Decomposition of Norway spruce needles and fine roots

Production of CO_2 and DOC

Hanna Larsson

Handledare: Dan Berggren Kleja, Karna Hansson (Inst f ekologi)
Examinator: Olle Andrén

KANDIDATARBETE I BIOLOGI, 15 hp

Sveriges lantbruksuniversitet
Institutionen för markvetenskap
Avdelningen för markkemi och jordmånslära
Examens- och seminariearbeten Nr 93

Uppsala 2008

ISSN 1102-1381
ISRN SLU-MLE-EXS--93--SE

Abstract

The relative amounts of CO_2 and DOC lost during decomposition of spruce needles and fine roots are poorly known. However, knowledge about this division is crucial for our understanding of carbon cycling in boreal forest ecosystems. In this paper, decomposition of Norway spruce needles and fine roots has been studied in a three-week-long column incubation experiment. Five different substrates were used; fresh needle litter, aged needles from the litter layer, seven-year-old roots from litterbag studies, fresh roots from mineral soil, and dead roots from mineral soil. Production of CO_2 and DOC from the substrates, DOC quality and adsorption of DOC to ferrihydrite was studied. Respiration rate was highest for needles and fresh material, while DOC production was highest from needles in a later decomposition stage and from fresh roots. Most carbon was lost as CO_2 from fresh needle litter, while DOC dominated carbon losses from seven-year-old roots from litterbag studies. The fraction of hydrophobic compounds in DOC and the proportion of DOC adsorbed to ferrihydrite were largest for substrates in late decomposition stages. Respiration rate seemed to be dependent on substrate origin (needle or root) while DOC production, DOC quality and adsorption were independent of origin.

Sammanfattning

Kunskaper om hur stor andel av kol som försvinner som CO_2 respektive löst organiskt kol (DOC) från barr och finrötter under nedbrytning är nödvändiga för att förstå kolomsättningen i boreala skogsekosystem. Dessa kunskaper saknas dock fortfarande i hög grad. Denna uppsats bygger på en tre veckor lång studie där fem olika substrat från gran (barr från fallförna, barr från markförna, sju år gamla rötter från förnapåsar, färska rötter från mineraljord samt döda rötter från mineraljord) inkuberades i glaskolonner. Produktion av CO_2 och DOC, DOC-kvalitet samt adsorption av DOC till ferrihydrit mättes för de olika substraten. Respirationshastigheten var högst för barr och färska substrat, medan produktionen av DOC var högst för barr i senare nedbrytningsstadier och för färska rötter. De största kolförlusterna från barr från fallförna skedde som CO_2 medan DOC dominerade kolförlusterna från de sju år gamla rötterna från förnapåsar. Andelen hydrofoba föreningar i producerat DOC samt andelen DOC adsorberat till ferrihydrit var störst för substrat i sena nedbrytningsstadier. Respirationshastigheten påverkades av om substratet var barr eller finrot, medan DOC-produktion, DOC-kvalitet samt DOC-adsorption var oberoende av ursprung.

Table of Contents

Introduction

Global climate change is more and more discussed in the society today. In this context, deeper knowledge of processes influencing the global carbon cycle is necessary. Forest ecosystems are important storages in the global carbon budget, and potential changes in processes taking place in forests may have large impact on the global carbon cycle. Of all terrestrial carbon, the world's forests have been estimated to contain about 80 % of the above-ground carbon and 40 % of the below-ground carbon (Dixon et al. 1994). The same review estimates the carbon density of European forests to be 32 Mg/ha in vegetation and 90 Mg/ha in soils. Examples of carbon fluxes from and within forest ecosystems are emissions of carbon dioxide from organic matter decomposition, production of dissolved organic carbon from decomposition of organic matter, and storage of carbon in forest soils through adsorption. In this paper, these processes are studied for Norway spruce substrates in a boreonemoral forest.

Sources and sinks of dissolved organic matter (DOM) in soils is one of the three main topics for further research to understand DOM dynamics stated by McDowell (2003). This includes how recent and older organic matter in the soil contributes to DOM flux as well as how decomposition and adsorption act as sinks for DOM in the soil, and the time scales of these processes. One considerable uncertainty seen in the literature is the relative importance of fresh litter versus older soil organic matter as sources of DOM in soil solution. Further, the contribution of root-derived DOM to the DOM released from the soil has not been measured (Kalbitz et al. 2000). The present paper aims at adding additional data to the discussions of these questions, as it compares the dissolved organic carbon (DOC) production from different substrates at different decomposition stages. To understand the proportion of DOM originating from different sources and its pathways in the soil is fundamental to understand and estimate the effect of various environmental changes on soil carbon dynamics (McDowell 2003).

Fine roots with a diameter of less than 2 mm have a typical life-span of about one year, but a large part of the net primary production (NPP) may be allocated to these tissues, giving them an important role in soil carbon flux (Kalyn & Van Rees 2006). Kalyn & Van Rees (2006) found that in a *Picea mariana* stand in Saskatchewan, Canada, the fine roots comprised 71 % of total NPP in the ecosystem, while they contributed to less than 1 % of the carbon biomass of the ecosystem. Further, the decomposition rate of fine roots is high relative to aboveground tissues (Ruess et al. 2003). Despite the significant carbon fluxes caused by fine-root decomposition, there are still few established principles of root decomposition compared to leaf litter decomposition (Silver and Miya 2001). Roots are exposed to a different environment during decomposition compared to aboveground litter; hence development of specific principles for factors controlling root decay is desirable (Silver and Miya 2001), but means practical problems as the environment must be disturbed as a part of the analysis. This paper does not study root decomposition under field conditions, but aims to show differences in decomposition products from roots and needle litter under the same conditions.

The objective for this work was to compare production of carbon dioxide and DOC during decomposition of different kinds of Norway spruce (*Picea abies)* litter. The quality of the produced DOC in terms of aromaticity and its binding to iron-oxide surfaces were investigated.

Theoretical background

Carbon mineralization

When plant litter is decomposed, carbon is lost either as CO_2 or stabilized as soil organic carbon (Rasse et al. 2005). Temperature is usually considered to be an important factor regulating the rate of carbon mineralization, where an increased temperature gives an increased decomposition rate. However, studies have shown that within a site, the initial stimulating effect of a stepwise temperature increase may decline with time, possibly due to decreased substrate availability (Eliasson et al. 2005). On the regional scale, temperature and topography, i.e. the degree of inundation, are among the primary controllers of litter decomposition in high-latitude soils (Hobbie et al. 2000). In these soils, cold temperatures and lack of oxygen in saturated soils are the main limiting factors for decomposition.

Substrate quality is another factor influencing the carbon mineralization rate. Tree litter is a complex material consisting of several groups of organic compounds which are more or less easily decomposed by microorganisms. Sugars, low molecular weight phenolics and some nutrients are lost from the material in early decomposition stages, as a result of the activity of microorganisms and dissolution and leaching processes (Berg and McClaugherty 2003). Larger organic compound such as cellulose, hemicellulose and lignin are more slowly decomposed. These three substances are the most abundant compounds in plant remains, while waxes and lipids, tannins, suberin and cutin are found in smaller amounts (Zech and Guggenberger 1996). The relative amount of different organic compounds varies between species and plant part. During decay, plant litter is reformed to new complex structures, due to condensation processes and import of nutrients to the structures (Berg and McClaugherty 2003, Hobbie et al. 2000).

The change in substrate quality during decomposition means that the decomposition rate of a substrate will change over time. In a study of Black spruce (*Picea mariana* L.) fine root dynamics the decomposition was rapid soon after the roots were identified as dead, but decreased with time (Ruess et al. 2003). The same study showed effect of changing root quality with root age, as the decomposition time increased only slightly over time for roots that had lived less than a year, but substantially for roots that had lived more than a year.

Chemical recalcitrance of plant material is generally attributed to the aromatic compound lignin, which requires strong oxidation agents to be degraded (Rasse et al. 2005). For a range of agricultural crops, Rasse et al. (2005) found that within a given species, the lignin content of roots is on average more than double that of shoots. The root tissues were in general more chemically recalcitrant than shoot tissues in the study. Berg and Meentemeyer (2002) points out the N concentration of litter as a factor regulating the decomposition rate of litter especially in late decomposition stages. An increased N concentration in the litter seems to increase the mass of organic material left when the decomposition more or less ceases.

Most of the carbon stored in northern soils has decomposition rates that are slower than those estimated for fresh litter (Hobbie et al. 2000). This indicates a dominance of recalcitrant compounds in these soils. A build-up of recalcitrant organic material may be the result of selective decomposition of easily degraded substances, or of a reformation through microbial processing (humification) or by fire (charcoal).

DOM and DOC

DOM in soil solution originates from plant litter, soil humus, microbial biomass and root exudates. It can be defined as organic molecules of different sizes and structures that pass through a filter of 0.45 μm pore size (Kalbitz et al. 2000). When studying carbon processes as in this paper, DOC is often in focus, while in studies of nutrient recycling, the Dissolved Organic Nitrogen (DON) and Dissolved Organic Phosphorous (DOP) might be in focus.

Most of the DOM can be classified into five general groups, dependent on the properties of the material: hydrophobic acids (polyelectrolytic aliphatic and aromatic acids, highly degraded lignin- and lignocellulose-degradation products), hydrophilic acids (more oxidized polyelectrolytic aliphatic and aromatic acids, very highly degraded lignin- and lignocellulose-degradation products), hydrophobic neutrals (fatty acids, waxes, less degraded lignin- and lignocellulose-degradation products), hydrophilic neutrals (carbohydrates, polyfunctional alcohols) and hydrophilic bases (amino acids, amphoteric proteins, amino sugars) (Zech and Guggenberger 1996). Another way of grouping DOM is based on its mobility in soil solution. Mobile DOM is situated in meso- and macropores and can be transported convectively, while DOM in micropores is immobile and can only interact with soil solution through diffusion (Kalbitz et al. 2000).

The amount and fluxes of DOM in soils are controlled by several factors and processes, both biotic and abiotic. The substrate quality seems to influence the production of DOM, as studies show higher DOM fluxes from coniferous than from hardwood stands (Kalbitz et al. 2000). However, in situ effects of quality in terms of nutrient composition (C/N and C/P ratios) have been difficult to quantify. Access to substrate for microorganisms, decomposer community and content of soluble organic C in the substrate are possible factors influencing the DOM production. Amount of litter fall and organic matter present in soil are suggested to influence DOM production, but such effects have not been quantified.

When measuring DOM it is important to keep in mind that both production and consumption of DOM can occur at all levels in the soil profile (McDowell 2003). However, it is generally assumed that adsorption of DOM to mineral surfaces in soil dominates over DOM decomposition in decreasing DOM content in soil solution (Kalbitz et al. 2000).

Adsorption of DOC to mineral soil

Sorption of DOM in the mineral horizons is likely the main process by which DOM is retained in forest soils (Kalbitz et al. 2005). Most of the DOC in the soil solution is removed in the top meter of mineral soil due to sorption processes (Chorover and Amistadi 2001). Estimated values of DOC flux from the forest floor to the mineral subsoil is between 115 to 500 kg C $ha^{-1}year^{-1}$ (Kalbitz et al. 2005). The sorption of organic matter to mineral surfaces seems to be influenced by the chemical composition of the organic compounds. Constituents with higher molecular weight has been shown to adsorb preferentially, and fractions rich in aromatic structures such as lignin-derived hydrophobic, fulvic and humic acids show stronger sorption than compounds rich in carbohydrates (Chorover and Amistadi 2001, Kaiser 2003). Chorover and Amistadi (2001) suggest that organic material with high molecular weight is enriched in aromatic groups. Acidity of the compounds seems to be a key factor, where sorption is favoured by increasing number of carboxyl groups per molecule and by increasing acidity of the carboxyl groups (Kaiser 2003). Kaiser (2003) found that the total and carboxylic acidity as well as the content of carboxyl C according to ^{13}C NMR spectroscopy were higher in hydrophobic, humic and fulvic acids than in hydrophilic substrates. Hydrophilic organic matter did always show a much weaker adsorption to goethite than hydrophobic, fulvic and humic acids. Kaiser (2003) argues that the main difference in sorption of different compounds is not due to the presence of aromatic or aliphatic structures per see, but to their attached carboxyl and other functional groups. The sorption of organic matter to goethite surfaces seems to increase with the number of acidic groups attached per aromatic structure. The position of the attached groups may also influence the sorption, where functional groups attached to the *ortho* positions seems to have highest affinity for surfaces of Fe and Al oxides.

Aromaticity and UV-absorbtivity

The specific UV absorbance of DOC has been shown to be strongly correlated to aromaticity of the compound, determined by NMR spectroscopy (Aitkenhead-Peterson & Kalbitz 2005). Kalbitz et al. (2003) use UV absorbance at λ = 280 nm as a parameter to investigate aromaticity of DOM, while

Weishaar et al. (2003) use UV absorbance at $\lambda = 254$ nm. The latter concludes that UV absorbtivity is a good measure of general chemical composition of DOC, but not of its reactivity. In the near UV spectrum ($\lambda = 200 – 380$ nm), conjugated systems such as those present in aromatic molecules, has the highest absorptivities while other electronic structures do not absorb in this spectrum (Weishaar et al. 2003). This makes it possible to measure characteristic bonding features in DOC, which is a mixture of substances with varying complexity. However, it should be noted that individual aromatic compounds have different absorbtivities.

Materials and methods

Site description

The material used in the study was sampled in Asa (57°08'N, 14°45'E), near Lammhult in Småland, southern Sweden. The site is one of three Norway spruce (*Picea abies*) stands used within the research program LUSTRA. Asa is located 190-200 meters above sea level in the boreonemoral vegetation zone (Berggren et al. 2004). Average annual air temperature is 5.5 °C and average annual precipitation 688 mm. The length of the growing season (temperature > 5 °C) is 190 days. Field samples for this study were collected in plots no 4-6 which have a mesic moisture regime. Plots no. 4 and 5 were clear cut from a mixed *Picea abies*/*Pinus sylvestris* stand (aged between 80 and 120 years) in 1966 and planted with four-year old *Picea abies* seedlings in 1967. Plot no. 6 was used as arable land before it was planted with four-year old *Picea abies* seedlings in 1960-1961.

According to FAO 1990 the soil is classified as a Haplic Podzol, which is developed in glacial till. The soil is classified as a stony sandy loam with a medium boulder frequency. Site productivity ranges from 10.1 to 11.3 $m^3*ha^{-1}*yr^{-1}$ and the field and ground vegetation is grass or no vegetation in plots no. 4-6 (Berggren et al. 2004).

Substrates

Five different substrates were compared in the study; fresh needle litter (fnl), aged needles from the litter layer (nll), fresh roots from mineral soil (frms), dead roots from mineral soil (drms) and seven-year-old roots from litterbag studies (lb7). All roots had a diameter of less than 2 mm. Roots from litterbag studies where previously cut in pieces of 1 to 4 cm length and put in litterbags in 1999. These samples were recollected in 2006 and put in freezer. Needles were randomly picked from litter samples collected in Asa in January 2007. Fresh needle litter samples were taken by shaking trees and collecting the falling needles, while aged needles from the litter layer where sampled from the forest floor. Green needles were left out when preparing the substrates. Fresh and dead roots from mineral soil were identified and sorted from samples collected in Asa in October and November 2007. The roots where cut in pieces of approximately needle length. Water content in the material was determined by weighting substrates, drying them in 105 °C for 24 h and measuring the weight loss.

Column incubation and measurements

Substrates were incubated in glass columns (*figure 1*), 35 cm long with a diameter of 2.4 cm, using a method adapted from Sjöberg et al. (2003). Each column had a bottom plug made of silicone, containing a glass drain pipe connected to a silicone tube closed with a clip. On top of the silicone plug, a glass fiber filter was placed to avoid leaching of particles. During the first two percolations filters with 0.7 μm pore size were used. During these percolations the filters caused problems with clogging in several columns, why they were exchanged for filters with 1.0 μm pore size before the third percolation. The columns were filled with substrate mixed with 25 g quartz sand (washed with acid and heated to 600°C to clean it from carbon) and a second glass fiber filter (0.7 μm pore size) was put on top. During incubation plastic films were put on the opening of the column to allow gas exchange but avoid evaporation of water. Four replicates of each substrate were made, in total 20 columns were incubated.

The columns were leached at unsaturated conditions at a tension of about -0.2 bar using a synthetic throughfall solution. The solution was prepared from salts and deionized water. Concentrations of the ions are presented in *Table 1*.

A solution with soil microorganisms was prepared using ground litter from plots 4, 5 and 6 in Asa. 14.55 g litter was grinded using a mixer and mixed with one liter deionized water. The mixture was left for sedimentation for about half an hour, and then the solution without large particles was taken out with a pipette. 5 ml of the solution was added to each of the columns. Columns were incubated in a dark room at a constant temperature of 15°C.

Table 1. Ion concentrations in the throughfall water solution.

Ion	Concentration [μM]
Na^+	0.66
K^+	0.54
Ca^{2+}	0.14
Mg^{2+}	0.1
NH_4^+	0.14
NO_3^-	0.14
SO_4^-	0.27
Cl^-	1.14

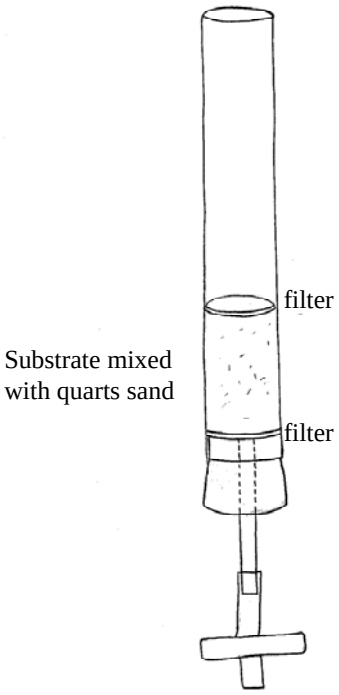

Figure 1. Sketch of the columns used for incubation of substrates.

Figure 2. Sketch of how CO_2 samples were taken out from the columns using a syringe.

Production of CO_2 was measured after 7, 14 and 21 days incubation. The columns were left without coverage for 30 minutes and air was blown into the columns to help mixing the air. Columns were then closed with silicon plugs and after 10 minutes samples were taken out using a syringe (*figure 2*). The silicon plugs were kept on and the columns incubated for about three to seven hours, then a second sample was taken out from each column. The samples were analyzed on a gas chromatograph (Hewlett Packard 5890A with helium in column). Before each respiration measurement, the columns were weighted to calculate water content.

The day after CO_2 measurements, the columns were percolated with 50 ml throughfall water solution at a velocity of 0.55 ml/min. Percolated water samples were filtered using 0.2 μm Acrodisc PF-filters. UV absorbance at 285 nm (Jasco V-530 spectrophotometer), DOC content (Shimadzu TOC-5000A analyzer) and pH (Radiometer Copenhagen PHM93 reference pH-meter) was measured for each sample.

Calculations

A standard series for CO_2 concentration was prepared using eight bottles flushed with N_2. CO_2 was injected using a syringe to obtain a concentration series of 0.032, 0.062, 0.10, 0.17, 0.23, 0.33, 0.50 and 0.66 % v/v CO_2. Using data for the standards, a linear regression was made for the correlation between

partial CO_2-pressure and area (mV*s). The regression equation was used to calculate the CO_2-pressure in the columns.

To assess the total amount of CO_2 respired, equilibrium calculations were made to calculate the concentration of inorganic carbon (CO_2, H_2CO_3 and HCO_3^-) dissolved in the water phase in the columns. The equilibrium constants log K_0 = 1.34 and log K_{a1} = -6.42 were used for the carbonate system at 15 °C (reactions below).

$$H_2CO^*_{3\,aq} \Leftrightarrow CO_{2\,g} + H_2O \qquad K_0 = \frac{P_{CO_2}}{\{H_2CO^*_3\}}$$

$$H_2CO^*_{3\,aq} \Leftrightarrow H^+{}_{aq} + HCO^-_{3\,aq} \qquad K_1 = \frac{\{H^+\}\{HCO^-_3\}}{\{H_2CO^*_3\}} \text{ where } H_2CO^*_{3\,aq} = CO_{2\,aq} + H_2CO_{3\,aq}$$

To convert between activities and concentrations, the relationship $a_i = c_i \cdot \gamma_i$ was used, where a_i is the activity of the compound, c_i the concentration and γ_i the activity coefficient of the compound. Ionic strength (I) of the rainwater solution was calculated using the formula $I = 0.5 \cdot \sum m_i \cdot z_i^2$ where m_i is the molality of the ion and z_i its charge. The activity coefficient γ_i was calculated using Davies equation: $-\log \gamma_i = 0.51 \cdot z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3 \cdot I \right)$. In this formula, z_i is the charge of the compound of interest. For HCO_3^-, the activity coefficient was calculated to be 0.948. The total amount of respired carbon (n_{cr}) was calculated using the formula $n_{Cr} = n_{Ca} + n_{Cw}$, where n_{Ca} is the amount carbon in the air and n_{Cw} the amount carbon dissolved in water. Background level n_{cr} were subtracted from final n_{cr} to assess respired amount of CO_2. The rate was obtained by dividing with the incubation time.

Adsorption experiment

Adsorption of DOC to oxide surfaces was investigated using synthetic ferrihydrite. Samples from the second percolation were pooled to obtain one sample from each substrate to use in the adsorption experiment. Ferrihydrite was synthesized using a method adapted from Swedlund and Webster (1999) and Schwertmann and Cornell (2000). To a solution containing 36 mM $Fe(NO_3)_3$ and 12 mM $NaNO_3$, 4 M NaOH was added dropwise under stirring, until pH 8.27 was reached. The resulting suspension was aged for 18 hours in 20 °C and then backtitrated to pH 4.0 with 0.1 M HNO_3. To release CO_2 the suspension was stirred for one hour. Suspension pH was adjusted to 4.6 with 4 M NaOH before addition to the samples. 1.40 ml ferrihydrite suspension was added to 15 ml sample. For each substrate 6 different samples were prepared and adjusted to different pH-values (4.0, 4.5, 5.0, 5.5, 6.0 and 6.5) by addition of 0.01 M NaOH or 0.01 M HNO_3. The samples were "end-over-end" shaken for 5 h in darkness, 20 °C, and then centrifuged for 20 minutes in 2000 rpm, 20 °C in a Beckman Coulter J6-MI Centrifuge. The supernatant was extracted and pH was measured. The resulting supernatant was filtered using 0.2 µm Acrodisc PF-filter and UV absorbance and DOC content was analyzed.

To confirm that there were no iron oxide particles in the filtered supernatants, original solutions and filtered supernatants were analyzed for iron using ICP Optima 3000 DV. The original solution was also analyzed for sodium, potassium, calcium, magnesium and aluminum.

Statistical analysis

Results of pooled losses of CO_2 and DOC during the three weeks were analyzed using one-way ANOVA (95 % confidence level) in Minitab 15 software. To assess statistical significant differences between any substrates, the mean of every treatment was compared with the mean of every other treatment using Tukey's test with 95 % confidence interval. Result graphs are presented with error bars showing standard error of the mean.

Results

Values of measured pH, CO_2, DOC, UV-absorbance and UV-absorbance/DOC for each week can be found in *Appendices 1-3*. Results from element analysis of pooled samples from week two are presented in *Appendix 4*.

Respiration

The total mass of respired carbon (the sum of CO_2, H_2CO_3 and HCO_3^- in the columns) per gram (dry weight) substrate and hour is higher for the needles than for the roots (*figure 3*). Respiration tends to be highest in the first measurement. Fresh needle litter had the highest respiration rate in the two first measurements, followed by aged needles from the litter layer. In the third measurement, the respiration rates of these two substrates are almost equal. For the roots, the fresh roots from mineral soil had highest respiration rate, followed by dead roots from mineral soil, both slightly decreasing with time. Roots from litterbag studies had the lowest respiration rate, which was almost constant over time.

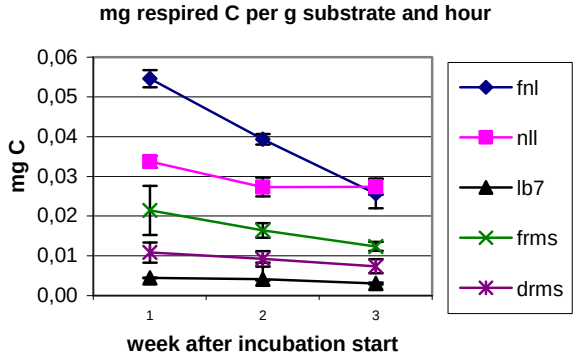

Figure 3. Respiration rates of different substrates after one, two and three weeks of incubation.

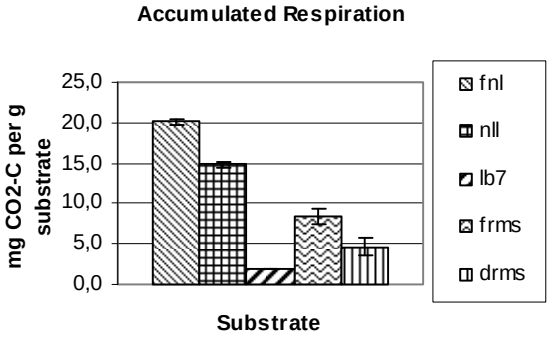

Figure 4. Accumulated respiration during three weeks of incubation (mg CO_2-C/g substrate).

The accumulated amount of respired CO_2-C (*figure 4*) is highest for fresh needle litter (fnl), followed by aged needles from the litter layer (nll). Fresh roots from mineral soil (frms) had higher accumulated respiration than dead roots from mineral soil (drms), and seven-year old roots from litterbag studies (lb7) respired least CO_2-C during the experimental period. These values indicate that needles contain larger amount of easily decomposed compounds compared to roots, resulting in higher respiration. Further, the fresh substrates have a higher respiration than substrates in later decomposition stages. ANOVA analyses showed a significant impact of substrate on respiration rate ($p < 0.001$). Tukey's test indicated significant differences between all substrates except between roots from litterbag studies and dead roots from mineral soil.

DOC production

Generally, there seems to be a decreasing trend in DOC-production over time (*figure 5*), most pronounced for fresh roots from mineral soil and aged needles from the litter layer, which had the highest DOC production in the first measurement. The DOC production from the fresh needle litter was quite low and almost constant.

Measured amount of DOC from the three percolations were accumulated, showing the total DOC production during the first three weeks of incubation (*figure 6*). The highest amount of DOC is produced from aged needles from the litter layer, followed by fresh roots from mineral soil and fresh

needle litter. Dead roots from mineral soil and roots from litterbag studies produced almost the same amount of DOC, with less variability for the roots from litterbag studies.

ANOVA analysis showed that substrate had a significant effect on accumulated DOC production ($p < 0.001$); however, the differences between all substrates were not significant. Accumulated DOC production from fresh needle litter was significantly lower than from aged needles from the litter layer, but could not be separated from roots from litterbag studies, fresh roots from mineral soil or dead roots from mineral soil. DOC production from aged needles from the litter layer was significantly higher than the production from roots from litterbag studies and dead roots from mineral soil, but could not be distinguished from fresh roots from mineral soil. Fresh roots from mineral soil had a significantly higher DOC production than roots from litterbag studies and dead roots from mineral soil while DOC production from the two latter could not be separated. These results indicate that DOC production peaks at a later decomposition stage than respiration, and that decomposition stage is more important than substrate origin for amount DOC produced.

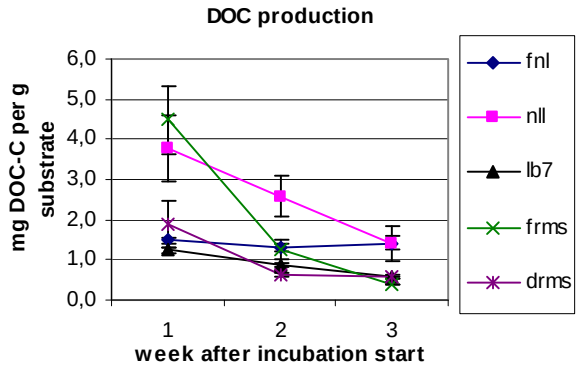

Figure 5. DOC production one, two and three weeks after incubation start (mg DOC-C/g substrate).

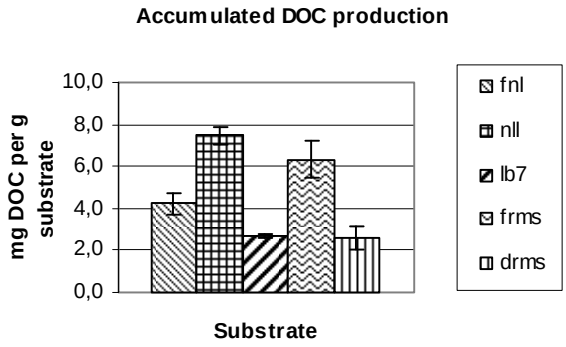

Figure 6. Accumulated DOC production during the first three weeks of incubation [mg DOC-C/g substrate].

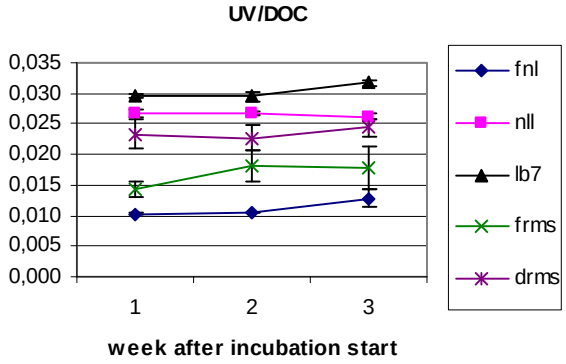

Figure 7. UV/DOC ratio for different substrates during the first three weeks of incubation.

UV/DOC as a measure of DOC quality (*figure 7*) seems to be constant or slightly increasing (meaning a higher proportion of hydrophobic compounds) over time during the three weeks of incubation. The differences between substrates are more pronounced for the studied time period. Seven-year-old roots from litterbag studies has the highest UV/DOC ratio followed by needles from the litter layer and dead roots from mineral soil. The ratio is lower for fresh roots from mineral soil and lowest for fresh needle litter. Highest UV/DOC ratios are measured for the substrates that were most decomposed at the start of the incubation experiment, indicating that the proportion of DOC

containing more aromatic structures increases during decomposition. The variability within the replicates is highest for fresh roots from mineral soil and dead roots from mineral soil. These substrates are the most heterogeneous, as they contain roots of different sizes (all less than 2 mm in diameter) and in the latter case roots that have been dead for a shorter or longer period.

Relative losses of CO_2 and DOC

To compare the decomposition process for different substrates, it is important to study the partitioning of losses as CO_2 and DOC, respectively. *Figure 8* shows the accumulated production of CO_2 and DOC, illustrating the total carbon losses per gram substrate during the first three weeks of incubation. The total losses are highest from the two needle substrates followed by the fresh roots. The two dead root substrates had the smallest losses. However, the interesting pattern in partitioning of losses are more clearly seen in *figure 9*, where total losses are considered as 100 %. In this graph it can be seen that although the respiration rate is low for the seven-year old roots from litterbag studies, the relative production of DOC is high in this group, nearly 60 % of total losses. For fresh needle litter, which had the highest total losses, the DOC production contributed to only about 20 %.

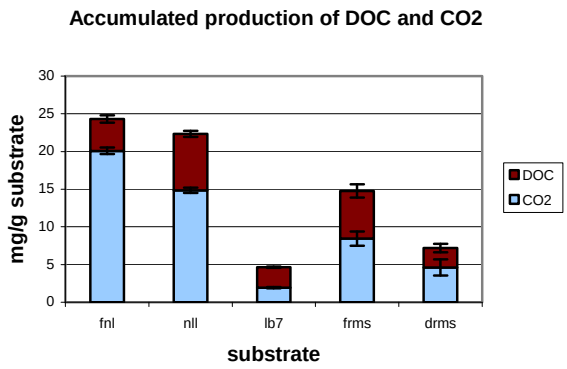

Figure 8. Accumulated production of CO_2 and DOC from different substrates, normalized to initial weight of substrate.

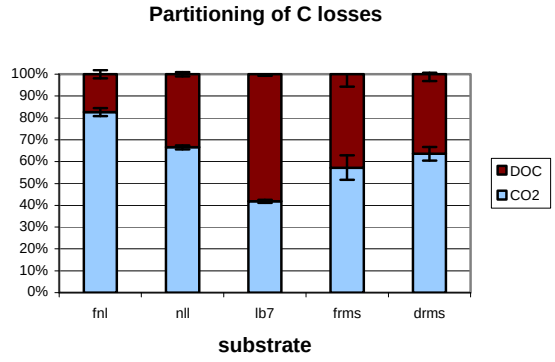

Figure 9. Relative contribution of CO_2 and DOC to total carbon losses.

DOC adsorption to ferrihydrite

Percentage DOC adsorbed to ferrihydrite is showed in *figure 10*. This figure indicates that there is a difference in proportion DOC adsorbed to the ferrihydrite between the substrates, but the adsorption seems to be independent of pH. The aged needles from the litter layer, the roots from litterbag studies and the dead roots from mineral soil form a group with high adsorption (70-90 %) for all pH-values. The adsorption of DOC from fresh roots from mineral soil ranges from 50 % to 70 % while the proportional adsorption of DOC from fresh needle litter is lowest (30-40 %). These results indicate that the degree of decomposition is more important for DOC adsorption than if the original tissue was a needle or a root.

To see if adsorption processes were influenced by substrate quality in terms of aromaticity the ratio $\frac{UV / DOC_{before}}{UV / DOC_{after}}$ was calculated for the different substrates at different pH-values. This is the ratio between UV/DOC before contact with ferrihydrite and UV/DOC after contact with ferrihydrite. A ratio of 1 means no effect of quality on adsorption, a ratio larger than 1 indicates preferential sorption of

hydrophobic compounds, while a ratio of less than 1 indicates a preferential sorption of hydrophilic compounds. In *figure 11*, showing the calculated ratios, it can be seen that hydrophobic compounds were preferentially adsorbed for all substrates, except for the dead roots from mineral soil where almost no effect of quality on adsorption was measured. However, the degree of impact varied between the substrates. Adsorption of compounds from fresh roots from mineral soil, aged needles from the litter layer and fresh needle litter was most affected by litter quality, while the effect on DOC from seven-year-old roots from litterbag studies was smaller.

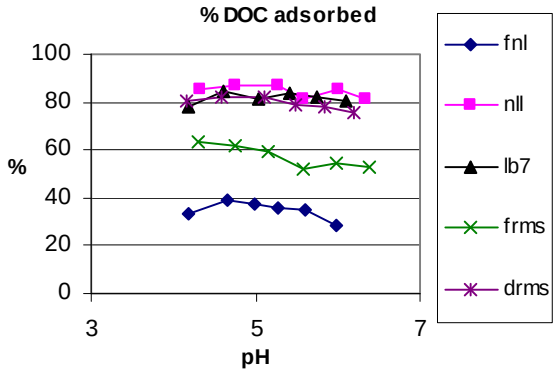

Figure 10. Percentage DOC adsorbed to ferrihydrite.

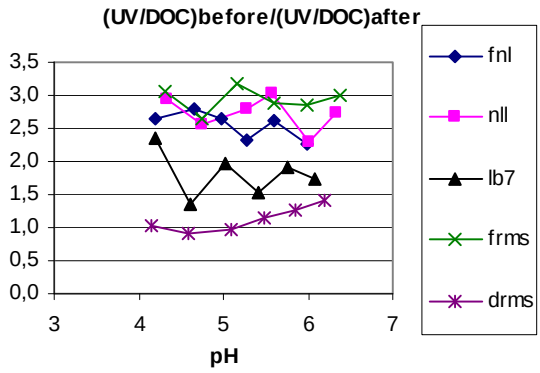

Figure 11. Effect of DOC quality on sorption

Discussion

The results from the present study can be an important input to further understanding of partitioning of losses during decomposition, especially for roots. The fraction of carbon lost as DOC from aged dead roots is high and very different from the partitioning of carbon losses from needles. Fröberg et al. (2007) concluded from several laboratory studies that recent litter has a large potential to produce DOC. In this study, the DOC production (accumulated values for the three weeks) is highest in aged needles from the litter layer and fresh roots from mineral soil (*figure 6*); while DOC production is lower from the two groups with dead roots, in agreement with these earlier studies. However, this comparison only accounts for the amount of carbon lost as DOC, not the relative amount of DOC lost during decomposition.

Further, Fröberg et al. (2007) found that DOC leached from added fresh litter had less UV absorbing moieties than DOC leached from organic horizons in the soil. This is in agreement with the results from this study, where fresh needle litter had the lowest UV/DOC ratio (*figure 7*) followed by fresh roots from mineral soil, while the substrates in later decomposition stage had a higher UV/DOC ratio.

This study only considers substrates from Norway spruce, a common species in Swedish forests. However, McDowell (2003) concludes in a review that tree species appear to have very little effect on DOC composition, despite the large variation in litter chemistry among species. Hence the general trends for DOC sorption found in this study might be valid even for substrates from other tree species.

Only one size group of roots was used in the study (root diameter < 2 mm). It could be interesting to compare decomposition of roots with different diameters, as the secondary thickening of roots in woody species changes the proportion of wood to more ephemeral tissues (Silver and Miya 2001). However, this would require more samples and probably a larger size of each sample to get enough material. Further, Silver and Miya (2001) found no statistically significant differences in decomposition rates between small (< 2 mm) and medium (2-5 mm) diameter roots, while large diameter roots (> 5 mm) decomposed significantly slower.

Chorover and Amistadi (2001) investigated sorption of organic material with different functional groups to goethite, birnessite and montmorillonite and concluded that the fractionation of organic material is influenced by the mineral surface chemistry. In this study, adsorption to ferrihydrite was investigated. As ferrihydrite is the most common iron oxide in Swedish soils (Eriksson et al. 2005), the results may indicate how DOC is adsorbed in Swedish mineral soils. The ferrihydrite used was synthetic, meaning that there was no organic material adsorbed to the oxide before the adsorption experiment. To further understand adsorption under field conditions, it would be interesting to study if the ferrihydrite can be saturated with DOC hence making the proportion DOC adsorbed lower.

This study is carried out under laboratory conditions and the incubation was made in 15 °C, a temperature higher than the average temperature in southern Sweden. It can also be questioned if the added solution prepared from forest litter represents the decomposer community in the forest soils. However, the study shows the relative amounts of CO_2 and DOC produced from different substrates under equal conditions. The fact that the columns are percolated the day after CO_2-measurements makes the experiment similar to natural conditions, where rain percolates the soil continuously during the decomposition process. As always one has to be aware of the complexity of nature when trying to scale up results obtained in lab conditions.

Within the substrate group *dead roots from mineral soil* the range in how long time the roots have been dead is quite wide. Despite this, the variance for the results within this group is not strikingly bigger than for the other groups.

Results from the decomposition study presented in this paper only contain data from one month incubation experiment. This time period is too short to be able to get a complete picture of how CO_2 and DOC production changes over time in the decomposition process. However, this study is a part of

an incubation experiment that will stretch over several months. Data from this longer study may show how decomposition patterns changes over a longer time period.

A further analysis to be made on percolated solution from the present experiment is measurement of the decomposition rate of DOC in soil solution. This can be related to one question posed by McDowell (2003) concerning what fraction of DOM produced that is actually measured, and what fraction is turned over too quickly to be measured.

Working with the experiment rose questions about biological aspects of decomposition of different substrates, i.e. if there are any differences in decomposer communities that degrade needles and roots. Very little research is made in this field and this could be an interesting topic for future research. McDowell (2003) points out development of an integrated conceptual approach addressing interactions between solid soil organic matter, microorganisms including fungi and DOM as recommended for future DOM research. McDowell (2003) also points out the importance of cooperation between soil chemists, microbiologists and ecologists to understand the ecological significance of DOM. This is something I can agree in, as a student meeting researchers from these fields with different perspectives in different courses.

Conclusions

Respiration and DOC-production from Norway spruce needles and fine roots, as well as degree of adsorption of DOC to ferrihydrite, is dependent on degree of decomposition of the substrate. Amount of respired CO_2 seems to be dependent on substrate origin, where respiration is higher for needles than for roots. DOC production, DOC quality and DOC adsorption to ferrihydrite appear to be independent of substrate origin and only dependent on decomposition degree. DOC-production peaks in later decomposition stages for needles and in an early stage for fine roots, while the relative contribution of DOC to total carbon losses is highest for roots in late decomposition stages. DOC-adsorption to ferrihydrite is highest for substrates in late decomposition stages with high UV/DOC ratio i.e. a large proportion of aromatic structures.

Acknowledgements

First I would like to thank my supervisors Dan Berggren Kleja (Department of Soil and Environment) and Karna Hansson (Department of Ecology). Dan for giving me the opportunity to do this work and interesting discussions, Karna for good company and discussions during the daily work. Thanks to Tomas Grönqvist (Department of Ecology), Gunilla Hallberg and Gunilla Lundberg (Department of Soil and Environment) for patiently helping us with equipment and measurements. I would also like to thank the staff at the department of Ecology for interesting discussions in the laboratory and during coffee breaks.

References

Aitkenhead-Peterson J A, Kalbitz K (2005) *Short-term response on the quantity and quality of rhizo-deposited carbon from Norway spruce exposed to low and high N inputs*. J. Plant Nutr. Soil Sci. 168:687-693.

Berg B, McClaugherty C (2003) *Plant Litter. Decomposition, Humus Formation, Carbon Sequestration*. Springer-Verlag, Berlin Heidelberg.

Berg B, Meentemeyer V (2002) *Litter quality in a north European transect versus carbon storage potential*. Plant and Soil 242:83-92

Berggren D, Bergkvist B, Johansson M-B, Langvall O, Majdi H, Melkerud P-A, Nilsson Å, Weslien P, Olsson M (2004) *A description of LUSTRAs Common Field Sites*. Reports in Forest Ecology and Forest Soils. No 87. Swedish University of Agricultural Sciences. ISSN 0348-3398

Chorover J, Amistadi M K (2001) *Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces*. Geochemica et Cosmochimica Acta 65:95-109.

Dixon R K, Brown S, Houghton R A, Solomon A M, Trexler M C, Wisniewski J (1994) *Carbon Pools and Flux of Global Forest Ecosystems*. Science 263:185-190

Eliasson P E, McMurtrie R E, Pepper D A, Strömgren M, Linder S, Ågren G I (2005) *The response of heterotrophic CO_2 flux to soil warming*. Global Change Biology, 11:167-181

Eriksson J, Nilsson I, Simonsson M (2005) *Wiklanders Marklära*. Studentlitteratur, Lund.

Fröberg M, Berggren Kleja D, Hadgedorn F (2007) *The contribution of fresh litter to dissolved organic carbon leached from a coniferous forest floor*. European Journal of Soil Science 58:108-114.

Hobbie S E, Schimel J P, Trumbore S E, Randerson J R (2000) *Controls over carbon storage and turnover in high-latitude soils*. Global Change Biology 6:196-210.

Kaiser K (2003) *Sorption of natural organic matter fractions to goethite (a-FeOOH): effect of chemical composition as revealed by liquid-state ^{13}C NMR and wet-chemical analysis*. Organic Geochemistry 34:1569-1579

Kalbitz K, Solinger S, Park J-H, Michalzik B, Matzner E (2000) *Controls on the dynamics of dissolved organic matter in soils: A reiew*. Soil Science 165:277-304.

Kalbitz K, Schmerwitz J, Schwesig E, Matzner E (2003) *Biodegradation of soil-derived dissolved organic matter as related to its properties*. Geoderma 113:273-291.

Kalbitz K, Schwesig D, Rethemeyer J, Matzner E (2005) *Stabilization of dissolved organic matter by sorption to the mineral soil*. Soil Biology & Biochemistry 37:1319-1331.

Kalyn A L, Van Rees K C J (2006) *Contribution of fine roots to ecosystem biomass and net primary production in black spruce, aspen, and jack pine forests in Saskatchewan*. Agricultural and Forest Meteorology 140: 236-243.

McDowell W H (2003) *Dissolved organic matter in soils – future directions and unanswered questions*. Geoderma 113:179-186.

Rasse D P, Rumpel C, Dignac M-F (2005) *Is soil carbon mostly root carbon? Mechanisms for a specific stabilization*. Plant and Soil 269:341-356.

Ruess R W, Hendrick R L, Burton A J, Pregitzer K S, Sveinbjornssön B, Allen M F, Maurer G E (2003) *Coupling fine root dynamics with ecosystem carbon cycling in black spruce forests of interior Alaska*. Ecological Monographs 73:643-662.

Schwertmann U, Cornell R M (2000) *Iron Oxides in the laboratory. Preparation and Characterization*. Wiley, Weinheim.

Silver W L, Miya R K (2001) Global patterns in root decomposition: comparisons of climate and litter quality effects. Oecologia 129:407-419.

Sjöberg G, Bergkvist B, Berggren D, Nilsson S I (2003) *Long-term N addition effects on the C mineralization and DOC production in mor humus under spruce*. Soil Biology & Biochemistry 35:1305-1315.

Swedlund P J, Webster J G (1999) *Adsorption and polymerization of silicic acid on ferrihydrite, and its effect on arsenic adsorption*. Water Research 33:3413-3422.

Zech W, Guggenberger G (1996) *Organic Matter Dynamics in Forest Soils of Temperate and Tropical Ecosystems*. In Piccolo A, (Ed.) *Humic substances in Terrestrial Ecosystems*. 101-170. Elsevier Science B.V. Amsterdam

Weishaar J L, Aiken G R, Bergamaschi B A, Fram M S, Fujii R, Mopper K (2003) *Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon*. Environ. Sci. Technol. 37:4702-4708.

Appendix 1: **Data from measurements week 1**

Substrate	Sample	pH	CO2 [mg C/h*gsubstrate]	DOC [ppm]	UV-abs	UV-abs/DOC
Fresh needle litter	1	5.55	0.0554	33.05	0.336	0.010
	2	5.72	0.0487	24.91	0.254	0.010
	3	5.5	0.0559	30.30	0.326	0.011
	4	5.32	0.0589	30.07	0.294	0.010
Aged needles from the litter layer	5	6.43	0.0353	122.00	3.5	0.029
	6	5.91	0.0361	52.82	1.348	0.026
	7	5.9	0.0294	52.83	1.373	0.026
	8	5.91	0.0358	74.05	2	0.027
Seven-year-old roots from litterbag studies	9	4.86	0.0045	23.84	0.716	0.030
	10	4.98	0.0046	24.66	0.709	0.029
	11	4.93	0.0046	22.72	0.682	0.030
	12	5.12	0.0042	29.27	0.865	0.030
Fresh roots from mineral soil	13	7.03	0.0251	80.63	1.287	0.016
	14	6.19	0.0036	139.60	1.693	0.012
	15	7.08	0.0320	63.89	1.103	0.017
	16	6.84	0.0316	75.64	0.887	0.012
Dead roots from mineral soil	17	6.73	0.0190	71.35	1.158	0.016
	18	6.39	0.0107	20.81	0.503	0.024
	19	6.22	0.0087	33.25	0.88	0.026
	20	6.48	0.0063	24.88	0.65	0.026

Appendix 2: **Data from measurements week 2**

Substrate	Sample	pH	CO2 [mg C/h*gsubstrate]	DOC [ppm]	UV-abs	UV-abs/DOC
Fresh needle litter	1	5.6	0.0364	21.630	0.223	0.010
	2	5.67	0.0413	25.580	0.269	0.011
	3	5.43	0.0420	27.720	0.292	0.011
	4	5.41	0.0380	29.990	0.32	0.011
Aged needles from the litter layer	5	6.53	0.0318	26.210	0.69	0.026
	6	6.65	0.0248	75.370	1.945	0.026
	7	6.02	0.0323	46.570	1.281	0.028
	8	6.84	0.0245	58.730	1.608	0.027
Seven-year-old roots from litterbag studies	9	5.04	0.0045	17.730	0.519	0.029
	10	5.2	0.0031	15.260	0.428	0.028
	11	5.03	0.0043	18.690	0.541	0.029
	12	5.04	0.0047	19.270	0.614	0.032
Fresh roots from mineral soil	13	6.95	0.0161	29.960	0.368	0.012
	14	6.67	0.0189	20.130	0.397	0.020
	15	6.35	0.0124	14.130	0.34	0.024
	16	6.71	0.0217	36.010	0.584	0.016
Dead roots from mineral soil	17	6.42	0.0152	14.440	0.289	0.020
	18	6.32	0.0088	9.800	0.178	0.018
	19	6.33	0.0075	12.490	0.318	0.025
	20	6.32	0.0059	14.420	0.392	0.027

Appendix 3: **Data from measurements week 3**

Substrate	Sample	pH	CO2 [mg C/h*gsubstrate]	DOC [ppm]	UV-abs	UV-abs/DOC
Fresh needle litter	1	6.09	0.0248	18.42	0.236	0.013
	2	6.1	0.0342	20.00	0.296	0.015
	3	5.41	0.0165	54.91	0.509	0.009
	4	5.94	0.0271	19.74	0.289	0.015
Aged needles from the litter layer	5	6.48	0.0266	22.51	0.604	0.027
	6	6.45	0.0236	15.01	0.377	0.025
	7	6.31	0.0261	32.04	0.838	0.026
	8	6.48	0.0332	22.35	0.600	0.027
Seven-year-old roots from litterbag studies	9	5.48	0.0030	12.40	0.397	0.032
	10	5.69	0.0024	10.86	0.329	0.030
	11	5.37	0.0031	11.56	0.379	0.033
	12	5.78	0.0036	9.99	0.318	0.032
Fresh roots from mineral soil	13	6.54	0.0139	7.39	0.083	0.011
	14	6.53	0.0142	8.60	0.111	0.013
	15	6.56	0.0091	7.09	0.184	0.026
	16	6.39	0.0123	7.93	0.168	0.021
Dead roots from mineral soil	17	6.51	0.0125	14.66	0.309	0.021
	18	6.31	0.0068	10.35	0.237	0.023
	19	5.98	0.0057	12.12	0.333	0.027
	20	6.19	0.0045	9.22	0.240	0.026

Appendix 4: **Concentration of elements in pooled samples**

Substrate	Sample	Fe [mg/l]	Na [mg/l]	K [mg/l]	Ca [mg/l]	Mg [mg/l]	Al [mg/l]
Fresh needle litter	1-4	0.01	3.31	2.90	1.07	0.52	0.26
Aged needles from the litter layer	5-8	0.02	2.78	4.91	4.52	1.18	0.38
Seven-year-old roots from litterbag studies	9-12	0.04	3.27	2.96	0.16	0.07	0.13
Fresh roots from mineral soil	13-16	0.12	6.50	4.64	0.29	0.25	0.30
Dead roots from mineral soil	17-20	0.09	5.02	2.63	0.21	0.12	0.25