Organic Matter Turnover in Forest and Arable Land

Temperature and Moisture Effects and Dynamics of Heavy Metals

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Doctoral thesis
Swedish University of Agricultural Sciences
Uppsala 2002

Acta Universitatis Agriculturae Sueciae
Silvestria 250

ISSN 1401-6230
ISBN 91-576-6334-3

Tryck: SLU Service/Repro, Uppsala 2002

Abstract

Lomander, A. 2002. *Organic matter turnover in forest and arable land – temperature and moisture effects and dynamics of heavy metals*. Doctoral dissertation.
ISSN 1401-6230, ISBN 91-576-6334-3.

Decomposition is crucial in the circulation of global C as well as that of other elements like heavy metals. The aims of this work were to investigate and model how temperature (-4, 0.3, 5, 15, 25 and fluctuating -4/5°C) and moisture (four levels between wilting point and 100% WHC) influence the decomposition rate in a heavy clay soil incubated in the laboratory. Concentrations of Cd, Zn, Mn, Cu and Pb in spruce needles incubated in litter-bags for 6-8 years in five spruce stands were also measured and their effects on decomposition rates discussed.

Decomposition rate increased significantly with increasing temperature and moisture. The decomposition rate was twice as high in the topsoil as in the subsoil samples. Temperature fluctuations did not increase decomposition rate compared with samples at constant +5°C. A two-component first-order model was superior to a single-component model to describe decomposition. Quadratic temperature and moisture response functions were used. The calculated minimum temperature (T_{min}) for decomposition was -0.83°C and Q_{10} increased from 2.2 at 25°C to 12.7 at 0.3°C. When analysing decomposition data compiled from the literature, the two-component model was again more accurate than the single-component. The goodness of fit did not differ between the temperature response models tested, but was affected by the reference temperature. Between 5 and 35°C, a Q_{10}-value of 2 was found to be adequate.

Concentrations of Cd, Zn, Cu and Pb increased, while concentrations of Mn generally decreased during spruce needle decomposition. Concentrations considered toxic to micro-organisms were not observed. Total amounts of Cd, Zn, and Mn decreased by at least 15, 24 and 43% while total amounts of Cu and Pb increased by over 40 and 230% respectively, before they became more constant or started to decrease. A PCA indicated that dynamics of total amounts were more similar between adjacent sites than between more distant sites.

The studies indicate that there is a need for more research, especially at low temperatures where decomposition rate is low. The paucity of high-precision measurements of decomposition below 5°C makes it difficult to draw conclusions about the temperature responses below this temperature. Concerning heavy metals, after about 8 years of decomposition in the field, between 20 and 40% of the litter still remained. We therefore lack a complete picture of heavy metal dynamics during the latter parts of the decomposition period.

Key words: C mineralization, CO_2 evolution, temperature response, moisture response, soil organic matter, soil C, heavy clay soil, mor layer, forest soil, *Picea abies,* heavy metal accumulation, heavy metal release

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Först syns det oändligt.
Tar sin början med ett intensivt nu.
Under åren man arbetar, stretar och gnor
är livet imorgon, om ett år och igår.

Brytpunkter kommer
Man får kanske följe, av best eller vän?
Man väljer själv dess karaktär
och ges en chans till det som är.

Contents

Appendix

Papers I-IV

The present thesis is based on the following papers, which will be referred to in the text by their Roman numerals.

I. Lomander, A., Kätterer, T., & Andrén, O. 1998. Carbon dioxide evolution from top- and subsoil as affected by moisture and constant and fluctuating temperature. *Soil Biology and Biochemistry* 30, 2017-2022.

II. Lomander, A., Kätterer, T. & Andrén, O. 1998. Modelling the effects of temperature and moisture on CO_2 evolution from top- and subsoil using a multi-compartment approach. *Soil Biology and Biochemistry* 30, 2023-2030.

III. Kätterer, T., Reichstein, M., Andrén, O. & Lomander, A. 1998. Temperature dependence of organic matter decomposition: a critical review using literature data analysed with different models. *Biology and Fertility of Soils* 27, 258-262.

IV. Lomander, A. & Johansson, M.-B. 2001. Changes in concentrations of Cd, Zn, Mn, Cu and Pb in spruce (*Picea abies*) needle litter during decomposition. *Water, Air and Soil Pollution* 132, 165-184.

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Introduction

The subject at hand includes a risk for an I-will-save-the–world attitude that can make a text like this one somewhat too severe. However, saving the world is, at least in this case, not my intention. The purposes of the following text are mainly to give you a brief introduction to the subject and hopefully to manage to put the work in the presented papers into context as well. Large efforts are today being dedicated towards improving our understanding of the global carbon (C) cycle, and there is great concern about human actions affecting climate and circulation of different heavy metals in the environment, which will influence soil organic C turnover.

This thesis contributes some new information regarding the decomposition process, especially its temperature response. New long-time observations of heavy metal dynamics in decomposing needle litter are also presented. Furthermore, some of the problems with regard to transfer of results from the laboratory and from field experimental set-ups to larger semi-natural and natural ecosystems are discussed.

Soil organic carbon

The Earth contains about 10^8 Gt (Gt=10^9 tonnes) of C, whereof the majority is found as organic compounds and carbonates in buried sedimentary rocks (Schlesinger, 1997). The amount of C that is actively circulating near the surface of the Earth is about 40 000 Gt, *i.e.* only 0.04% of the global C pool. This portion is usually divided into four pools, whereof the oceanic pool containing 38 000 Gt C is by far the largest. On land, the largest pool of C, 1500 Gt, is contained as soil organic matter. This is twice as much as the content of the atmospheric pool, 750 Gt, and almost three times the estimated amount of C (560 Gt) in vegetation (Schimel, 1995).

There are some general trends for the distribution of soil organic C among different soil types. Soils developed under cold conditions contain more C than soils developed under warm conditions and wet soils contain more C than dry soils. Grassland soils contain more soil C than forest soils and uncultivated soils more than cultivated soils. Soil texture is also an influencing factor and soil C increases with increasing clay content (see *e.g.* Batjes, 1996; Brady & Weil, 1996).

The CO_2 flux from soils to the atmosphere is estimated to be about 50-70 Gt C yr^{-1} (Raich & Schlesinger, 1992) and is assumed to be more or less balanced by net primary production, NPP (Schlesinger, 1997). Burning of fossil fuels results in a flux of 6 Gt C yr^{-1} to the atmosphere, and emissions from land use changes are estimated to about 0.9 Gt C yr^{-1}. Although this makes up a net flux of 6.9 Gt C yr^{-1} to the atmosphere, the atmospheric CO_2 content is presently rising by approximately 3.2 Gt C yr^{-1}, (Schimel, 1995). This leaves about 3.7 Gt that probably is taken up by large sinks in terrestrial and/or oceanic ecosystems. The rise in atmospheric CO_2 content from about 280 ppm before the industrial revolution (Sowers & Bender, 1995) up to the present day level of 370 ppm is a severe problem, since CO_2 is a greenhouse gas (Petit *et al.*, 1999). It means that infra-red radiation is absorbed which otherwise would be emitted from the surface of the Earth into space, which affects the heat balance of the Earth. During the past century, the global mean temperature has increased by 0.6ºC (Kaufmann & Stern, 1997) and even higher increases of the global mean temperature over the period 1990 to 2100 are estimated. These are based on the assumption that present global warming will accelerate the decomposition rates of soil organic matter stores, turning them into sources of CO_2, resulting in a positive feed-back to further global warming (Kirschbaum, 2000).

As early as 1927, Lundegård noted that soil respiration was correlated with various factors including temperature, moisture and the nutrient content of the soil. Together with chemical and physical characteristics of the organic material, these parameters are considered to be the major factors controlling decomposition rates of soil organic matter (see *e.g.* Swift *et al.*, 1979). Oxygen availability (see *e.g.* Nyhan, 1976), the type of micro-organisms present (see *e.g.* Wilson & Griffin, 1975) and faunal abundance and activity (see *e.g.* Petersen & Luxton, 1982) are also important factors. Since the pool of soil C is twice as large as the pool of atmospheric C, relatively small changes in the former could have a significant impact on the CO_2 content of the atmosphere.

The effects of temperature and/or moisture on decomposition in sandy, silty or loamy soils developed under tropical or temperate conditions have been reported by several authors. Corresponding studies on decomposition rates in soils in boreal (cold) regions are fewer and mainly made on litter or humified organic matter and light mineral soils. Studies on the effects of temperature and moisture on decomposition rates in cold heavy clay soils are lacking. The high soil C content of these heavy clay soils and the fact that they constitute about 59% of Swedish agricultural soils (Andrén & Kätterer, 2001), emphasise the importance of studies of factors controlling the decomposition rate in these soils. Since the texture itself affects temperature and moisture, as well as the quality and quantity of the available organic material, it may be difficult to interpret and compare the results between soils of different textures. However, a first step could be to study and model the effects of temperature and moisture on decomposition rates without taking account of the texture. This has mainly been done in the first two papers included in this thesis. As a further step (Paper III), our decomposition data from the cold heavy clay soil were combined with other data on the effect of temperature on decomposition for different soil types. The temperature response model used for our cold heavy clay soil, as well as three other temperature response models, were then tested for their ability to describe the dynamics of decomposition in the soils.

Decomposition does not only involve evolution of CO_2, but also release of different elements. The release of elements from decomposing litter is known to quantitatively be one of the major processes in nutrient cycling in natural unmanaged ecosystems. Elements are released from litter either through leaching by soil water or through the decomposition of the organic components by the soil organisms. Elements like K, Na, Mg and Mn, which are usually scarce in the structural components of the cell wall, are often subject to initial leaching losses, while elements like N, P, S and Ca, which are often bound in structural compounds, are mainly released through decomposition. Decomposition also involves production of humic substances, whose affinity for different elements also probably affects the release of the elements. For example Cu and Pb complexes with humic substances are characterised by a relatively high stability compared with those with Mn, Zn and Cd (see *e.g.* Stevenson, 1996). This may to some extent explain the lack, or slow release, of elements that form high stability complexes (Brynhildsen, 1991).

The concentration of a certain element in the litter over time indicates the relationship between the release of the element and litter dry-mass from a compartment during decomposition. If the concentration remains constant, the release of the element is similar to the mass loss of the litter. If the concentration decreases, the release of the element is faster than the mass loss. If the concentration increases the element is accumulated either biologically or chemically. One reason for the increase in concentration may be that the element is being released more slowly relative to the rate of litter mass loss. Provided that the litter is not artificially protected from the surrounding environment, there is probably a continuous flux of elements through the litter. If the input of elements to the litter exceeds the losses, the total amount of the element in the litter will also increase.

Heavy metal dynamics were included with organic turnover in this thesis for the following reasons: First, temperature and moisture influence organic matter decomposition rate and can therefore affect the release of heavy metals. Second, although strained, both topics relate to the influence of the greenhouse effect and how to cope with it. The greenhouse effect probably involves a change in climate and, as discussed earlier, this requires an increased knowledge of how temperature and moisture affect decomposition rates. It also leads to an increasing interest in the use of bio-fuels such as slash, i.e. branches and needles remaining after clear-cutting. To compensate for the nutrient removal, the ash of the bio-fuel is re-circulated to the ground. However, to evaluate the effect of ash application, ash and slash need to be compared in terms of their heavy metal dynamics and studies of heavy metal dynamics in needles could constitute a first step here. Background information and a summary of previous data within this area are presented in the section Heavy Metals. At present, long-term studies over the heavy metal dynamics in decomposing organic matter are lacking. However, this thesis presents the results of heavy metal dynamics in needle litter decomposing in the field for 6 to 8 years.

The influence of temperature on decomposition

It is well established that C mineralization increases with increasing temperature, from null at about –6.5ºC or less (Flanagan & Veum, 1974; Coxon & Parkinson, 1987; Clein & Schimmel, 1995), up to an optimum of about 30-35ºC (see *e.g.* Waksman & Gerretsen, 1931; Jenny *et al.*, 1949; Kirschbaum, 1995) or even 45-65ºC in soils where thermotolerant or thermophilic microorganisms are present (Drobnik, 1962). Cycles of freezing-thawing seem also to have a promoting effect on mineralization in the long run, since they usually cause fragmentation, increased leaching and enhanced susceptibility to microbial attack (see *e.g.* Coxon

& Parkinson, 1987; Skogland *et al.*, 1988; Taylor & Parkinson, 1988). The respiratory burst having its maximum immediately after freezing has been explained by surviving bacteria utilising the bacteria killed by the freezing (Skogland *et al.*, 1988). Herrmann & Witter (2002) also tried to characterise the source of organic matter becoming available during freezing-thawing cycles. They observed that although microbial biomass contributed almost 65% of the increased flush in C mineralization upon freezing-thawing, the amount of mineralised C only represented 5% of the microbial biomass C.

The response of C mineralization rate to temperature is in many studies traditionally described by the Q_{10} relationship (the factor by which the activity increases when the temperature increases by 10ºC), originally developed by Van´t Hoff , 1898 (see review by Kirschbaum, 1995). Other exponential functions like the conventional Arrhenius equation (Arrhenius, 1889), which assumes a constant activation energy for the chemical processes, have been used as well (see *e.g.* Moore, 1986; Lloyd & Taylor, 1994; Leirós, *et al.*, 1999). Although both of these models have been reported to be successful in fitting data obtained in a specific experiment, they are not sufficiently sensitive, especially at lower or higher temperatures (Lloyd & Taylor, 1994). To improve the temperature sensitivity, Lloyd & Taylor (1994) modified the Arrhenius equation by deriving a formulation which let a parameter, E_0, decrease with increasing temperature (for a more detailed description of the equations see Paper III). This equation (the Lloyd & Taylor function) provides a similar (Kätterer *et al.*, 1998; Leirós *et al.*, 1999; Fang & Moncrieff, 2001) or a better (Lloyd & Taylor, 1994) description of the temperature response at lower temperatures. Apart from exponential relationships, several other functions have been used to describe temperature responses: linear functions (see *e.g.* Gupta & Singh, 1981; Honeycutt *et al.*, 1988; Rochette *et al.*, 1991), power functions (see *e.g.* Kucera & Kirkham, 1971; Fang & Moncrieff, 2001) logistic functions (Jenkinson, 1990) and S-shaped functions (De Neve et al., 1996).

To be able to compare the effect of temperature on C mineralization in different soils, the responses are often recalculated to Q_{10} values. A constant Q_{10} value of about 2 has traditionally been used in ecosystem process models when modelling the seasonal cycle of CO_2 evolution from soils (Raich *et al.*, 1991), and compiled literature values from year-round field studies give an average Q_{10} value of 2.4 (Raich & Schlesinger, 1992). Several papers report on the variation in Q_{10} with different factors like temperature, moisture, quality of the organic material, organism community and time. Most commonly it is reported that Q_{10} increases with decreasing temperature, from being about 2.5 or less at 20 ºC, to 4.5 at 10 ºC and about 8 or higher at 0 ºC (see *e.g.* review by Kirschbaum, 1995; Dalias *et al.*, 2001b). However, reports also occur of constant (Chapman & Thurlow, 1998; Reichstein *et al.*, 2000) or even increasing Q_{10} values (Nadelhoffer *et al.*, 1991; Howard & Howard, 1993) with increasing temperature.

Several authors have investigated the effect of both temperature and moisture on C mineralization. How soil water content influences the temperature response is contradictory (Fang & Moncrieff, 2001). For example, Chapman & Thurlow (1998) report no effect on the temperature response after a reduction in the water content. Clark & Gilmour (1983) report decreasing Q_{10} values with increasing moisture in a silty loamy soil, from 2.7 for unsaturated to 1.4 for saturated conditions. The same trend was found by Hogg *et al.*, (1992) who calculated Q_{10} to vary between 1.9 and 2.2 for drained and between 1.0 and 1.5 for flooded peat samples. On the other hand, Silvola *et al.* (1996) found increasing Q_{10} values with increasing water content of peat, from 2.0 with the water table below 20 cm to 2.9 with the water table above 20 cm. This trend is also seen in an older study of moisture and temperature effects on peat by Svensson (1980). Possible reasons for these discrepancies may be that the definition of water content differs between the studies and that the physical structure of the different types of organic matter affects the water availability for the microbes. The water content levels are usually also few in comparison to the temperature levels included in the temperature response studies, making it harder to get significant trends.

Besides general rate variations with temperature and moisture, there is also evidence that different organism communities respond differently to temperature and moisture. Nicarlarot *et al.* (1994) found a greater sensitivity to temperature for holocellulose decomposition (Q_{10}=4.5) than for glucose decomposition (Q_{10} =2.9) and Coûteaux *et al.* (2001) suggest different temperature responses for the decomposition rates of labile and resistant soil organic matter. Another factor is that organisms may be adapted to a certain climate. For example, micro-organisms in cold soils are adapted to these conditions and thus show comparatively high activity at low temperatures (Kirschbaum, 1995). Another example of adaptation of the organism community and its effect on the temperature response is discussed by Bunnell *et al.* (1977). They found higher Q_{10} values for newly dead litter (Q_{10}=8.79) than for one year old litter (Q_{10}=2.56) in the litter layer. They explain this by a lower colonisation of the younger substrate by psychrophilic fungi and a lower respiration rate at lower temperatures. They also found an increase in Q_{10} with increasing depth in the humus layer and it is suggested that the microbial populations have a narrower temperature range with depth since surface layers are subject to wider ranges in both temperature and moisture. Contrary to this, Bowden *et al.* (1998) found CO_2 evolution from mineral soil to be less responsive to temperature than CO_2 evolution from the humus layer. It has even been suggested that decomposition of resistant organic carbon in the mineral soil does not respond to temperature at all (see *e.g.* Liski *et al.*, 1999; Giardina & Ryan, 2000). The result by Liski *et al.* (1999) is primarily derived from a compartment model of soil organic matter. Ågren (2000) criticises the assumption of fixed residence times of organic material in the compartments, while the respiration rates increase with temperature. As a consequence, the C content of a compartment will decrease with increasing temperature due to increasing respiration. The assumption of fixed residence times of organic material in the compartments is hence according to Ågren (2000) an assumption of a temperature dependence which has been countered by Liski *et al.* (1999) by letting the turnover rates of soil organic matter become less temperature sensitive. However, contrary to most other studies of temperature responses, Giardina & Ryan (2000) base their conclusion on decomposition rates estimated for undisturbed soils in the field. This could be one explanation for the differences in temperature responses between different types of studies.

Summing up, modifications of the Arrhenius equation seem to provide a better description of the temperature response of decomposition than the Q_{10}

relationship, especially at lower temperatures. However, to be able to compare temperature responses between soils, Q_{10} is still used. Concerning factors affecting the Q_{10} value, the temperature effect has been most frequently studied and generally results in decreasing Q_{10} values with increasing temperature. The effect of moisture on the temperature response is not clear and studies including more than two moisture levels are called for. Increased knowledge of the effect of organism community on the Q_{10} value is also essential. This is closely connected to the effects of substrate quality and microbial climate adaptation on the Q_{10} value. However, one should also bear in mind that the resulting temperature responses are probably also dependent on the pre-treatment of the soil samples, the time of incubation and the choice of method for analysing the results. First, concerning the pre-treatment of soil samples, Gödde *et al.* (1996) calculated Q_{10} =3.3 for sieved samples and 2.6 for intact samples, although they do not discuss the result further. However, even more important is probably the risk for substrate depletion and the fact that changed composition of microbial species with time of incubation could lead to incorrect Q_{10} values (see *e.g.* Kirschbaum, 1995; McHale *et al.*, 1998; Reichstein, *et al.*, 2000). Finally, the choice of method for analysing the temperature responses, *i.e.* calculating temperature responses on initial rates, accumulated values or whole time series, affects the Q_{10} value (Kätterer *et al.*, 1998; Reichstein *et al.*, 2000). The effect of the choice of methodology when analysing temperature responses is discussed further under the section Results and Discussion.

The influence of moisture on decomposition

Since the influence of water content on decomposition can only be compared if water contents are expressed on a tension basis, comparisons between studies can in several cases only be done qualitatively. It is well known that decomposition rates increase with increasing water content (see *e.g.* Nyhan 1976; Clark & Gilmour, 1983; Howard & Howard, 1993). Microbial tolerance to low water potentials varies widely. Significant decomposition of straw down to about –21 MPa has been shown by Bartholomew & Norman (1949). The decomposition below the wilting point (-1.5MPa) is mainly carried out by fungi (see *e.g.* Swift *et al.*, 1979) and some ascomycete fungi or yeasts may show activity even down to –65 MPa (Leistner & Rodel, 1976). Bacterial decomposition is more sensitive to water tension, since bacteria can only remain active if nutrients can diffuse towards them and waste products away from them. Their activity therefore declines sharply as water potential falls and is negligible at –1.5 MPa (see *e.g.* Wilson & Griffin, 1975; Orchard & Cook, 1983). Decomposition rate usually reaches a maximum within the range –0.01MPa and -0.05 MPa, whereafter it decreases again due to oxygen deficiency for the microbes (Wilson & Griffin, 1975; Orchard & Cook, 1983; Howard & Howard, 1993).

Cycles of drying and rewetting of soil samples have been shown to cause large and rapid increases in decomposition rates (see *e.g.* Orchard & Cook, 1983; Bloem *et al.*, 1992). This has mainly been explained by: 1) increased solubility of humic substances; 2) a higher turnover of C due to new microbes regrowing on microbial cells killed during desiccation or by osmoregulatory shock on rewetting; and 3) release of protected organic matter by disruption of aggregates (Magid *et al.*, 1999). However, Magid *et al.* (1999) state that the reported increased decomposition rates more are due to increased temperature, rather than pure moisture effects.

The response of decomposition to moisture is often described as a log-linear function of the soil water potential (see *e.g.* Stott *et al.*, 1986; Moore, 1986; Andrén & Paustian, 1987). Quadratic (Paper II), polynomial (Bowden *et al.*, 1998) or other functions (Howard & Howard, 1993) have also been used. Compared to studies of the response of decomposition to temperature, studies and modelling of the moisture response of decomposition are scarcer. One reason may be the technical problems with controlling and comparing the water content of the soils. This is especially a problem when soil samples are homogenised for incubation, since the pF-curve for each individual sample is then changed compared with that of the undisturbed soil in the field.

Heavy metals

Although it is true that some emissions of heavy metals originate from natural sources like parent material and sea spray, most of the heavy metals deposited from the atmosphere have anthropogenic origins (Nriagu, 1984). The term "heavy metals" usually refers to elements having a density greater than 5.0 g cm^{-3}. In the following text I will, however, concentrate on cadmium (Cd), zinc (Zn), copper (Cu), lead (Pb) and manganese (Mn).

Copper has been used for more than 10 000 years (Scheinberg, 1991), mainly for wire, brass and bronze alloys. Smelters have been built around several mining sites and there are zones around these where effects of Cu deposition can be seen in the form of litter accumulation due to decreased microbial respiration (see *e.g* Rühling & Tyler, 1973; Derome & Lindroos, 1998). Emissions from fossil fuel combustion significantly contribute to the deposition of Cu (Rühling *et al.*, 1996). The first signs of atmospheric Pb pollution date back to 3500-4000 BP (Renberg *et al.*, 2000). With the industrial revolution Pb atmospheric pollution started to increase, accelerated after the First World War with a more common use of leaded fossil fuels, and peaked in 1970 (see *e.g.* Ewers & Schlipköter, 1991; Renberg *et al.*, 2000). Metalliferous mining, smelting and traffic are the main Pb pollution sources (see *e.g.* Ross, 1994; Rühling *et al.*, 1996). Zinc has been used in brass production since 400 AD, but was first purified in India during the 13th Century (Ohnesorge & Wilhelm, 1991). Today metal industries are the main sources of Zn emissions (see *e.g.* Rühling & Tyler, 1973; Tyler, 1984; Ross, 1994). Manganese was first recognised in 1774, by Scheele (Anonymous, 1964). Since 1939, Mn has been used primarily in the metallurgical industry (see *e.g.* Ross, 1994). Finally, Cd was discovered in 1817 but it is only since 1950 that problems with Cd have been recognised (Stoeppler, 1991). Cadmium is mainly spread to the environment by the use of phosphate fertilisers and through emissions from waste incineration and combustion of fossil fuels. Mining and metal industries are other emission sources (see *e.g.* Rühling & Tyler, 1973; Rühling *et al.*, 1996)

The atmosphere is an effective transport medium for metals, usually in the form of particles, from the various sources. These can be transported up to hundreds of kilometres away from the pollution source and through deposition under gravity (dry deposition) or wash out (wet deposition) they will affect the ecosystem (see *e.g.* Alloway, 1995). For trace metals that are transported long distances it is thought that wet deposition is the dominant process bringing metals to the ecosystem, since the majority of the mass of the metals consists of particles that have a low deposition velocity. Therefore, in less polluted regions like Sweden, which is affected by long range transport of Cd and Pb in particular, the contribution from wet deposition is usually high (Lindberg & Harris, 1981; Ross, 1990; Grömping *et al.*, 1997). It also explains why the highest deposition will be found in areas with the highest precipitation and/or near large emission sources. The concentrations of Cd, Zn, Pb, Cu and Mn found in precipitation are generally highest in southern Sweden, decreasing towards the north (Ross, 1987). Deposition of Cd and Pb is generally higher in the south-western part of Sweden and decreases towards the north, although concentration maxima are found around sources like for example the smelter Rönnskärsverken (Cd) or along road sides (Pb). For Cu and Zn, the deposition pattern is different since the effects of local point sources are more pronounced (Andersson *et al.*, 1991; Rühling *et al.*, 1996).

Forest canopies are effective collectors of dry deposited metals because of their large effective surface area (Lindberg & Turner, 1988; Anghern-Bettinazzi *et al.*, 1989; Ukonmaanaho *et al.*, 2001). Litterfall, besides throughfall and stemflow, is one of the major pathways of heavy metals to the soil in forest ecosystems. Studies of coniferous forest ecosystems in the south of Sweden have shown that Pb and Cd deposited on the soil by precipitation and litterfall are mainly of atmospheric origin. The dominating parts of the essential elements Mn, Cu and Zn in leaf litter originate from soil uptake and translocation (see *e.g.* Bergkvist, 1987; Andersson *et al.*, 1991).

Besides deposition, root uptake is crucial in the uptake and accumulation of essential elements like Cu, Zn and Mn in forest vegetation. Since Cd is chemically similar to Zn, a certain uptake of Cd also occurs (see *e.g.* Balsberg-Pålsson, 1989; Stoeppler, 1991; Alloway, 1995). The uptake and transport of Pb from roots to shoots is usually very low (Chappelka *et al.*, 1991). Accumulated Pb in the plant therefore mainly originates from atmospheric deposition and is located on the surface of the tissue (see *e.g.* Andersson *et al.*, 1991; Berthelsen *et al.*, 1995; Ukonmaanaho *et al.*, 2001). A net accumulation with age of Cu, Pb, Zn and Mn in living needles has been recorded (see *e.g.* Nilsson, 1972; Heinrichs & Mayer, 1980).

A high degree of retention of heavy metals in forest organic horizons is well documented, both from areas in the vicinity of pollution sources (see *e.g.* Tyler, 1978; Heinrichs & Mayer, 1980; Derome & Nieminen, 1998) as well as from more undisturbed areas (see *e.g.* Friedland *et al.*, 1986; Saur & Juste, 1994; Ukonmaanaho *et al.*, 2001). One reason is the stability and low mobility of the chemical complexes formed between heavy metal ions and negatively charged organic groups on the humus compounds. Complexes of Cu and Pb with humic substances are characterised by a very high stability, while those of Mn, Cd and Zn are of a comparatively low stability (see *e.g.* Ross, 1994; Stevenson, 1996). However, appreciable amounts of heavy metals are also released from the mor layer (see *e.g.* Bergkvist, 1987; Bergbäck & Carlsson, 1995; Ukonmaanaho *et al.*, 2001). Copper, Pb and Mn are mainly transported in complexed form, bound to dissolved organic acids, while Cd, and Zn are mainly transported as free ions or inorganic complexes in the soil solution (see *e.g.* Livens, 1991; Ross, 1994; Stevenson, 1996).

Several studies concern the dynamics of macro-nutrients but investigations on heavy metal dynamics at sites considered as low-polluted are scarce. The different methods used to study the phenomenon and to present the results makes it difficult to compare the resulting heavy metal dynamics between the studies. However, in Tables 1 and 2 initial concentrations as well as time series for changes in heavy metal concentrations and amounts are summarised. Only studies where locally produced above-ground leaf/needle litter has been incubated in forest stands considered as low-polluted are presented. Generally, Mn, which is highly mobile and not limiting for micro-organisms, tends to decrease rapidly in both concentration and total amount as decomposition proceeds. Increases in Mn concentrations are reported as well and are probably dependent on pH or the

Table 1. Initial concentrations of Mn (mg g^{-1}), Cd (μg g^{-1}), Zn (μg g^{-1}), Cu (μg g^{-1}) and Pb (μg g^{-1}) for above-ground litter locally produced at sites considered as low-polluted.

References	Litter type	Mn	Cd	Zn	Cu	Pb
Lousier & Parkinson, 1978	Aspen (*Populus tremuloides*)	0.05		240	3.5	
Laskowski *et al*., 1993	Beech-Pine (*Fagus sylvatica-Pinus sylvestris*)	1.023	0.76	70.77	5.02	17.60
Rustad, 1994	Red spruce (*Picea rubens*)	1.01				
Liu *et al*., 2000	*Pinus Yunnanensis*	0.05		3.0		
McEnroe & Helmisaari, 2001	Scots pine (*Pinus sylvestris*)	0.11	0.66	33.0	10.78	11.95

Table 2. Changes (increases = +, decreases = –, no change = 0 and not measured = .) in heavy metal concentrations (c) and amounts (a) in locally produced above-ground litter decomposing for 1, 2, 3 and 5 years in forest stands considered as low-polluted. All changes are in relation to the initial concentrations presented in Table 1.

References	Litter type	c/a	Mn	Cd	Zn	Cu	Pb
			1, 2, 3, 5	1, 2, 3, 5	1, 2, 3, 5	1, 2, 3, 5	1, 2, 3, 5
Lousier & Parkinson, 1978	Aspen	c	+ + + +		+ + + -	+ + + +	
	Aspen	a	+ + + +		0 + + -	+ 0 0 +	
Laskowski *et al*., 1993	Beech-Pine	c	. + . . .	. + . . .	. + . . .	. + . . .	. + . . .
	Beech-Pine	a	+ - . .	+ + . .	+ + . .	+ + . .	+ + . .
Rustad, 1994	Red spruce	c	- - - -	. . . .	. . . .	. . . .	. . . .
	Red spruce	a	- - - -	. . . .	. . . .	. . . .	. . . .
Liu *et al*., 2000	*Pinus yunnanensis*	c	+ + . .		+ + . .		
		a	- - . .		- - . .		
McEnroe & Helmisaari, 2001	Scots pine	c	- - . .	+ + . .	+ + . .	+ + . .	0 + . .
	Scots pine	a	- - . .	+ + . .	- - . .	+ + . .	0 + . .

redox-potential of the soil (Lousier and Parkinsson, 1978). Concerning Cd and Zn, most of the shorter studies indicate that concentrations as well as total amounts increase during decomposition. However, some studies on Cd and/or Zn dynamics for two years or longer show no significant changes in their amounts with time or even a net release of them (Table 1; Laskowski & Berg, 1993; Krakina *et al.*, 1999; Paper IV). The dynamics of Cu are mostly characterised by increasing concentrations as well as total amounts (Table 1; Laskowski & Berg, 1993; Krakina *et al.*, 1999; Paper IV). There are also several reports of suddenly appearing increases in Cu concentrations, by over hundreds of percent, whereafter the concentrations decrease anew (see *e.g.* Lousier & Parkinson, 1978; Laskowski *et al.*, 1993; Paper IV). No explanations for these "bursts" in Cu concentrations and amounts have been found, but since they have been observed in several independent studies, they cannot be dismissed as outliers. The highest increases in concentrations as well as in total amounts (>200%) are generally reported for Pb. Only in studies lasting longer than five years were constant or even decreasing amounts of Pb observed (Paper IV).

Studies on heavy metal dynamics in decomposing litter combined with measurements of the heavy metal fluxes to and from the decomposing litter as well as exact climatic data for the site are scarce. One reason for this is probably that existing publications are mainly of a descriptive character and focus on finding a factor that might affect the decomposition rate. This makes it hard to be anything but speculative about the reasons for changing heavy metal concentrations and amounts. The increase in total amount reported for some heavy metals is due to a net influx of elements to the litter. Wet and dry deposition, as well as throughfall, probably constitute major heavy metal sources. The sources may also be in the form of dissolved organic acids (*e.g.* Pb, Cu, Mn), free ions and inorganic complexes (*e.g.* Mg, Ca, Cd, Zn; see Ross, 1994; Stevenson, 1996) leached for example from overlying litter. Accumulation and transport of heavy metals in fungi are probably also an explanation (see *e.g.* Giesler *et al.*, 2000) since ingrown mycelia were not separated from the analysed litter.

The idea that initially high carbon to heavy metal ratios in litter would imply immobilisation of heavy metals until the decomposition has caused extensive C losses, in the same way as has been observed for *e.g.* nitrogen, has been discussed by many authors (see *e.g.* Krakina *et al.*, 1999). However, studies on the dynamics of heavy metals in litter have yielded differing results even for litters of one species and with similar initial heavy metal concentrations. A probable reason for this is that the fluxes of the heavy metals are dependent on site conditions (*e.g.* deposition level, tree stand density, tree species, age of the stand, parent material) as well as of the climate of the site (*e.g.* precipitation, temperature, growing season; Kurka *et al.*, 2001).

Tyler (1992) reports that several biological processes in the mor layer are affected by concentrations of Cd, Cu, Pb or Zn at about 3-4, 20, 150 and 300 $\mu g\ g^{-1}$ dry mass respectively. A negative effect of the metals on decomposition could either be due to toxicity, caused by the free ion of the metal, or due to a reduced microbial availability of the organic material, caused by complex binding to the heavy metals (Brynhildsen, 1991; Giller *et al.*, 1998). According to Giller *et al.* (1998) it is not possible to distinguish a metal toxicity effect from an effect of metal addition on substrate availability. However, at forest sites near smelters or other heavy metal pollution sources, where heavy metal concentrations in the mor layer greatly exceed mentioned values, accumulation of litter has been observed due to suppression of decomposition (see *e.g.* Rühling & Tyler, 1973; Freedman & Hutchinson, 1980; McEnroe & Helmisaari, 2001). Even for unpolluted sites it has been suggested that the high retention of heavy metals in the long run could lead to toxic concentrations and decreased decomposition rates (Laskowski & Berg, 1993). However, there is always a risk when correlating the decrease in litter decomposition over time with for example the change in heavy metal concentrations in the litter. This is because other variables, like the quality of the organic material, also change with time and their effects on the decomposition rate should therefore be taken into account. Furthermore, in a cold climate, more than 50% of the litter may still remains after three years (Johansson, 1986) and only few studies have been carried out where the dynamics of heavy metals have been followed for longer periods than about three years. Therefore, to more exactly reveal the patterns of heavy metal dynamics in decomposing litter, long-time studies at well-characterised unpolluted sites are needed. These studies are also of great importance to verify if heavy metal concentrations high enough to affect litter decomposition may be reached even at unpolluted sites. In a broader context these types of studies are also, as mentioned earlier, called for in the evaluation of effects of wood-ash application. However, this topic will not be treated further in this summary.

Modelling of decomposition

Different mathematical models have been used to describe soil organic C turnover. Depending on the desired degree of analytical simplicity, predictive power, generality and interest of the investigator, the models might include temperature and moisture as well as the efficiency of decomposing organisms as rate determining factors. The quality of the organic soil C may also be included in the model. Most simply, soil organic C may be considered as being homogeneous (one-pool models). More complicated models consider soil organic C as being heterogeneous and/or include a decrease in quality with decomposition (*e.g.* parallel first-order, consecutive, continuous quality decreasing and asymptotic models). Here follows a short summary of the principles for some of the more simple mathematical models used to describe decomposition.

The probably most widely used model for describing decomposition of soil organic matter is based on first order kinetics (see *e.g.* Jenny *et al.*, 1949; Howard & Howard, 1974; Wadman & de Haan, 1997). This model is based on the assumption that a constant fraction is lost from the organic pool, which is treated as a homogeneous substrate (see *e.g.* Andrén & Kätterer, 2001 and papers cited therein). The estimated decomposition rate of the organic pool is hence specific to the studied soil and a specific set of environmental conditions, including temperature and moisture at the site or in the laboratory.

Soil organic matter consists of a wide range of organic compounds with different decomposability. By using different types of multiple component models, the decomposability of different fractions of the original organic matter and/or secondary products produced from the decomposition process can be separated (Andrén & Paustian, 1987). The simplest approach, the parallel first order model, describes decomposition of two or more independent pools of organic matter according to first order kinetics (see *e.g.* Jenkinson, 1977; Lomander *et al.*, 1998; Dalias *et al.*, 2001a). Closely related to this is the consecutive first order model. It assumes that the more stable organic pool is transformed into a more labile pool (by for example solubilization) from which all mass loss occurs. This model gives the same decomposition rates for the organic pools as the two-component model, although the size of the pools at a given time will differ (Andrén & Paustian, 1987). The approaches referred to generally provide a better description of decomposition than an one-pool model.

Decomposition of organic matter implies not only mass loss due to CO_2 evolution, but production of new organic compounds that may be chemically more resistant to decomposition than the original material. Furthermore, decomposing organisms are involved in the process. To handle this, models built on the concept that decomposition is a cascade of decomposition processes, with carbon mineralization being carried out by decomposing organisms in each step, have been created. Examples of this are the four component model described by Andrén & Paustian (1987), as well as the ICBM models (see *e.g.* Andrén & Kätterer, 1997; Kätterer & Andrén, 2001 and papers cited therein). In all cases the transformations between the pools follow first-order kinetics. Although in several cases successful, this division of the organic matter into discrete pools is artificial and could be replaced by a continuum. This has been achieved by introducing organic matter quality as a variate (Bosatta & Ågren, 1985; Ågren & Bosatta 1996). Among the models listed here, this model probably describes decomposition most realistically. However, compared with the ICBM models it is far more complicated to understand mathematically.

During decomposition studies, the initially high decomposition rate usually decreases with time. In some cases it has even been assumed that decomposition rates go towards zero with time, before all of the organic material has been decomposed. The remaining amount of organic material will hence reach an asymptote, a certain limit value, valid for that particular type of organic matter and at that specific environment. Based on the theory of undecomposable organic fractions, asymptotic functions have been used to describe decomposition, especially in the case of mass loss from litter incubated in litter bags (see *e.g.* Howard & Howard, 1974; Berg & Ekbohm, 1990; Berg *et al.*, 1995). However, assuming an undecomposable fraction implies that sooner or later all carbon on the Earth will end up in there, which is hardly realistic.

Although not very common today, linear models (zero-order kinetics) have also been used. According to them, the flux from the organic pool is constant over time and does not depend on the amount of remaining organic matter. According to Taylor & Parkinson (1988) linear models seem to be more common for substrates with a large labile fraction, like herbaceous litter, as well as for litter with a small amount of labile litter that decomposes slowly, like wood. Furthermore, they conclude that decomposition, especially of substrates with a large or a small labile fraction, might appear linear if it is not monitored for an enough long period.

Objectives

The aim was to study and model the effect of temperature and moisture on the decomposition rate of soil organic C. No studies of temperature and moisture effects on organic material in cold and heavy clay soils have been conducted before. Therefore this type of soil was chosen for temperature and moisture incubations at the laboratory.

Concerning heavy metals, studies following heavy metal dynamics in decomposing litter for longer periods than 3-5 years have not been presented before. Since it is impossible for a PhD-student to have time to conduct and evaluate long-time incubations, stored samples from earlier studies had to be used. In my case, only material from spruce litter incubations was available and it was used with the aim of studying the dynamics of heavy metals in spruce needle litter during decomposition (6-8 years), at five sites considered as low-polluted, in southern Sweden.

The specific objectives were:

1. To quantify the influence of temperature and moisture as well as freezing-thawing cycles on CO_2 evolution rates in a cold heavy clay soil.
2. To quantify differences in CO_2 evolution rates between topsoil and subsoil and after addition of roots or stubble.
3. To test whether a multi-compartment modelling approach was superior to a single-component approach, when analysing temperature and moisture influence on CO_2 evolution rates from a cold heavy clay soil, as well as on a larger data set including CO_2 evolution rates from different types of soils.
4. To find response functions adequately describing the temperature and moisture effects on CO_2 evolution from a heavy clay soil.
5. To compare results from the laboratory incubations with measurements and model outputs from field investigations of the same soil.
6. To quantify changes in concentrations and amounts of Cd, Zn, Cu, Pb and Mn during decomposition.
7. To compare the dynamics of total heavy metal amounts between sites differing in climate, soils, vegetation and heavy metal deposition, investigating factors controlling the elemental changes in the litter during decomposition.
8. To evaluate whether concentrations considered as being toxic to micro-organisms would be reached or not during the decomposition process.

Materials and methods - an overview

Measurements of CO_2 evolution rates (Paper I)

On 29 October 1994, topsoil (0-25 cm) and subsoil (30-55 cm) samples were taken from four conventionally fertilised plots cropped with reed canary grass (*Phalaris arundinacea L.*), at Ultuna, Sweden (59º48'N, 17º38'E). The soil was classified as an Oxyaquic Eutrochrept (Soil Survey Staff, 1998), and had a clay content of about 53% between 0 and 55 cm depth (Andrén *et al.*, 1990b).

The samples were stored at +4°C until January 1995, when subsamples were bulked into one topsoil and one subsoil sample. The soil was crumbled into fragments and visible organic debris was removed. Remaining debris was quantified by washing, sieving and weighing of subsamples. Topsoil and subsoil samples were homogenized carefully and put separately into vessels (466 ml) made of standard styrene-acryl nitril plastic (SAN; Figure 1). Lids with rubber septa and rubber seals were used to close the vessels periodically to accumulate $CO_2(g)$ for measuring the CO_2 evolution. Thereafter the water contents of the samples in the vessels were adjusted to four levels between the wilting point and 100% water holding capacity (WHC), *i.e.* 17, 26, 36, 50 and 16, 23, 31 and 41 g H_2O 100 g^{-1} dry soil for topsoil and subsoil, respectively. Three replicates of each water content were finally incubated at six different temperatures (-4, 0.3, 5, 15, 25 and fluctuating -4/+5°C). Two additional treatments containing topsoil (36 g H_2O 100 g^{-1} dry soil, 25°C) with addition of roots or stubble of reed canary grass were also made.

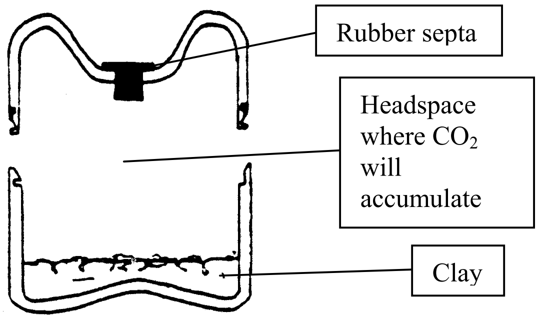

Figure 1. Vessel with rubber septa used for the accumulation of CO_2.

Decomposition was measured as the rate of CO_2 evolution at one-week intervals during the first month, at two–week intervals after a month, three-week intervals after two further months and four-week intervals after a total of 6 months of incubation. Before starting the measurements the vessels were opened and held under a fan to equilibrate the CO_2 concentration in the atmosphere of the vessel with the surrounding atmosphere. Thereafter the vessels were closed and CO_2 was accumulated for 15 minutes before a gas sample was withdrawn using a 100 µl syringe and injected into a gas chromatograph, to provide a back-ground value. The time between the background measurement and the final measurement, taken in the same way as the background measurement, was adapted to the microbial activity for that specific temperature and moisture level. Cumulative amounts of evolved CO_2-C were calculated by assuming that the amount of evolved C measured at one date remained constant until the next measurement or, for the samples in fluctuating temperature, until the next change in temperature.

The SAS procedure GLM was used for analysis of variance. Since the measurements of the CO_2 evolution from low-activity samples seemed to be less reliable, samples incubated at lower (≤5ºC) or higher (≥5ºC) temperatures were analysed separately. LSD tests (95% confidence limit) were used to confirm pairwise differences between means (SAS Institute Inc., 1982).

Modelling temperature and moisture responses (Paper II)

Two models, a two-component and a three-component parallel first-order model were fitted to the measured CO_2 evolution rates that differed significantly from zero (Paper I) using a least-squares fitting procedure (proc NLIN in SAS; SAS Institute Inc., 1982). For the two-component models, the organic material was divided into two independent pools, labile and refractory, and for the three-component model into three pools, labile, refractory and either added stubble or roots. Corresponding decomposition rate constants were assumed to be equally modified by quadratic functions for the effects of temperature (Ratkowski *et al.*, 1982) and moisture. See Figure 2 for model structure. However, the Q_{10}-function for the effect of temperature was also tested. The temperature response was normalised for 25ºC and the moisture response for the highest water content in the topsoil (50%) and in the subsoil (41%).

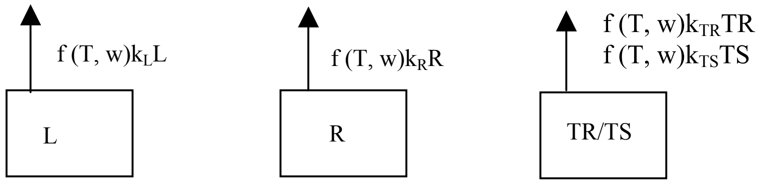

Figure 2. Structure of the two- or three component parallel first-order model describing CO_2 evolution from independent pools of soil organic matter. The components are labile (L) and refractory (R) for the two-component model and labile (L), refractory (R) and roots (TR) or stubble (TS) for the three-component model. Flux equations are written close to their respective arrows. The parameters are 1) the decomposition rate constants for L (k_L), R (k_r) and TS (k_{TS}) or TR (k_{TR}) and 2) a response function f(T, w) representing the modification of the rate constants for the effects of temperature and moisture.

Kätterer & Andrén (1996) used a simulation model to estimate C mineralization in the field from which soil was incubated in our experiment. After taking differences in temperature and moisture into account, the modelled amount of C mineralised in the field was compared with the modelled amount of C mineralized at the laboratory.

An analysis of our model was also performed to illustrate how the CO_2 evolution rates from the labile and refractory pools affected the total CO_2

evolution rates from samples incubated under cold and warm conditions. The purpose was to demonstrate the importance of basing temperature responses on repeated measurements of CO_2 evolution rates.

Analysing literature data considering temperature dependence of decomposition (Paper III)

By reviewing published incubation studies in which C mineralization was measured, a data set was compiled. The main criteria for selection were: 1) incubation of the same substrate in at least two different temperatures and 2) available time series comprising at least four measurements for each substrate and temperature. The measurements of CO_2 evolution significantly different from zero, presented in Paper I, were also included in the data set. From the resulting data set several studies were excluded. For example, only consistently increasing response functions were considered; substrates showing decreasing decomposition rates with temperature or no effect of increasing temperature on the decomposition rate were also excluded from the data set, as well as experiments with incubation temperatures ≥40ºC.

After scaling the data to a common unit, CO_2 evolution rates or cumulative CO_2 evolution were analysed by both a first-order one-component model and a parallel first-order two-component model. For the two-component model, decomposition rate constants of the organic pools were assumed to be equally affected by temperature. See Figure 2 for the structure of the models.

After normalising for a reference temperature, the following four temperature response functions were tested for their ability to describe the temperature dependence of the C mineralization:

1) An Arrhenius-type function
2) A two-parameter function proposed by Lloyd and Taylor (1994)
3) The exponential Q_{10}-function
4) A quadratic function proposed by Ratkowski *et al.* (1982)

For description of the functions, see Paper III.

Studying heavy metal concentrations in decomposing needle litter (Paper IV)

Litterbag incubations were carried out in five monocultural stands of Norway spruce (*Picea abies* (L.) Karst) in southern Sweden (between lat. 56-58ºN). The sites Remningstorp and Tveten are situated in the inland province Västergötland; Tönnersjöheden and Mästocka are on the west coast in Halland province and Farabol is on the south-east coast in Blekinge province.

Litterbags containing locally produced brown needle litter of Norway spruce (*Picea abies* (L.) Karst), were placed on the litter layer in each stand during spring 1979. A randomised block design, containing 25 blocks (1×1 m) within an area of 150 m^2 was used. During the first two years, litterbags were generally collected twice a year, and thereafter once a year until it was no longer possible to identify incubated needles from other plant residues (after about 6-8 years). On each sampling occasion, one litterbag from each of the 25 blocks in each stand was collected, resulting in 25 samples per stand and occasion. After collection, the samples were brought to the laboratory where plant remnants were removed before loss of dry mass (85ºC, 48 h) for each litterbag was measured. Thereafter, the samples were pooled to form one sample for each site and sampling occasion. The samples were then milled (Ø < 1 mm) and stored at room temperature until June 1996, when analyses of Cd, Zn, Mn, Cu and Pb were performed (0.5 g sample in 5.0 ml conc HNO_3 for 25 minutes at 175ºC in a tight Teflon bomb in a micro-wave oven). Contents of Zn, Mn and Cu in the digests were analysed by inductively coupled plasma (ICP-AES), while contents of Cd and Pb were analysed by graphite furnace atomic absorption spectrometry (AAS).

PCA ordinations of the data (Proc PRINCOMP, SAS Inst., 1987) were made. One objective was to try to identify potential factors controlling the changes in heavy metal amounts in the needle litter at the different sites. Another was to more clearly reveal potential similarities and differences between the elements with respect to their changes in amounts during litter decomposition.

Results and Discussion

The influence of temperature and moisture on CO_2 evolution

The CO_2 evolution rate generally increased significantly with increasing temperature and moisture (Figures 3 and 4). Even at water contents corresponding to the wilting point, there were higher CO_2 evolution rates when soil was incubated at 25ºC than at 15ºC. Accelerated decomposition as a result of increasing temperature, regardless of decrease in precipitation, is reported by Hornsby *et al.* (1995), who used microcosms in the field to control temperature and water content of the litter samples. They concluded that C loss in the field is primarily limited by temperature and secondarily by moisture. This is also reported by Bowden *et al.* (1998) who studied CO_2 and CH_4 evolution from incubated humus material and mineral soil at the laboratory. Contrary to this, Taylor & Parkinson (1988) observed that increased temperature at low moisture content had little effect on decomposition rate of leaf litter, while the decomposition was more responsive to temperature at higher moisture contents. In modelling, the decomposition rate usually is assumed to depend on both temperature and moisture, *i.e.*, their effects are assumed to be multiplicative. Therefore, the effects of the temperature and moisture are synchronised - if it is too dry, the temperature will not matter.

Comparing the accumulated amounts of CO_2 at a specific time of incubation, the soil samples with weekly fluctuating temperature (-4/5) generally evolved less CO_2 than the soil samples with constant temperature (5ºC). Even when standardizing for the incubation time at 5ºC, treatments with weekly fluctuating temperature generally evolved less CO_2 than the treatments at a constant 5ºC. The CO_2 evolution from the samples with weekly fluctuating temperature was in some cases not significantly different from, or was even significantly lower than, the CO_2 evolution from the samples incubated at 0.3ºC. There are several possible explanations for why freezing/thawing did not enhance CO_2 evolution. Perhaps we

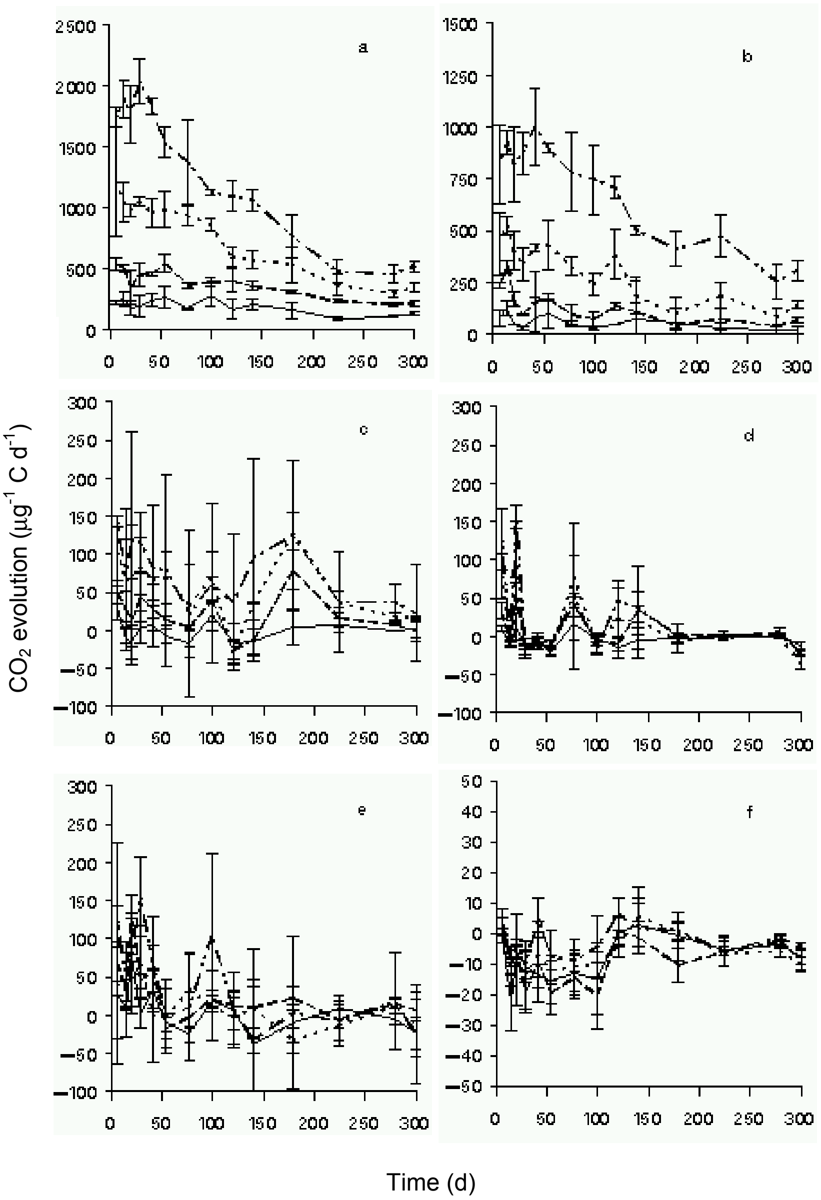

Figure 3. CO$_2$ evolution rates (µg C g^{-1} C day^{-1}) during 300 days for topsoil. The treatments are combinations of the temperatures 25 °C (a), 15 °C (b), 5 °C (c), fluctuating –4/+5 °C (d), 0.3 °C (e) and –4 °C (f) and the water contents 50 (-¨-¨), 36 (¨¨¨) 26 (----) and 17 (—) g H$_2$O g$^{-1$} soil.

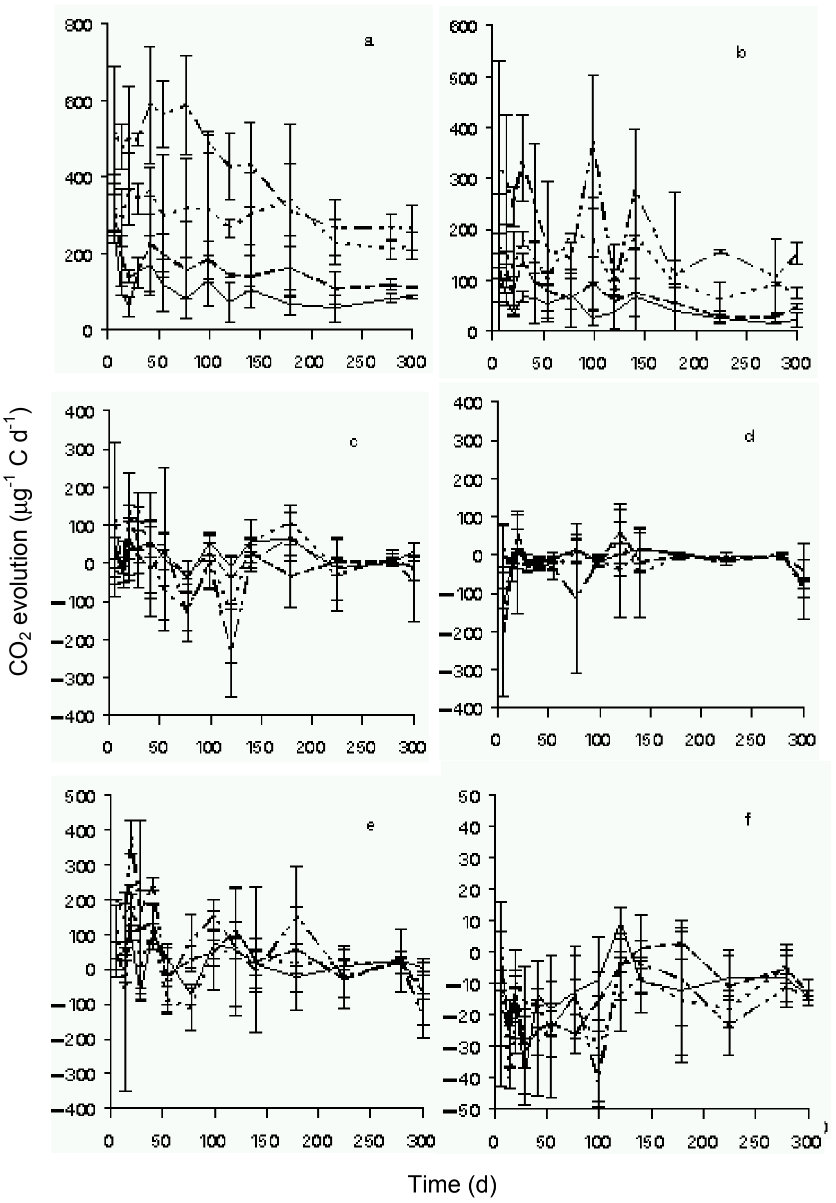

Figure 4. CO$_2$ evolution rates (µg C g^{-1} C day^{-1}) during 300 days for subsoil. The treatments are combinations of the temperatures 25 °C (a), 15 °C (b), 5 °C (c), fluctuating –4/+5 °C (d), 0.3 °C (e) and –4 °C (f) and the water contents 41 (-¨-¨), 31 (¨¨¨¨), 23 (----) and 16 (—) g H$_2$O g^{-1} soil.

did not catch the peaks in CO_2 evolution since the respiratory burst after freezing has its maximum immediately after thawing and is highest during the first freeze/thaw-cycles (see *e.g.* Skogland *et al*. 1988; Herrmann & Witter, 2002). The incubation periods at 5ºC could also have been too short for the microbial biomass to recover and respire as much as it would have done at a constant 5ºC. Another reason could be that freezing was not a new phenomenon in this soil and that the crumbling of the soil samples opening up new C-sources for the microorganisms had a more profound effect and masked the effect of freezing/thawing on decomposition.

At constant -4ºC, as well as from several other treatments resulting in low activity, especially in the subsoil, it was not possible to detect any CO_2 evolution. This may be a true result or a false one since the precision of the method (discussed later) seemed to decrease with decreasing CO_2 evolution rate from the samples. Andrén & Paustian (1987) and Andrén *et al*. (1990a) did not find significant litter mass loss in the field of similar soils, when frozen. However, several studies report significant decomposition at sub-zero temperatures (*e.g.* Flanagan & Veum, 1974; Coxon & Parkinson, 1987; Clein & Schimel, 1995). For example Clein and Schimel (1995) show that the potential winter (temperatures at or below zero) C loss may constitute 10-30% of the total annual C loss due to decomposition from tundra and taiga soils.

In our case the CO_2 evolution increased with increasing moisture content (Figure 3). At the highest water content we had expected a decrease in CO_2 evolution due to oxygen deficiency (see *e.g.* Wilson & Griffin, 1975; Taylor & Parkinson, 1987; Devêvre & Horwáth, 2000), but this was not observed. One explanation is that we did not achieve anaerobic conditions, probably due to incubation of too thin soil samples. Since our experiment only contained four different moisture levels, another explanation may be that the optimal water content for CO_2 evolution was somewhere in between our two highest water contents and therefore missed.

CO_2 evolution rates in relation to the quality of the organic material

Generally, CO_2 evolution rates decreased with time, as the more easily decomposable compounds became depleted. For most of the subsoil samples and for topsoil samples with low activity, a decrease followed by an increase in the CO_2 evolution rate was observed after about 150 days of incubation (Figure 3). No similar results are found in the literature. However, the results may be due to changes in the microbial population.

During the first 140 days of incubation, topsoil with added stubble had the significantly highest CO_2 evolution rate, topsoil with addition of roots intermediate and pure topsoil the lowest (Figure 1 in Paper I). Thereafter, there were no significant differences between the treatments. According to the model (Paper II), stubble decomposed (3.6% d^{-1}) about three times faster than did roots (1.3% d^{-1}) and after 300 days of incubation the added material had decomposed almost completely (99 and 86% for stubble and roots, respectively). This probably indicates that stubble contained a larger fraction of easily available organic C than roots.

Relative to the initial amount of C in the soil samples, the amount of accumulated CO_2 from the topsoil was generally almost twice as high as from the subsoil at the end of the incubation. The optimised k_L and k_R of the labile and refractory pools were generally 1.3 and 2.0 times higher respectively in the topsoil than in the subsoil. This difference in CO_2 evolution rate is in accordance with other studies. Due to the low input of organic C in relation to the organic C content in the subsoil compared to that in the topsoil, the mean age of the organic C is usually higher in the subsoil than in the topsoil. A higher mean age usually implies that the organic C has become more stabilised and hence is more resistant to decomposition. This may explain the decrease in decomposability with depth in the soil profile (see *e.g.* Andersson, 1991; Brady & Weil, 1996).

Modelling the effects of temperature and moisture on CO_2 evolution

Single-component models have preferably been used to analyse soil incubations in the laboratory (see *e.g.* Jenny *et al.*, 1949; Olson, 1963; Wadman & de Haan, 1997). Therefore, when analysing our own data sets (Papers II and III), both single and multi-component models, as well as different combinations of temperature and moisture response functions, were fitted to the data. When analysing our own measurements of CO_2 evolution (Paper I) a two-component model with quadratic temperature (Ratkowski *et al.*, 1982) and moisture response functions resulted in the highest coefficient of determination (R^2_{adj}=0.96 and 0.81 for topsoil and subsoil respectively; Paper II). Also when analysing literature data (Paper III), the two-component model gave the best description of the dynamics of decomposition.

The main advantages of using this type of model when analysing the moisture and temperature responses are that all empirical information can be used for the analysis and that changes in CO_2 evolution rates over time can be handled. Calculated temperature responses using only initial rates are sensitive to the precision of one measurement at the same time as the information from the rest of the experiment is neglected. At the start of an incubation, soil CO_2 evolution may still also be affected by the pre-treatment of the soil sample, enhancing the risk for over-estimation of CO_2 evolution rates, especially at high temperatures. However, using rates obtained on later days or cumulative values to calculate temperature responses may be even less appropriate. The risk for exhaustion of readily available substrate under conditions favourable for microbial activity compared with less favourable conditions, as well as the risk for accumulation of metabolites inhibiting decomposition at the end of long incubations, have been discussed (Kirschbaum, 1995). To illustrate this effect of assumed substrate depletion on CO_2 evolution, a model analysis was constructed (Paper II). It showed that CO_2 evolution rates became relatively higher at the end of the incubation in the cold treatment, where a substantial amount of easily available organic material remained. Under certain conditions, rates in the cold treatment even exceeded those in the warm treatment (see Figure 4 in Paper II). The risk for drawing wrong conclusions about the temperature dependence of decomposition using one single measurement for the estimation of the responses is in this case obvious. As a result of the relatively higher CO_2 evolution rate in the cold treatment, the Q_{10} values decrease with time. When the easily decomposable fraction is also depleted in the cold treatment, the Q_{10} values increase again (Reichstein *et al*., 2000).

As mentioned above, the use of time series containing discrete measurements of CO_2 evolution is preferable to accumulated values (Hess & Schmidt, 1995). The accumulation of data implies an accumulation of systematic error and a dampening of random error (noise). The result may be better (higher significance) but unreliable estimates of model parameters.

Temperature and moisture response functions

In 1994, Díaz-Raviña *et al.* showed that the quadratic function, originally proposed by Ratkowski *et al.* (1982) to explain temperature responses of growth of pure bacterial cultures, was also suitable for predicting microbial temperature responses in soils. In our case T_{min}, a hypothetical value at which the CO_2 evolution is modelled to cease, was optimised to –0.83ºC for topsoil data, when normalised for 25ºC (T_{ref} =25; Paper II). This is considerably higher than the values T_{min} = –6ºC and –10ºC estimated by Díaz-Raviña *et al.* (1994). Similar low values are also reported by Seyferth (1998), who estimated T_{min} to about –6ºC for CO_2 evolution from humus layers at Skogaby and Hasslöv, and by Reichstein *et al.* (2000) who optimised T_{min} to –5.1 and –6.2ºC, respectively for the A-horizon and the Oe/Oa-layer at the Stillberg Alp. However, T_{ref} differs between these studies and as discussed below, this type of comparison should bee made with care.

Fitting different temperature response functions to decomposition data compiled from the literature (Paper III) showed that the choice of T_{ref} influenced all other parameter values. The activation energy E (J mol^{-1}; Arrhenius-type function) and Q_{10} were not greatly affected by the choice of T_{ref}, while T_{min} decreased from 3.54ºC to –5.17ºC when T_{ref} was increased from 10 ºC to 40ºC. Therefore comparisons with other studies especially considering T_{min}, as well as interpreting T_{min} as a temperature where biological activity is supposed to cease, should be made with care. The highest R^2 value (0.96) for all four tested response functions was reached for T_{ref}=30ºC.

In Paper II, our temperature response was also recalculated to Q_{10}-values to make the result more comparable to other studies. It resulted in decreasing Q_{10}-values with increasing temperature from 12.8 at 0.3ºC to 2.2 at 25ºC. This is in accordance with several other studies. For example Kirschbaum (1995), analysed literature data for C mineralization and found Q_{10} values of about 8 and higher at 0ºC. Dalias *et al.* (2001b) studied C mineralization after incubation of seven soils taken from coniferous forests located in different climatic zones of Western Europe. They found Q_{10}-values decreasing from about 5 at 4-10ºC to less than 1 at 23-30ºC. On the other hand there are studies reporting constant (Reichstein *et al.*, 2000) or even increasing Q_{10}-values (Q_{10}-varied between 2.01-2.83) with increasing temperature (Howard & Howard, 1993).

Due to the mathematical formulation of the Q_{10}-function, extremely high Q_{10}-values are reached when the temperature-activity factor approaches zero. Therefore, the models proposed by Ratkowski *et al.* (1982) and Lloyd and Taylor

(1994) are probably more adequate for the lower temperature range. An empirical model by Fang and Moncrieff (2001) is also more suitable for this low-temperature range. When modelling the temperature effect of C mineralization at larger scales, a Q_{10}-value of 2 has traditionally been used (Raich *et al.*, 1991). This is probably adequate when temperatures range between about 5 and 35ºC. At temperatures exceeding 35ºC, a bell-shaped function, considering the decrease in temperature response above the temperature optimum, has been suggested by Kirschbaum (1995). However, as discussed by several authors, interactions with other factors that may influence the C mineralization response to temperature must be considered, for example substrate quality (see *e.g.* Bunnell *et al.*, 1977; Chapman & Thurlow, 1998; Coûteaux *et al.*, 2001) and moisture (Anderson, 1991; Howard & Howard, 1993; Chapman & Thurlow, 1998). The duration of the incubation (Reichstein *et al.*, 2000; Dalias *et al.*, 2001a; Luo *et al.*, 2001), closely linked to the change in substrate quality and change of microbial community with time, is also an interacting factor. More research within this area is therefore needed to understand and quantify the effect of these interacting factors on the temperature response.

Usually, the moisture response is described as a log-linear function of the soil water potential (see *e.g.* Orchard & Cook, 1983; Andrén & Paustian, 1987). However, quadratic, linear or other functions have also been proposed (Howard & Howard, 1993; Leirós *et al.*, 1999). In our case, a log-linear function was not relevant since we did not measure the soil water potential of the soil samples. Linear and different polynomial functions were therefore tested. The best description of the moisture response for our soil was provided by a quadratic function of the moisture content (% H_2O).

Both in Paper II and III, we assumed that the CO_2 evolution rate constants (k_L and k_R) were equally affected by temperature and moisture. As mentioned above, several studies indicate that the temperature response may differ between substrates (see *e.g.* Bunnell *et al.*, 1977; Chapman & Thurlow, 1998; Coûteaux *et al.*, 2001). Our assumption was tested in Paper III and we found that k_L and k_R were equally affected by temperature. This means that the fit of the model was not affected by the assumption. One has to bear in mind that k_L and k_R are highly correlated parameters and not measured CO_2 evolution rates from two different measured pools of organic material. We therefore do not eliminate the possibility that the temperature and moisture response may differ between different types of organic matter.

Methodological aspects (Papers I and II)

The objective of the first part of the study, to investigate the effect of increasing temperature and moisture on CO_2 evolution, was achieved. However, on several occasions, the precision of the method was probably not good enough for the low activity treatments. This may explain why the CO_2 evolution measured from, *e.g.* subsoil samples incubated at 5 or 0.3°C or from topsoil and subsoil incubated at -4°C was in several cases not significantly different from zero or in some cases even negative. Different methods for measuring respiration in organic material were compared by Van Cleve *et al.* (1979). They report values for CO_2 evolution measured by KOH adsorption to be higher than those measured by infra red gas analysis (IR) and considerably higher than measurements by gas chromatography (GC). The lower values for the GC were attributed to the closed system employed. This implied that the gas diffusion was not increased as it is with the KOH-CO_2 sink method. Although the sensitivity between the methods mentioned differed by more than ten times (the sensitivity decreased in the following order IR > GC > KOH), the authors do not recommend one specific method. Instead they emphasise the importance of carefully working out the conditions under which any of the techniques may be used for the respiration measurements. In view of this, measurements of CO_2 evolution by IR or KOH adsorption, in parallel to the GC analysis performed, would perhaps have been an improvement of the study.

Besides improving the sensitivity of the analysis equipment, further methodological development could be done to increase the accuracy of the measurements, especially at low activities. Larger soil volumes could be used and the time of CO_2 accumulation in the vessels could probably be increased. An increased number of replicates would probably also enhance the precision.

One could also perhaps expect that the overall temperature and moisture responses might be different in the laboratory compared to the field, if the available organic material differs in quality and quantity. There are several possible reasons for such expectations. Pre-treated soil samples with comparatively high amounts of easily available organic material may initially show higher respiration rates during the incubations than undisturbed soil samples. The easily available organic material is decomposed faster at higher than at lower incubation temperatures. After a certain time the CO_2 evolution decreases significantly either due to a depletion of the easily available fraction or build-up of waste products (see *e.g.* Kirschbaum, 1995). This decrease in CO_2 evolution rates would probably be more pronounced in the pre-treated than in the undisturbed soil samples. This effect could also be expected for undisturbed soil samples incubated at temperatures uncommonly high for that specific site. Consequently, after a certain time there will be more easily available soil C left in the low than in the high temperature incubations. The undisturbed soil samples will probably also contain more easily available soil C than the pre-treated ones. This causes relatively higher CO_2 evolution rates for the low temperature and undisturbed samples. Especially for the pre-treated samples, this results in a risk for over-estimations of the temperature response when using initial measurements and a risk for under-estimations when using later measurements. Although our approach accounts for the changes in substrate quality with time without affecting the response to temperature or moisture, we cannot account for the effect of the pre-treatment on the CO_2 evolution rates. Another reason discussed by several authors (see *e.g.* Andersson, 1991; Liski *et al.*, 1999; Coûteaux *et al.*, 2001) is the assumed difference in temperature response between organic fractions.

Finally, an interesting speculation but one beyond the subject of this thesis is the hypothesis that the pre-treatment of the soil sample, as well as the incubations of soil samples at temperatures considerably higher than in the field, will affect the microbial community and as a consequence also the effects of temperature and moisture on decomposition (Luo *et al.*, 2001). As pointed out by Ågren (2000) the different temperature responses found for forest soil organic C and agricultural soil organic C (Persson *et al.*, 1999) could be a result of a difference in the relative importance of fungi and bacteria as decomposers.

One conclusion from this section is that the effects of the pre-treatment must be investigated more carefully. Despite this, few papers comparing or discussing the effect of the pre-treatment are available. For example, Fang & Moncrieff (2001) studied the CO_2 evolution from intact incubated soil cores and concluded that there was no effect of incubation time on the respiration. Gödde *et al.* (1996) reported without further comments on the result higher Q_{10}-values for sieved (3.3) than for intact soil samples (2.6). The results of these two papers are in agreement and support the former discussion about the risk for over-estimations of the temperature response when the soil becomes pre-treated. However, to be able to predict a temperature and moisture response that is more close to that in the field, measurements of CO_2 evolution performed on undisturbed soil samples are needed. This would probably not increase the precision of the measurements even if the number of replicates were increased, since the samples would be more heterogeneous. But it would be one of the most important improvements since the overall goal is to understand decomposition in the field.

Heavy metal dynamics in decomposing needle litter

Concentrations and amounts of Pb, Cu, Zn, Cd and Mn were recorded in decomposing needle litter for 6 to 8 years. At all sites concentrations of Cd, Zn, Cu and Pb increased, whereof Cu and Pb most, during needle decomposition (see Figures 2 and 3 in Paper IV). The increase in concentration of these heavy metals is in accordance with several other studies of litter decomposition at low-polluted sites (see *e.g.* papers reviewed in Table 2). However, during the latter part of the incubation our concentrations became more constant or even decreased. In a few cases, decreasing Zn concentrations after initial increases are reported (Lousier & Parkinsson, 1978; Liu *et al.*, 2000) and Liu *et al.* (2000) also report constant Zn concentration during litter decomposition at one of their sites. One reason why there are few reports of decreasing concentrations may be the time of incubation. Most studies follow litter decomposition for about 2-4 years and in our case the tendency to more constant or even decreasing concentrations appeared after about 3 to 4 years of incubation or more.

The concentration of Mn decreased at all sites but one, where pH in the mor layer was higher than at the other sites. Since the solubility of Mn decreases with increasing pH, Mn was probably not leached from this site (Remingstorp) to the same extent as from the other sites. The same relationship between pH and Mn in the litter and mor layers has been found by other authors (see *e.g.* Nilsson, 1971; Lousier & Parkinsson, 1978; Fritze, 1988). Other studies report either increases (Berg & Tamm, 1994; Liu *et al.*, 2000) or decreases (see *e.g.* Berg & Laskowski, 1997; Liu *et al.*, 2000; McEnroe & Helmisaari, 2001) in Mn concentrations during litter decomposition, without relating the dynamics of Mn to pH.

As a result of the strong retention of heavy metals to organic material, heavy metals may be released more slowly than carbon during decomposition. This results in increasing metal concentrations with time. It has therefore been suggested that concentrations high enough to affect microbial activity could be reached, even at low-polluted sites (Laskowski & Berg, 1993). The fact that the concentration of heavy metals increases with time, while the mass loss decreases, can make it tempting to interpret the decreased decomposition as a toxicity effect due to increased heavy metal concentrations. However, if the heavy metals in this case cause part of the decrease in the decomposition rate, which we cannot prove, it would rather be due to stabilisation of the organic matter than due to toxicity (Giller *et al.*, 1998). As pointed out by Palmborg *et al.* (1998), the covariation with the quality of the organic material must also be considered. During decomposition, the litter becomes more resistant as easy available carbon sources are depleted and the concentration of lignin increases. Covariation with other variables like climate and tree stand characteristics have also been discussed (Kurka *et al.*, 2001).

In 1992, Tyler stated that there is a risk for reduction of the microbial activity in the mor layer at total concentrations over 3-4µg Cd g^{-1}, 300 µg Zn g^{-1}, 20 µg Cu g^{-1} or 150 µg Pb g^{-1}. None of these values were reached during our experiment. It is also important to bear in mind that the concentrations given by Tyler refer to the entire mor layer. Comparing Tyler´s values with our mean values of the heavy metal concentrations for the whole incubation period would therefore be more correct and would mean even lower concentrations for our litter. The conclusion may therefore be that no effect of increases in heavy metal concentrations on microbial activity in the mor layer could be expected under low-polluted conditions, as was the case in our investigation.

At the end of the incubation, total amounts of Cd, Zn and Mn had decreased by at least 15, 24 and 43%, compared to the initial amount (Figure 3 in Paper IV). However, shorter periods of accumulation of Cd and Zn occurred, especially during the first years of incubation. Total amounts of Cu and Pb increased most. Copper increased over 40% before it started to decrease and Pb increased more than 230% before the amount became more constant or started to decrease. Similar results for the amounts of Mn, as well as for Cu and Pb, are reported by Lomander & Johansson (1998) when following elemental release from green spruce and pine needles decomposing between three and five years at nine clear-cut stands. Other studies also report large increases in total amounts of Cu and Pb (generally 50-700%) during litter decomposition (Lousier & Parkinsson, 1978; Laskowski *et al.*, 1993; McEnroe & Helmisaari, 2001). It is somewhat surprising that all studies I have found report constant or increasing amounts of Cd during decomposition (Laskowski *et al.*, 1993; Lomander & Johansson, 1998; McEnroe & Helmisaari, 2001). The results concerning Mn and Zn dynamics are more inconsistent. Both increases (Laskowski *et al.*, 1993; Lomander & Johansson, 1998) and decreases (Lousier & Parkinsson, 1978; Liu *et al.*, 2000; McEnroe & Helmisaari, 2001) in total amounts of Zn have been reported, as well as of Mn (Lousier & Parkinsson, 1978; Rustad, 1994; Lomander & Johansson, 1998; Liu *et al.*, 2000).

The similarity in dynamics of total amounts of Cd, Zn and Mn observed in our study was also confirmed by a PCA ordination, as were those of Cu and Pb. This is in accordance with the general reactions of the elements in the soil. Lead and Cu are generally more strongly bound to soil organic material and thus less mobile than Cd and Zn (see *e.g.* Evans, 1989; Ross, 1994; Stevenson, 1996).

An increase in the total amount implies that, at least occasionally, there has been a net transport of the heavy metal into the litterbags. Since no measurements of the heavy metal fluxes to and from the litterbags were conducted during our experiment, we can only speculate about sources of the influx. As PCA ordination indicated (Figures 4 and 5 in Paper IV), atmospheric deposition as well as throughfall (see *e.g.* Skrivan *et al.*, 1995; Nieminen *et al.*, 1999) probably contribute to the increases in the total amounts. As regards Pb, isotope ratios indicate that the Pb in the mor layer of present-day Swedish forest soils comes nearly exclusively from atmospheric pollution and only to a minor extent from the underlying mineral soil (Bindler *et al.*, 1999). Newly fallen litter, which with time will cover the litter-bags, can therefore also act as a source and /or a sink of heavy metals for the underlying litterbags. Furthermore, the analysed litter was not separated from fungal mycelia, which may constitute a significant pool of organic material. Since fungi even at unpolluted sites may have a high capacity to accumulate heavy metals, they may affect the overall mobility of metals in the system (see *e.g.* Lepp, 1992; Krantz-Rülker *et al.*, 1993).

The relative heavy metal amounts on a sampling occasion differed more between sites than within sites (Figure 4 in Paper IV). An observation on one sampling occasion can be considered to be a combination of the effects of the length of the litter incubation in the field and of the site, *i.e.* seasonal, climatic and edaphic effects, as well as of forest management factors such as thinning intensity. The changes in total heavy metal amounts were quite similar at the sites Tönnersjöheden and Mästocka and at the sites Remningstorp and Tveten, while the changes at Farabol were intermediate. This grouping of the sites is similar to the grouping of the sites due to similarities in deposition, climate and site properties. One conclusion can therefore be that the prevailing conditions at the sites have an influence on the change in amounts of heavy metal in the litter during decomposition. This is supported by Kurka *et al.* (2001) who discuss the close link between decomposition, chemical properties of the humus layer and stand characteristics.

Conclusions

> *"Omniam mirari etiam tritissima" – varthän man än vänder blicken*
> *finns något värt en avhandling*
> -Carl von Linné

Decomposition

This work contributes with new measurements of CO_2 evolution rates from two depths of a cold heavy clay soil, incubated at different combinations of temperature and moisture. However, since the precision of the method was probably not good enough for the samples with low activity, *i.e.* topsoil below 5°C and subsoil below 15°C, there were problems with getting significant results for these samples. In relation to later published studies, low temperature measurements are still in great demand. In our case, further methodological development is needed to increase the accuracy of the measurements, especially at low activities. Larger soil volumes could be used and the time of CO_2 accumulation in the vessels could probably be increased. An increased number of replicates would probably also enhance the results.

A quadratic function, which had previously only been used for pure bacterial cultures, was introduced and gave the best description of the temperature response in our cold heavy clay soil. On a larger data set, including different soil types, the goodness-of-fit did not differ between the four different temperature response functions tested but was affected by the choice of reference temperature, especially for T_{min}. This stresses the importance of taking account of T_{ref} when comparing the temperature responses. However, a Q_{10}-value of 2 was found to be adequate to describe the temperature dependence of decomposition for the whole data set between 5 and 35 ºC. For single studies of CO_2 evolution, especially below 5ºC, Q_{10}-values deviated from 2 and for our heavy clay soil Q_{10} decreased with increasing temperature. Functions not based on Q_{10}, like the quadratic function, would probably be more accurate at conditions where temperatures are below 5ºC for longer periods. Due to the mentioned paucity of data from low temperature incubations, this is only a hypothesis and more experimental work is required.

By using a two-component parallel first-order model when analysing the moisture and temperature responses, the whole data set can be used for the analysis and changes in CO_2 evolution rates over time due to substrate quality changes can be handled. The model analysis presented shows the risk for over- or under-estimations of the temperature response if based on initial or late measurements. Some authors have continued the discussion about the effect of quality change or time of incubation on temperature responses but hopefully it will be paid even more attention since this problem is of great concern when transferring results from the laboratory to the field.

We assumed that the CO_2 evolution rate constants for our heavy clay soil, k_L and k_R, were equally affected by temperature and moisture. This has properly been criticised by several authors, although a test did not show any difference in the effect of temperature on k_L and k_R. Quantification and continuous long-time measurements of different C pools at different temperature and moisture combinations would have been preferable. Although important, it would be expensive to conduct an experiment such as that.

An extrapolation of the results from our laboratory study to field conditions resulted in a 6-fold over-estimation of the CO_2 evolution. The pre-treatment of the incubated soil samples affects the quantity and the quality of the organic material and probably increases the CO_2 evolution compared with the field situation. It probably also affects the predicted temperature and moisture response in the laboratory. I therefore re-emphasise the importance of measurements of CO_2 evolution on undisturbed soil samples in predicting a temperature response that is more close to that in the field.

Heavy metals

Concentrations of Cd, Zn, Cu, Pb and Mn in decomposing needle litter were successfully followed for 6 to 8 years. The concentration of Mn decreased at all sites but one, while the concentrations of Cd, Zn, Cu and Pb increased during needle litter decomposition at all sites. During the latter part of the experiment, concentrations became more constant or even decreased. However, to be able to state whether these trends are significant, studies lasting longer than 6 years are needed under low-temperature conditions.

Concentrations considered to being toxic to micro-organisms in the mor layer were probably not reached during the experiment. The decrease in mass loss of the needle litter with time can therefore presumably be described by the depletion of the labile fraction as discussed in Papers I, II and III. Stabilisation of the organic material by heavy metals may also contribute.

This study indicates that climatic conditions, deposition and site properties may have an influence on the change in total amounts of heavy metals in the litter during decomposition. To more exactly identify the effects of these parameters, measurements of local deposition, throughfall, leaching and the growth of fungal mycelia into the litterbags would be necessary, as well as continuous climatic data for the sites. The variation in measurements within and between sites was large, especially for Cd. More replicates would therefore be needed and the heavy metal analyses should be performed more often. I also emphasise the importance of long incubations. The risk for losing litter fragments from the litter-bag, or not being able to completely separate *e.g.* ingrown roots from the incubated litter, increases with time. It would therefore demand a modification of the litter-bag method or a complete change of method.

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Acknowledgements – Ett varmt tack

Först vill jag tacka min huvudhandledare Maj-Britt Johansson som givit mig möjlighet att utföra mitt avhandlingsarbete här på ”Skoglig marklära”. Du har generöst låtit mig ta del av data från dina många fältförsök. Jag vill även rikta ett stort och varmt tack till mina biträdande handledare. Thomas Kätterer, du var den som först riktigt väckte mitt intresse för kolmineralisering, modellering och statistik. På ett fängslande sätt lärde du mig dessutom grunderna i SAS-programmering, trots att det kom att ta dig åtskilliga timmar av ”fnutt-letande”. Din tålmodighet med alla ogenomtänkta manus beundrar jag. Olle Andrén, du har med din erfarenhet, klarsynthet och känsla för språk varit en stor kunskaps- och inspirationskälla. Jan Eriksson har med stor noggrannhet ägnat mycket tid åt diverse tungmetallbryderier och manus.

Jag vill också tacka alla vänner och arbetskamrater vid Insititutionen för skoglig marklära, men speciellt skulle jag vilja nämna några. Erik Karltun har gett värdefulla kommentarer till detta manus. Kjell Larsson och Janne Edelsjö har hjälpt till med analyser och annat arbete på lab. Våra fantastiska sekreterare, Annika Lundberg och Kristina Lindström, har hållit reda på allt, inte minst alla ledighetsansökningar. Åke Nilsson har fixat med datorkrångel och tillsammans med Gertrud Nordlander visat på en rad SAS-finesser. Johan Stendahl har också gett goda råd om olika dataprogram. Torbjörn Nilsson har alltid haft just det jag saknat; artiklar, böcker, datorprogram... Jorge Mendoza och Lars Rosenqvist har bidragit med inspiration och uppmuntran, något som är av stort värde då det ibland går riktigt tungt. Hillevi Eriksson och Agnetha Alriksson fungerade som diskussionspartners och stöd, främst under den första tiden.

Dessutom vill jag tacka: Tryggve Persson för lån av ”Tryggve-burkar” och för en aldrig sinande entusiasm inför diverse resultat, Mikael Sjöberg för hjälp med GC:n, Ulrike Seyferth för praktiska tips angående burkförsök, Anke Herrman för synpunkter angående frys/tining-cykler, Bengt Olsson för idéer och litteraturtips angående tungmetalldynamik, David Hagerberg för kritiskt granskande av min tungmetalluppsats, samt David Tilles och Mary McAfee för att de gjorde min swenglish mer like english. Betygsnämnden bestående av Riitta Hyvönen-Olsson, Ernst Witter, Bo Svensson och Ewa Bringmark (suppleant), lade ned ett enormt arbete på att kommentera manuset innan det trycktes.

Jag vill även nämna några andra Ultunavänner som haft särskild betydelse under denna tid. Gudrun Sjöberg, du har i många år nu varit på samma plats och i samma fas i livet som ”en annan”. Anna Cigwald-Lööf, - många goda råd om informationssökning har det blivit. Helena Bengtsson, du har delat med dig av dina erfarenheter och det har hjälp mig mycket.

Slutligen, vill jag tacka min föräldrar, svärföräldrar och min familj. Jonas, dä´ skull´ bihöjv´ nämnes först bordi ållihop. Får äuto schölpa der haim å äuto de´ ståurstöde å trösta fra´ däj, he´ ji åldri kånt djere de´ here erbajde´. Nä skå´ he vel bläi maijr täin ivi för familjo o´ er rolian sek so´ger ibi skåojo, renn o´ änte mäinst botaderlende.

Mina älskade ungar, Axel och Hugo, nu har mamma jobbat klart! Då far hon upp i taket och sedan landar hon. Sen' så är det klart, så är det slut, så är det färdigt, så är det klart, så kommer hon hem….