F layer, and then fell to reach its lowest value in the H layer. The N concentrations were also generally higher on the mesic than on the sub-xeric sites, and higher in the south than in the north (Figure 4B). There were some interactions, however, with the layer: on the mesic sites the N concentrations were higher in the south in all soil layers, but on the sub-xeric sites the N concentration in the L and F layers was higher in the south, whereas in the H layer it was higher in the north. The N stock was the largest in the H layer, and was generally higher on the mesic than on the sub-xeric sites, and also higher in the south than in the north (Figure 5B). The C/N ratio was the highest in the L layer and the lowest in the F layer, and significantly higher in the north than in the south and higher on the sub-xeric than on the mesic sites (Table 4). The AIR/N ratio was higher on the sub-xeric than on the mesic sites, and higher in the north than in the south, with the exception of the H layer on the sub-xeric sites, which was higher in the south.

Correlations between Parameters in the L Layer and the C Stocks in the F and H Layers

Stepwise regression analyses were carried out to determine which parameters in the L layer best explained the C stocks in the F and H layers on the

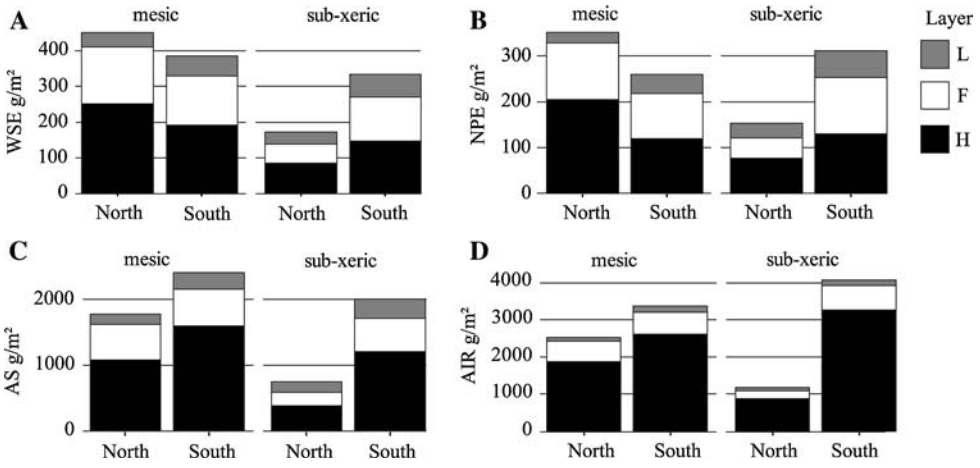

Figure 3. Stocks of the organic fractions in L, F, and H layers in mesic and sub-xeric sites in north and south boreal forests.

Table 4. The C/N, AIR/N and AIR/AS Ratios in the L, F, and H Layers of Mesic and Sub-Xeric Sites in North and South Finland

Plot	Layer	C/N	SD	AIR/N	SD	AIR/AS ratio
Mesic						
North	L	49.5	2.6	29.4	2.8	0.8
South	L	34.5	2.4	18.8	1.7	0.8
Total	L	43.1	2.5	24.9	2.3	0.8
North	F	41.8	2.3	31.4	3.3	0.9
South	F	27.9	2.0	26.8	4.8	1.0
Total	F	35.8	2.2	29.5	3.9	1.0
North	H	49.2	3.8	74.8	17.7	1.7
South	H	26.1	2.6	62.6	24.2	1.6
Total	H	39.3	3.3	69.5	20.5	1.6
Sub-Xeric						
North	L	67.7	3.5	36.9	3.8	0.7
South	L	52.1	2.6	29.6	1.8	0.8
Total	L	61.0	3.1	33.7	3.0	0.7
North	F	31.3	11.7	36.9	14.4	1.1
South	F	34.5	2.6	33.8	7.0	1.2
Total	F	32.7	7.8	35.5	11.3	1.1
North	H	41.0	6.5	85.4	31.4	1.9
South	H	34.1	3.8	99.8	39.8	2.3
Total	H	38.1	5.4	91.6	35.0	2.1

AS = acid soluble fraction; AIR = acid insoluble fraction; AIR/AS ratio = AIR (%)/AS (%).

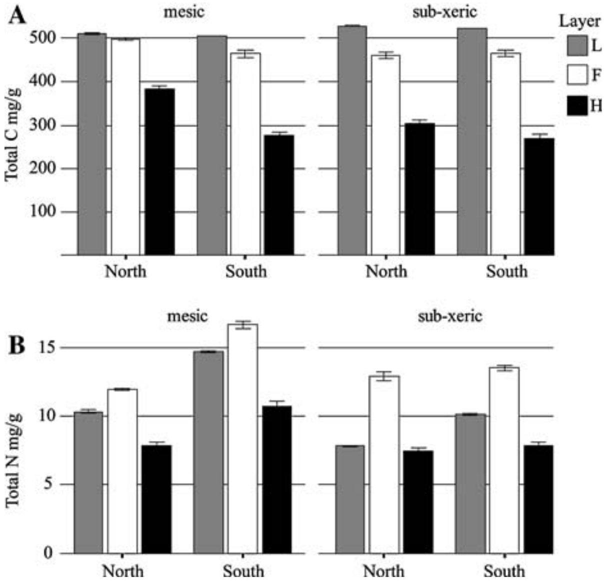

Figure 4. Concentrations of C and N in L, F, and H layers in mesic and sub-xeric sites in north and south boreal forests.

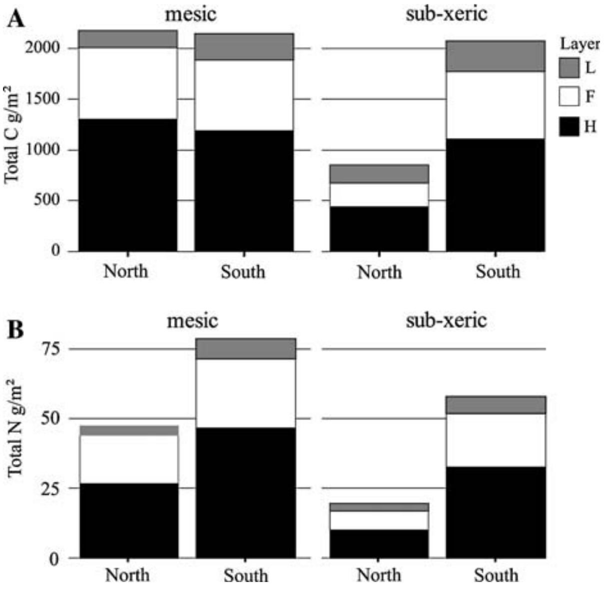

Figure 5. Total C and N stocks in L, F, and H layers in mesic and sub-xeric sites in north and south boreal forests.

different site types. On the sub-xeric sites, the concentrations of AS and NPE in the L layer explained 17% ($P = 0.039$; stepwise linear regression) of the variation in the total C stock in the F layer. The total C concentration in the F layer, and the combined concentrations of AIS and WSE in the L layer explained 47% of the variation in the total C stock in the H layer ($P = 0.034$). On the mesic sites, the concentration of total N, AIS, and NPE in the L layer explained 43% of the variation in the total C stock in the F layer ($P < 0.001$). The C:N ratio and AIS:N ratio in the L layer explained 54% ($P = 0.001$) of the variation in the total C stock in the H layer.

Litter Decomposition Rates

We found no differences in the decomposition rates during 1 year of incubation in the field between the sites, the site types, or between the climatic zones (Table 5, ANOVA, $P > 0.05$). The mass loss % within 1 year of incubation in the field was highest in *V. myrtillus* litter, whereas the needle litter and moss litter decomposition were still at the net immobilization phase with a net increase of the dry weight during the incubation in many cases. We did not detect any regrowth of the mosses in the litter bags, and the weight increase during the incubation is thus due to microbial growth into the litter mass.

DISCUSSION

Chemical Changes in the Soil OM along the Decomposition Continuum

In this study we analyzed the proportions of different organic fractions down a vertical gradient in

Table 5. Decomposition Mass Loss in *Vaccinium myrtillus* Leaf Litter, Conifer Needle Litter, and Moss Necromass Incubated in the Field for 1 Year in South and North Boreal Sites

Decomposition mass loss (% y^{-1})	*Vaccinium myrtillus*		Conifer needles		Mosses	
	Sub-xeric	Mesic	Sub-xeric	Mesic	Sub-xeric	Mesic
South boreal sites						
Tammela	64.8 (0.7)	65.6 (0.6)	34.6 (0.5)	22.2 (0.3)	25.6 (2.7)	6.4 (4.6)
Punkaharju	63.0 (2.0)	68.5 (1.2)	29.6 (1.7)	30.0 (2.4)	16.0 (4.3)	4.2 (5.2)
Juupajoki	59.2 (1.0)	65.3 (1.2)	3.9 (3.2)	29.7 (4.9)	10.8 (9.5)	8.1 (13.7)
North boreal sites						
Kivalo	66.0 (0.6)	63.5 (0.2)	19.2 (3.0)	20.6 (1.9)	−38.4 (7.2)	42.2 (5.7)
Pallasjärvi	58.3 (0.7)	67.5 (0.5)	28.4 (2.8)	32.8 (1.2)	3.8 (4.8)	22.3 (1.1)
Sodankylä	62.5 (1.3)	67.9 (2.0)	17.9 (0.9)	23.8 (3.3)	−16.3 (7.7)	−35.5 (14.9)

Values are means + standard error in parentheses (n = 4).

the decomposition continuum (sensu Berg 2000), and compared the change in the proportions and total stocks of different organic fractions in the individual organic horizons on nutrient-poor and nutrient-rich forest sites under two boreal climatic zones. Consistent with our predictions, the concentrations of WSE and NPE decreased along the decomposition continuum from the L to the F and from the F to the H layers, and the H layer contained only about 30% of the WSE and 50% of the NPE present in the L layer. These results confirm the data from litter decomposition experiments which indicate that, in the early stages of decomposition, water soluble and other labile compounds in plant litter are more rapidly degraded than the insoluble AS and AIR fractions (Berg 2000; Girisha and others 2003). We found a peak in the AS concentrations in the F layer, which supports the assumption that long-chain carbohydrates are more slowly decomposable than NPE and WSE compounds, but at a faster rate than the AIR fraction (Berg 2000).

Due to differences in the decomposition rate between individual substrates, litter of highly divergent origin should be converted into relatively homogeneous humus material (Melillo and others 1989). Therefore, we predicted that the differences in the L layer between the site types and climatic zones would be greater than in the F and H layers. Our data did not support this expectation. We found no differences in the AIR concentrations between the site types in the L layer, whereas the concentration of AIR in the H layer was 5–10% higher in the sub-xeric than mesic forests. Thus, contradictory to our hypothesis, differences between the forest types were amplified from the L to the H layer. This finding suggests that the conditions under which the decomposition processes take place determine the OM quality in the H layer to a greater extent than the initial quality of the litter.

In the early stage of litter decomposition, the proportion of C released is generally greater than that of N, which results in increasing N concentrations and amounts (Gosz 1973; Prescott and others 1993; Berg and Cortina 1995; Berg 2000). After the C/N ratio in the OM reaches the C/N ratio of the microbial flora, C and N are thought to be released from the litter in the same proportion (Berg and McClaugherty 1987). In the vertical decomposition continuum, however, the N concentrations increased from the L to the F layer, but in the H layer the N concentrations were at their lowest irrespective of the forest type, climatic factors, or C/N ratio of the soil, thus contradicting our hypothesis. Our data demonstrate that, in the vertical decomposition continuum, the H layer became depleted in N in relation to C. Litter production by the roots, which plays an important role in boreal C cycles (Ruess and others 1998), does not follow the same vertical distribution, and this could disturb the vertical gradient in the C/N ratio. However, the increasing concentrations of AIR along the decomposition continuum indicate that the OM in the lower layers is in the late stage of decomposition. We suggest that plant N uptake from the H layer could reduce the N concentrations in the H layer and, in the long term, N consumption by the plant roots outweighs C mineralization from soil OM.

Organic Fractions in Different Climatic Zones and Forest Site Types

In all the layers, the WSE and NPE concentrations were higher in the north than in the south. Concurrently, the AIR concentration in the H layer was significantly higher in the south than in the north. Although both the AIR concentration and C/N ratio have been widely used as indices of decomposability, and are considered to depict the same processes, we found that the C/N ratio was higher in the north but the AIR concentration was higher in the south. These results reflect differences in both the litter input and conditions for decomposition processes between the south and the north. McTiernan and others (2003) found that the residual OM produced by standard litter was more recalcitrant in a wet and warm climate than that under a cold and dry climate. The climatic differences in OM quality have been attributed to higher soil temperatures that stimulate the decomposition of easily decomposable substrates in the litter, thus depleting the litter of labile C substrates and eventually enhancing the accumulation of the recalcitrant AIR fraction (Berg 2000; Kirschbaum 2006). As OM decomposition rates are generally higher in the south than in the north, the soil OM in the F and H layers in the south boreal zone is probably at a later stage of decomposition than in the north. Our finding that the differences in the AIR concentrations between the climatic zones were amplified from the L to the H layer also supports this conjecture.

Although climate is an important factor influencing decomposition at a large scale (Berg and Meentemeyer 2001), the quality of the litter determines the decomposition and OM accumulation rates on a small scale (Berg and others 1993; Sariyildiz and Anderson 2003; Girisha and others 2003). In both climatic zones and in vertical soil layers, the concentrations of NPE and WSE were lower and that of AIR higher on the sub-xeric than on the mesic sites, which was consistent with our hypothesis. The ground vegetation of sub-xeric sites is dominated by dwarf shrubs that produce litter rich in lignin and phenols (Wardle and others 2003; Vargas and others 2006), and the slow decomposability of dominant vegetation is thus reflected in the soil OM in the late stage of decomposition. Because the L layer is a combination of freshly fallen plant material and more decomposed material, the AIR fraction most probably contains true lignin and tannins derived from plant cells (see Sjöberg and others 2004; Wardle and others 2003; Kögel-Knabner 2002). However, in the F and H layers, the most recalcitrant AIR fraction mainly consists of alkyl C and O-alkyl compounds. Lorenz and others (2000) found that a black spruce forest floor in northern Ontario was actually very poor in aromatic compounds. Although Almendros and others (2000) showed in black spruce soils that the proportion of compounds with O- and di-O-alkyl intensities decreased and that of aromatic and phenolic regions increased down the vertical soil gradient, NMR studies indicate that the aromatic and phenolic substances in this fraction consist of tannins rather than lignins, and that the AIR fraction is a mixture derived from lignin, tannin, and insoluble alkyl-C from cutin and surface waxes (Lorenz and others 2000; Preston and others 2006).

Factors that Determine the Soil C Stocks in Organic Horizons of Boreal Forests

The composition and total amount of C stocks in the soil are determined by both the quantity and quality of the litterfall and the conditions under which litter and soil OM decomposition take place (Kalbitz and others 2006; Sariyildiz and others 2005). Total C stocks were significantly higher in the mesic than sub-xeric forests, and higher in the south than north boreal forests. Earlier investigations show that the litterfall from trees is higher in south than north boreal forests (Berg and others 1995; Vucetich and others 2000; Ukonmaanaho 2007). However, total litterfall does not decrease toward the north to the same extent, because of increasing quantities of litter from the understorey vegetation. In another study conducted in the same study sites, it was shown that one-fourth of the litter stock originated from the ground vegetation in the south boreal, but more than half of the litter stock was from the ground vegetation in the north boreal sites, showing that the contribution of understorey vegetation to both quality and quantity of soil OM is greater in the north than south boreal forests (Sari Hilli and others, unpublished). This is also likely to contribute to the OM quality in different climatic zones. Although the absolute quantity of the moss litter was higher in the south, the proportion of moss litter in the litter stocks was highest in the mesic forests in the north boreal zone (Sari Hilli and others, unpublished), which could partly explain the low AIR concentrations in the soil OM in the north boreal forests.

Quantitative differences in the litter production between the different forest types are not always directly reflected in the total organic C stocks (Preston and others 2006). In our study, the total C storage in the sub-xeric forests varied greatly between the climatic zones, but in the mesic forests, there were no differences in the C storage between the north and the south. Our litter decomposition trials demonstrated that, for example, leaves from *V. myrtillus*, the dominant understorey dwarf shrub in these forests, decompose at a fast rate, and are therefore unlikely to contribute to the soil C stocks to a considerable extent. Mosses, by contrast, decomposed at a very slow rate, and for this reason, contribute considerably to OM accumulation in boreal forests (Hobbie and others 2000). In the north boreal sub-xeric sites, the amount of moss litter was much lower than in other areas (Sari Hilli and others, unpublished), which probably explains the low accumulation rates of soil OM in these systems. In south boreal sub-xeric sites, however, mosses form thick carpets on the forest floor, which is also reflected in the large OM stocks in the systems.

Correlation analysis between the parameters of the L layer and the stocks of C in the F and H layers showed a positive correlation between the total C stocks and N concentrations on the mesic sites, and a positive correlation between the C stocks and concentrations on the sub-xeric sites. This indicates that the factors regulating OM accumulation may vary according to the nutrient level of the forest site type. Other studies have also demonstrated a relationship between high N concentrations and OM accumulation (Berg 2000; Berg and others 2001; Kindel and Garay 2002; Mäkipää 1995; Nilsson and Wilkund 1995; Mälkönen 1990). Traditionally it was assumed that high concentrations of lignin and other polyphenols in the litter enhance the accumulation of soil OM, especially in N-rich conditions due to chemical reactions between lignin degradation products and N compounds (Berg and others 1987; Coûteaux and others 1998). More recent chemical studies have questioned these views (Hedges and others 2000; Sjöberg and others 2004; Lützow and others 2006), and the mechanisms for a negative effect of N additions on microbial activities in boreal forests are not entirely understood (Sjöberg and others 2004). For future research, experimental investigations on the effects of N availability on the decomposition rates of various types of organic substrates should bring more light to the mechanisms of how soil nutrients determine OM accumulation rates in boreal forests.

As a conclusion, our study demonstrates that the organic fractions vary along climatic and productivity gradients, and therefore respond differently to environmental conditions, such as temperature. Therefore, the stocks of different organic fractions, not only the total C stocks, are important in the responses of soil C balance to climate change in boreal forest ecosystems. Because the AIR fraction is the most important in the total accumulation of soil OM, future investigations should involve a detailed chemical characterization of the composition of AIR fractions in different climatic zones and productivity levels.

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