

Factors influencing limit values for pine needle litter decomposition: a synthesis for boreal and temperate pine forest systems

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Received: 4 August 2009 / Accepted: 27 December 2009 / Published online: 10 February 2010
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Abstract We synthesized available data for decomposition of pine (*Pinus*) needle litter in pine forests to determine the litter chemical characteristics and climate factors that explained variation in the limit value, i.e. the level of accumulated mass loss at which the decomposition process either continues at a very low rate or possibly stops. Our data base included 56 separate studies on decomposition of pine needle

litter, spanning Scots pine, lodgepole pine, Aleppo pine, stone pine and white pine, mainly incubated at the site of collection. Studies had 5 to 19 samplings, on average 10, and the decomposition was followed to a mass loss ranging from 47 to 83%, on average 67%. The periods from 3.0 to 5.4 years, on average 3.9 years, were of sufficient duration to allow estimates of limit values of decomposition. We used a

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linear mixed model with regression effects to relate limit values to potential explanatory variables, namely the sites' long-term mean annual temperature (MAT) and mean annual precipitation (MAP) and to substrate-chemistry factors. Regarding the latter, we explored two models; one that included initial concentrations of water solubles, lignin, N, P, K, Ca, Mg, and Mn and one that included only lignin, N, Ca, and Mn to focus on those nutrients known to influence lignin degradation. Using backward elimination significant explanatory variables were determined. For litter decomposed in its site of origin we found the limit value to depend mainly on the initial concentration of Mn, with higher Mn concentrations resulting in higher accumulated mass loss. Thus, litter with higher Mn reached a higher limit value and left a smaller stable fraction. This is likely due to the fact that Mn is an essential component of ligninolytic enzymes important for degrading litter in the later stages of decomposition. Manganese has received little attention in decomposition studies to date. Given its significance in this synthesis, the role of Mn in influencing variation in the late stages of decomposition among ecosystems and among litters of other genera besides *Pinus* deserves further attention.

Keywords Litter decomposition · Limit values · Maximum decomposition · Nitrogen · Manganese · Calcium

Introduction

The very late decomposition stages of plant litter have been studied much less thoroughly than the early ones, and both the late and the near-humus stages deserve further attention to elucidate the factors that regulate late-stage decomposition rates. Some studies have reported that rates decline as decomposition progresses (e.g. Fogel and Cromack 1977; Johansson et al. 1995) and even may approach zero (Howard and Howard 1974; Berg and Ekbohm 1991). In such cases the accumulated mass loss approaches a maximum or “limit” value for decomposition, modeled as the asymptote of a mathematical function. Such an estimated limit value may not represent an absolute cessation of decomposition but could represent a stage

with an extremely low decomposition rate, and as such deserves exploration in terms of the factors (abiotic and biotic) that influence it.

Although limit values likely do not indicate completely undecomposable organic matter, the residual organic matter remaining once the limit value has been reached could consist of a moderately stabilized fraction that decomposes very slowly or that requires certain environmental or biotic conditions to decompose. Further, relating the limit value to climate, litter properties, or other environmental factors could provide important insights into the decomposition process. Thus estimating limit values complements other approaches such as modeling the slow, late stages of decomposition using two- or three-compartment exponential decomposition models (Lousier and Parkinson 1976; Couteaux et al. 1998).

A limit value may be useful for calculating carbon sequestration rates in forest soils, an idea that has been validated using budgets for soil organic matter (SOM) accumulation for boreal and temperate ecosystems of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). Further, as a limit value represents an extrapolation of the decomposition process such a validation is necessary and we used data from Wardle et al. (1997), who described more layers in boreal forest stands that have been growing continuously for over 2900 years. Berg et al. (2001) and Berg and Dise (2004) showed that this accumulation could be predicted using estimated limit values and measured litter-fall data. Further, Berg et al. (1999), using litter nitrogen (N) concentration as an internal marker, validated the concept using an alternative approach.

The reasons highly recalcitrant residues develop in some litter types, whereas others seem to be completely degradable, are not clear, but may relate to the nutritional requirements and constraints of the decomposing microbial community. For example, for several of the lignin-degrading white-rot fungi, high concentrations of low-molecular weight N compounds suppress the synthesis of the lignin-degrading enzymes (Keyser et al. 1978; Eriksson et al. 1990; Carreiro et al. 2000). Further, N has repeatedly been reported to react with remains of degrading lignin to form recalcitrant condensation products. Such products form chemically (Nömmik and Vahtras 1982; Stevenson 1982) rather than biologically and may be highly resistant to biological degradation. Piccolo and

Spaccini (1999) suggested that at least part of such bonds create a hydrophobic surface thereby resisting decomposition. The higher the concentrations of lignin and N in a litter material the more likely it seems that such covalent bonds will be formed. Using 106 sets of foliar litter comprising 21 tree species (both coniferous and deciduous) representing a wide range in chemical composition, Berg (2000a) found a highly significant negative relationship between limit values and initial N concentrations in litter.

The findings of a suppressing effect of N on the formation of the ligninase system in several fungal species was followed by the discovery of the enzyme manganese peroxidase (MnP) (Perez and Jeffries 1992), produced by wood-degrading white-rot basidiomycetes (see Hatakka 2001). Among the ligninolytic enzymes, MnP is the most wide-spread peroxidase produced by fungi (Hofrichter 2002). Positive relationships between decomposition rates of plant litter and the initial concentration of Mn in litter were seen for decomposing needle litter of Norway spruce (Berg et al. 2000) and leaves of common oak (*Quercus robur* L.) (Davey et al. 2007). Further, positive relationships between Mn concentration and annual mass loss were seen for pine needle litter in late decomposition stages (Berg et al. 2007; Virzo De Santo et al. 2009). Thus, it seems reasonable that Mn availability may in some cases limit lignin degradation and that an effect of Mn is not limited to just a few litter species. Consistent with Mn effects on decomposition rates, positive relationships have been found between limit values and litter Mn concentrations (Berg et al. 1996) indicating greater accumulated mass loss for litter with higher initial Mn concentrations.

The aim of the present synthesis paper is to determine climate factors and litter chemical characteristics related to limit values (Fig. 1) for pine needle litter

decomposing in pine ecosystems. We reviewed all available long-term (>3 years) decomposition studies of pine needle litter in pine stands; available studies encompassed five pine species. We focused on a single genus to minimize variation among substrates in morphological characteristics as well as unmeasured chemical properties, with the aim of isolating the chemical characteristics of litter that relate to its limit value. Although we included some data for transplanted litter we primarily focused our synthesis on studies that incubated litter at the site of collection. This ensured the relationship between litter chemistry and limit values from the same conditions that determined the litter quality. To our knowledge, our synthesis resulted in the largest data set to date for a single genus (*Pinus*) across a climatic gradient.

Materials and methods

Sites

We restricted our data synthesis to forest stands with monocultures of pine. Fifteen sites were located in Sweden and included 15 Scots pine stands with paired stands of lodgepole pine (*Pinus contorta* var. *contorta*) (Table 1) at two of the sites. Two stands of white pine (*Pinus strobus*) were located in Minnesota (USA) and two stands of Aleppo pine (*Pinus halepensis*) were located in northern Libya.

The stands in Sweden are located from 56°36' N to 65°47' N, from just north of the latitude of Copenhagen to about the Arctic Circle. All these stands are described by Berg et al. (1997). The two Minnesota stands are located c. 60 km north of Minneapolis at a latitude of 45°24' N (Hobbie 2005, 2008). The two

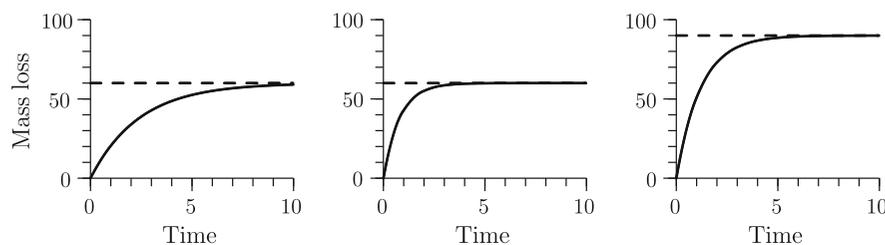


Fig. 1 Three illustrations of model 1 for various choices of limit value m (dashed line) and initial rate of decomposition k : $m = 60\%$ and $k = 25\% \text{ year}^{-1}$, $m = 60\%$ and

$k = 75\% \text{ year}^{-1}$, and $m = 90\%$ and $k = 75\% \text{ year}^{-1}$. Two of the illustrations have the same value of m , and two have the same k . Time is in years and mass loss in percent

Table 1 Number of incubations of litter per pine needle type/species and site

Litter type/species	Site																	Sum	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17		
Experimental litter																			
Lodgepole pine (green)				1														1	
Scots pine (green)				2					2									4	
Lodgepole pine (brown)				4														4	
Stone pine (brown)				1														1	
Local litter (brown)																			
Lodgepole pine	2				3													5	
Scots pine	2	1	1	17	1	1	3	1	4	1	1	1	1	1	1			37	
Aleppo pine																	2	2	
White pine																		2	2
Sum	4	1	1	25	4	1	3	1	6	1	1	1	1	1	1	2	2	56	

The sites in Sweden are listed as 1–15. Sites 16 and 17 each with two stands are located in Libya and in Minnesota (USA), respectively

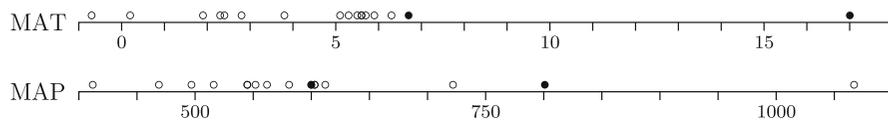


Fig. 2 Distribution of sites with regard to mean annual temperature (MAT, °C) and mean annual precipitation (MAP, mm). Sites no 1–15 (*open circles*), sites 16 and 17 (*filled circles*) (cf. Table 1). Multiplicity of overlapping points is not shown

Aleppo pine stands are located at a latitude of 32°49' N (Faituri 2002).

The ranges for mean annual temperature (MAT) and mean annual precipitation (MAP) among all sites are given in Fig. 2.

Database

The data

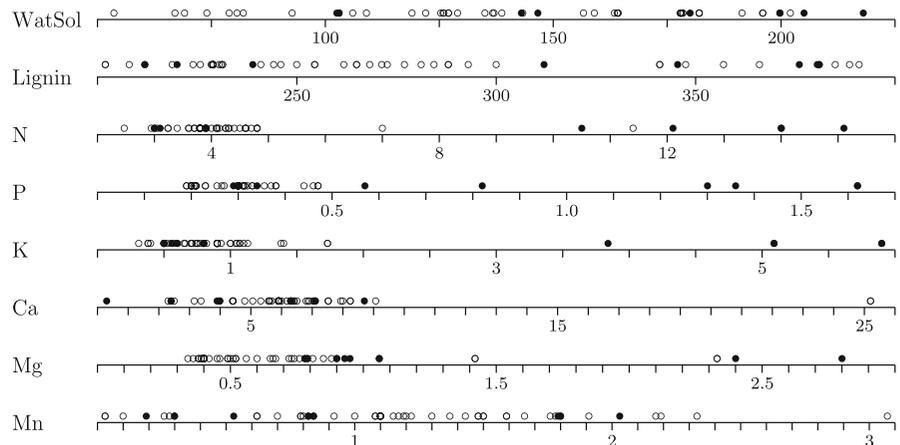
In most stands, only local needle litter (litter originating in the study site) was decomposed with the following exceptions: at one of the Swedish sites, site 4 (Jädraås), the range of substrate-quality was extended by incubating brown needle litter of stone pine (*Pinus pinea*), green needles of Scots pine, green needles and brown needle litter of lodgepole pine and at site 9 green needles of Scots pine (Table 1). Data from individual studies are also found in Berg et al. (1991), Hobbie (2005, 2008),

Johansson et al. (1995), Berg and Lundmark (1985, 1987), and Faituri (2002).

Available site and litter-quality variables and units

We included only studies that presented specific climate and litter chemistry data. For climate variables we required mean annual temperature (MAT, °C) and mean annual precipitation (MAP, mm). For litter-chemistry variables, we required that datasets include initial litter concentrations of water soluble cell contents (WatSol), lignin and the nutrients N, phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and Mn (Figs. 3 and 4). The data shown in Fig. 3 come from all sites, whereas those of Fig. 4 are restricted to the climatically more uniform area of Sweden. The gravimetric lignin analyses according to Klason (e.g. Bethge et al. 1971) and to Effland (1977) are based on methods which do not discriminate between lignin and polymer compounds newly formed through decomposition processes in

Fig. 3 The variability in litter-chemistry variables for ‘Gradient all stands’ with 56 sequences. *Open circles* correspond to local brown litter (46 sequences) and *filled circles* to experimental litter, ten sequences (cf. Table 1). Multiplicity of overlapping points is not shown. Unit: mg g^{-1}



litter, such as humic acids. We have used only the initial concentrations of lignin in the newly shed litter in our analyses, so for the sake of simplicity, we use the term ‘lignin’ hereafter.

Concentrations of nutrients, WatSol and lignin are given in mg g^{-1} and limit values in % accumulated mass loss.

Extent of decomposition in time and as measured accumulated mass loss

The decomposition was followed to different extent among the different studies viz. in time and in accumulated mass loss. The litter of Aleppo pine was followed for 3.0 years and until 47.7% accumulated mass loss. That of white pine was followed for 4.83 years and until 69.5 and 74.7% mass loss. The litter of stone pine was followed for 3.04 years until 58.1% mass loss. Most data sets (sequences)

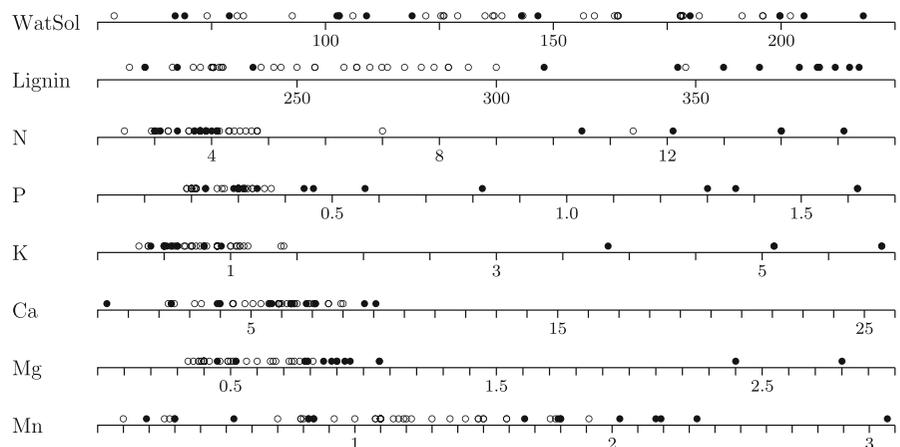
originated from lodgepole pine and Scots pine. For the former decomposition was followed until 3.00–4.01 years and a mass-loss between 52.2 and 75.5% and for Scots pine 2.95–5.04 years and between 48.4 and 80.8% accumulated mass loss. For the whole data set the studies had 5 to 19 samplings, on average 10, and the decomposition was followed over periods of 3 to 5.4 years, on average 3.9 years to an average mass loss of 67%.

Incubations

Litter in Sweden and Libya

The litter was incubated in 8×12 cm polyester litter bags (1 mm mesh), with 1–2 g of air-dried (room temperature) litter in each bag and 20–25 replicate litter bags in each sampling. Dry mass was determined on 20–25 subsamples dried at 85°C . For a description

Fig. 4 The variability in litter-chemistry variables for ‘Gradient all Swedish stands’ with 52 sequences. *Open circles* correspond to local Scots pine brown litter (37 sequences) and *filled circles* to experimental and local litter from lodgepole pine, Scots pine and stone pine, 15 sequences (cf. Table 1). Multiplicity of overlapping points is not shown. Unit: mg g^{-1}



see e.g. Berg et al. (1982, 1993). The incubations in Sweden ranged over a period of 20 years.

Litter in Minnesota (USA) was incubated in 400 cm² litter bags of fine-mesh polyester (200 μm) bottoms and 0.3 mm tops. Approximately 6 g (air-dried) of needle litter were placed in each bag. At each sampling 6 replicate samples were taken over a period of 5 years (Hobbie 2005). Litter was dried at 65°C to determine dry mass.

Chemical analysis

The methods for analyzing water solubles and lignin are given by Berg et al. (1982, 1993) and by Hobbie (2005). The lignin analyses are based on the sulfuric acid–lignin method (Bethge et al. 1971; Berg et al. 1982) and that of Effland (1977), respectively.

The analytical methods for analyzing nutrients for the Swedish samples changed over the period from 1982 until 2002, but were made by two well coordinated laboratories and the results are comparable (Berg et al. 1993). The same analysis methods were used for the Libyan samples. The analysis methods for the Minnesota samples are given by Hobbie (2005).

Terminology

The term ‘batch’ is used for litter with the same chemical composition. Further, litter from a given batch is used to give just one or a few ‘sequences’ of values. The term ‘sequence’ has been used for all values of accumulated mass loss for a given batch of litter that has been incubated at a given date. The limit value is denoted by m (model 1), m^* gives the estimated limit value from decomposition data using model 1, and \hat{m} refers to limit values obtained by regression (model 2).

Statistical method

As the first step of data analysis, we used the observed sequences of accumulated mass loss to estimate the parameters m and k of the model

$$y_i = m(1 - e^{-kt_i/m}) + \varepsilon_i \quad (1)$$

where y_i is the observed mass loss at time t_i , and ε_i is the random deviation from the modeled mass loss.

The model is meaningful if $k > 0$ and $0 < m < 1$, i.e. $0 < m < 100\%$. The parameters m and k can be interpreted as the limit value for mass loss and the initial rate, respectively. This follows since $m(1 - e^{-kt/m}) \rightarrow m$ as $t \rightarrow \infty$ and $m(1 - e^{-kt/m}) \approx kt$ for small values of t . This model is also considered in Berg and Ekbohm (1991) and is equivalent to the asymptotic mathematical models treated in Howard and Howard (1974) and Wieder and Lang (1982). Some illustrations of model 1 for different choices of m and k are given in Fig. 1. The estimates of m and k , restricted as above if needed, were found by least squares using the procedure Nlin of the statistical package SAS Institute Inc. (2004) for the numerical calculations.

The obtained estimates m_{ijl}^* of the limit value m at site i , batch j , and sequence l were used as response values in the linear mixed model:

$$m_{ijl}^* = \mu + \beta_1 x_{i1} + \beta_2 x_{i2} + s_i + \gamma_1 z_{ij1} + \dots + \gamma_8 z_{ij8} + b_{ij} + e_{ijl} \quad (2)$$

where μ is the overall mean, β_1 and β_2 are the regression coefficients for the explanatory variables x_{i1} and x_{i2} representing MAT and MAP, respectively, s_i is the random effect of site, following a normal distribution $N(0, \sigma_s^2)$, $\gamma_1, \dots, \gamma_8$ are regression coefficients for the explanatory variables z_{ij1}, \dots, z_{ij8} denoting WatSol, lignin, N, P, K, Ca, Mg, and Mn, respectively, b_{ij} is the $N(0, \sigma_b^2)$ -distributed random effect of batch within site, and e_{ijl} distributed as $N(0, \sigma_e^2)$ is the residual error.

Reduced versions of model 2 were also considered by using only lignin, N, Ca, and Mn among the substrate variables. Although calcium is not specifically involved in the ligninase system we included Ca among these variables because of its strong and general influence also on lignin degradation. When only site 4 was studied the model was simplified by removing the effects $\beta_1 x_{i1}$, $\beta_2 x_{i2}$, and s_i of MAT, MAP, and sites, respectively. The reduced model with the substrate-chemistry variables restricted to lignin, N, Ca, and Mn was also used for site 4.

The explanatory variables of model 2 were tested in steps by successively removing the least significant of them until all remaining variables were significant at the level 0.05. The purpose was to investigate to what extent the variables can explain the observed

differences, if any, in decomposition among the types of pine litter. In parallel with the step-wise tests, the variance components σ_s^2 , σ_b^2 and σ_e^2 were estimated. The correlations were calculated of the directly estimated limit values m_{ijl}^* in model 1 and the limit values \hat{m}_{ijl} estimated by regression, model 2. The correlations only serve as descriptive measures as the observations have a dependence structure from the effects of sites and batches.

As the data result from observational studies, there was limited possibility of establishing efficient designs with the aim to detect significant relationships using model 2. In a standard regression model, the efficiency is characterized by the range of the explanatory variables and their correlations. The ranges are illustrated in Figs. 2–4 and the correlations for two sets of selected sequences are given in Table 2. Although model 2 includes more effects than a standard regression model, the correlations can be used to catch a glimpse of the potential to find significant variables. The more the correlations deviate from zero the greater the multicollinearity among the variables, i.e. reduced chances to obtain significant results for individual explanatory variables when they are analyzed in a model with other variables. These effects are considered in the “Results and discussion” section.

Overview of the analysis

We studied the limit values (m^*) obtained by model 1 in four main steps, first by combining all values, and then by analyzing subsets defined as three separate

climatic gradients. We first let the backward elimination procedure select significant explanatory variables in model 2 using both climate variables (cf. Fig. 2) and all eight litter chemistry variables (Figs. 3 and 4) after which we analyzed the data using only the previously recognized causal chemistry variables, i.e. concentrations of lignin, N, Ca, and Mn (e.g. Eriksson et al. 1990; Hatakka 2001), plus the two climate variables. An overview of the number of available decomposition sequences for all sites is evident from Table 1.

In a first analysis we included all available data from all stands, combining (i) locally collected pine needle litter and experimental (i.e. non-local) litter (56 sequences) and (ii) local litter only (46 sequences). We call this analysis ‘Gradient, all stands’ (Figs. 2 and 3).

In a second analysis we included all available data for pine needle litter (52 sequences) incubated in a climatic gradient over Sweden, namely locally collected Scots pine and lodgepole pine litter plus experimental litter. We call this analysis ‘Gradient, all Swedish stands’. MAT ranged from -0.7 to 6.3°C and MAP from 412 to 1067 mm (Fig. 2). The ranges for litter-chemistry variables are given in Fig. 4.

In a third analysis we included all data for locally collected, brown Scots pine needle litter incubated in a climatic gradient over Sweden (37 sequences). We call this ‘Gradient, Swedish local brown Scots pine litter’. The ranges for MAT and MAP were the same as for ‘Gradient, all Swedish stands’ (Fig. 2), but the variation of the litter chemistry variables was restricted to the open circles in Fig. 4.

Table 2 Correlation coefficients based on all 56 sequences with local as well as experimental litter (above diagonal), and for 37 Scots pine sequences restricted to local brown litter (below diagonal)

	MAT	MAP	WatSol	Lignin	N	P	K	Ca	Mg	Mn
MAT	1	0.17	-0.02	0.12	-0.04	-0.05	0.04	0.76	0.52	-0.46
MAP	0.38	1	0.02	-0.01	0.08	0.00	-0.02	-0.16	0.04	-0.18
WatSol	0.05	-0.08	1	-0.76	0.31	0.38	0.46	-0.13	0.08	-0.46
Lignin	-0.10	-0.02	-0.92	1	-0.21	-0.17	-0.13	0.28	0.21	0.49
N	0.22	0.22	-0.03	0.13	1	0.88	0.61	-0.35	0.25	-0.35
P	0.01	-0.01	0.27	-0.20	0.33	1	0.77	-0.23	0.36	-0.25
K	0.28	-0.16	0.53	-0.44	0.34	0.56	1	-0.08	0.31	-0.40
Ca	-0.31	-0.46	0.13	-0.23	-0.63	-0.31	-0.29	1	0.48	-0.14
Mg	-0.24	-0.52	-0.02	0.07	-0.15	-0.04	0.10	0.32	1	-0.36
Mn	-0.35	-0.23	-0.17	0.22	-0.43	-0.10	-0.52	0.44	-0.02	1

In a fourth analysis we used all needle litter data for a Scots pine forest stand at one site (no. 4), (i) local plus experimental litter (25 sequences), (ii) local litter from different batches (17 sequences; Table 1). With all litter incubated in the very same stand the average climate was constant as were other stand factors such as soil properties and ground vegetation.

Results and discussion

Accuracy of the limit value

We estimated 56 limit values m^* using model 1, each one with a certain accuracy. Figure 5 illustrates the results for model 1 in three cases with varying species, climate situations and limit values. It is seen that the limit value m^* is essentially reached in 10 years or earlier. The confidence intervals also show that the estimated limit values have a limited uncertainty motivating them to serve as response variables in model 2. Out of the 56 sequences, 9 gave an upper confidence limit above 100%, mainly due to a high estimate of m^* from mass-loss values. In 11 cases, mostly with lodgepole pine, the value of m^* was set to 1 as the model-based estimate was larger than 100%.

One factor determining the accuracy of an average mass-loss value is the number of replicate samples. The main part of the decomposition studies were based on 20 or 25 replicates in each sampling giving a standard error in each sampling in the range of 0.23 to 1.65 percentage units (e.g. Berg et al. 1982, 1991). Most of the data in this study has been reported earlier (Berg and Ekbohm 1991; Berg 1998), resulting in asymptotic standard errors for limit values

varying from 0.9 to 11.1 and from 2.2 to 11.7, respectively. Except for three extreme cases with standard errors 27.7, 22.5, and 14.8, the uncertainty of the data added here is of the same magnitude.

‘Gradient, all stands’ and ‘Gradient all Swedish stands’ using all available data, both locally collected and experimental pine litter data

Local plus experimental needle litter (21 stands, 56 sequences)

Using all available data with a range in estimated limit values m_{ijl}^* (model 1) from 54 to 100%, we obtained a simple final version of model 2 based on two litter-chemistry variables only, with limit values positively related to Mn and negatively related to K (Table 3). Of the two factors, Mn was more significant ($p < 0.0001$) than K ($p = 0.0025$). The climatic factors were not significant. The correspondence of the directly estimated values m_{ijl}^* of model 1 and the regression-estimated values \hat{m}_{ijl} of the final version of model 2 is shown in Fig. 6. The analysis using previously recognized causal variables (lignin, N, Ca, Mn) (Berg et al. 1996; Berg and McLaugherty 2008) in addition to MAT and MAP gave Mn as the single positively related variable ($p < 0.0001$; Table 3).

Local plus experimental litter, Swedish stands (17 stands, 52 sequences)

Of the two climate variables and eight substrate-chemistry variables the backward elimination selected Mn ($p < 0.0001$) and K ($p = 0.0027$; Table 3). When using the recognized causal litter-chemistry variables and the two climate variables we

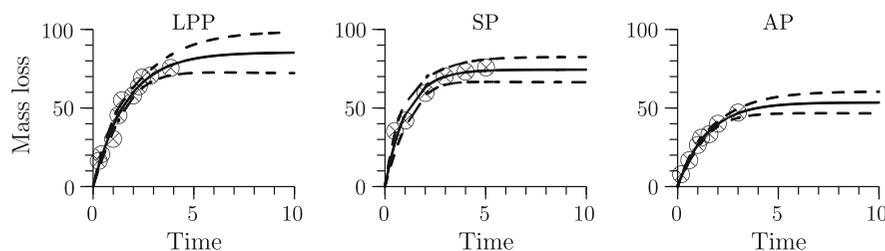


Fig. 5 Results for model 1 by three sequences representing the species lodgepole pine (LPP, boreal site, Mn concentration 1.66 mg g^{-1}), Scots pine (SP, temperate site, Mn concentration 0.92 mg g^{-1}), and Aleppo pine (AP, subtropical site, Mn

concentration 0.03 mg g^{-1}). $m^* = 85, 74,$ and 54% , respectively. *Solid curves* give estimated mass loss, *dashed curves* 95% confidence intervals (approximate width: ± 2 standard error), and \otimes observed values

Table 3 Estimates and standard errors of regression coefficients and variance components in the final versions of model 2, where $\hat{\sigma}_s^2$, $\hat{\sigma}_b^2$, and $\hat{\sigma}_e^2$ are for sites, batches and residuals,

respectively. Descriptive correlation coefficient r of the direct estimates of m^* in model 1 and regression estimates of \hat{m} in model 2

Final version of model 2	$\hat{\sigma}_s^2$	$\hat{\sigma}_b^2$	$\hat{\sigma}_e^2$	r
‘Gradient all stands’, locally collected plus experimental litter, 56 sequences				
All variables—two final variables				
$\hat{m} = 69.8 \quad -2.9K \quad +11.6Mn$	55.5	0	57.2	0.68
$s.e. = -4.0 \quad 0.9 \quad 2.4$	30.2	–	12.8	
Causal variables only—one final variable				
$\hat{m} = 63.8 \quad +14.2Mn$	47.9	25.9	49.4	0.61
$s.e. = 3.9 \quad 2.5$	35.4	30.6	21.6	
‘Gradient all Swedish stands’, local plus experimental litter, 52 sequences				
All variables—two final variables				
$\hat{m} = 68.9 \quad -2.8K \quad +11.8Mn$	21.4	0	55.8	0.70
$s.e. = -4.0 \quad 0.9 \quad 2.4$	13.8	–	12.1	
Causal variables only—one final variable				
$\hat{m} = 62.3 \quad +14.7Mn$	25.5	0	66.1	0.62
$s.e. = 3.7 \quad 2.3$	16.2	–	14.1	

First part: all pine litter data from 17 Swedish stands, 2 stands in Libya and 2 in Minnesota (USA) (‘Gradient all stands’), in all 56 incubations of needle litter in pine forests. *Second part:* all pine litter from the Swedish stands (‘Gradient all Swedish stands’), in all 52 incubations of needle litter in pine forests. All available eight substrate-chemistry variables, WatSol, lignin, N, P, K, Ca, Mg, and Mn, plus 2 site variables, viz. MAT and MAP, were tested in one run. In a second run only recognized substrate-chemistry variables based on causal relationships were used, namely lignin, N, Ca, and Mn plus MAT and MAP. Unit for \hat{m} is %

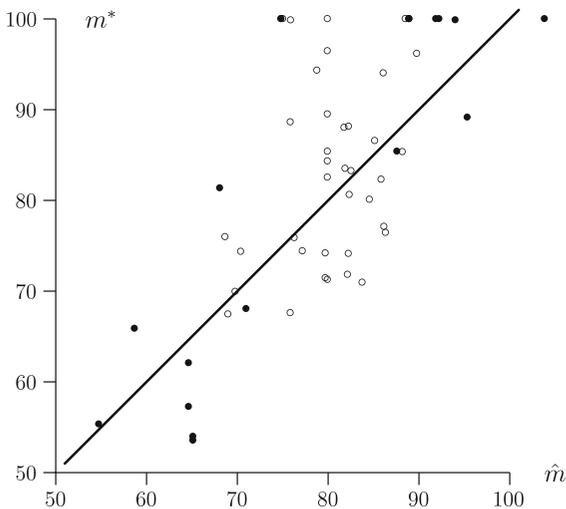


Fig. 6 Plot of predicted limit values \hat{m} (model 2) versus directly estimated limit values m^* (model 1). The straight one-to-one line with \hat{m} and m^* equal corresponds to an ideal perfect fit. Open circles correspond to Scots pine local brown litter, 37 sequences. Filled circles correspond to experimental and local litter from green and brown lodgepole pine, green Scots pine, stone pine, white pine, and Aleppo pine, 19 sequences. The descriptive correlations given in Tables 3 and 4 are $r = 0.68$ for all circles and $r = 0.32$ for open circles only. Unit for \hat{m} and m^* : %

obtained an equation with Mn as single factor ($p < 0.0001$; Table 3).

‘Gradients with only locally collected brown pine litter data

Gradient all stands. All pine needle litter decomposing in its own stand (local litter, 21 stands, 46 sequences)

The final model (Table 4) included Mn ($p = 0.0002$), Ca ($p = 0.0043$), and Mg ($p = 0.017$). The analysis with the recognized causal variables resulted in Mn as the single explanatory variable ($p = 0.0014$; Table 4).

‘Gradient, Swedish local brown Scots pine litter’ (15 Scots pine stands over Sweden, 37 sequences)

The levels of the estimated limit values m_{ijl}^* according to model 1 ranged between 67 and 100%. The stepwise regression procedure resulted in a model with one explanatory variable, namely Mn ($p = 0.019$) (Table 4). The same final model was obtained when

Table 4 Estimates and standard errors of regression coefficients and variance components in the final versions of model 2, where $\hat{\sigma}_s^2$, $\hat{\sigma}_b^2$, and $\hat{\sigma}_e^2$ are for sites, batches and residuals,

Final version of model 2	$\hat{\sigma}_s^2$	$\hat{\sigma}_b^2$	$\hat{\sigma}_e^2$	r
‘Gradient all stands’, locally collected litter only, 46 sequences				
All variables—three final variables				
\hat{m} = 68.8 -2.1Ca +18.5Mg +12.0Mn	35.7	0	58.1	0.63
s.e. = 5.8 0.7 7.4 2.9	23.1	–	14.5	
Causal variables only—one final variable				
\hat{m} = 69.2 +9.9Mn	63.7	0	60.9	0.51
s.e. = 4.2 2.9	34.4	–	15.5	
‘Gradient Swedish stands, local brown Scots pine litter only’, 37 sequences				
All variables—one final variable				
\hat{m} = 69.9 +9.0Mn	24.4	0	63.6	0.32
s.e. = 4.9 3.7	17.7	–	16.8	
Causal variables only—same result as for all variables				

For only locally collected needle litter 46 incubations remained in the same climatic gradient, and 37 incubations remained for local brown Scots pine litter. All available eight substrate-chemistry variables, WatSol, lignin, N, P, K, Ca, Mg, and Mn plus two site variables, MAT and MAP, were tested in one run. In a second run only recognized substrate-chemistry variables based on causal relationships were used, namely lignin, N, Ca, and Mn plus MAT and MAP. Unit for \hat{m} is %

the analysis was restricted to the four recognized causal variables and two climate variables.

Variation among sites and batches

The results in the preceding subsections show that MAT was not selected as a covariate. A reason to this can be that the tests of MAT and MAP effects are weakened by the residual variation among sites, not explained by the variables MAT and MAP. Such residual variation may include e.g. effects of mineral soil, differences in vegetation and possibly in pine species. Further, a variation in weather in the period of incubation would not be covered by the rather rough measures MAT and MAP. The estimates of the variance for sites σ_s^2 ranged between 38 and 105% of the estimates of the residual variance σ_e^2 (Tables 3 and 4) meaning that the variation in site properties was a major fraction of the variation not explained by litter properties. We may compare the variance for sites σ_s^2 both as such and relative to the residual variance σ_e^2 for a specific case with local brown litter. ‘Gradient all stands’ with 46 sequences (Table 4) encompasses 4 pine species, very different climates and likely very different soils. The variance for sites has a value of 35.7 and is 61% of the residual variation. For the considerably more limited gradient

respectively. Descriptive correlation coefficient r of the direct estimates of m^* in model 1 and regression estimates of \hat{m} in model 2

with Swedish stands encompassing 37 sequences and just one litter species the variation for sites was 24.4 and 38.4% of the residual variance. This may support a conclusion that although Mn was identified as a dominant litter property, species may be of importance even within a genus as well as site properties including soil and possibly variation in climate not reflected by MAT and MAP. The estimates of the batch variance σ_b^2 were mostly zero.

Locally collected litter, Mn concentration versus MAT

In a climatic gradient Berg et al. (1995) found a highly significant and negative relationship between Mn concentration in the newly shed pine needle litter and mean annual temperature, suggesting that pine litter Mn concentration may also reflect the local climate. We therefore applied a simplified version of model 2 for data on Swedish local brown litter ($n = 37$) with Mn as the response variable and MAT as the single explanatory variable, excluding the effect of the other substrate-chemistry variables and effect of batches (b_{ij}). The resulting equation for the concentration was $Mn = 1.56 - 0.096MAT$ with $p = 0.09$ for the slope coefficient. The estimates of the variance components for sites and residual error

were both 0.10 and the descriptive correlation between MAT and Mn was $r = -0.35$. Using the initial Mn concentration for all local brown litter (46 sequences, ‘all local litter’) the corresponding equation for the concentration was $Mn = 1.66 - 0.10MAT$, $p = 0.005$. The variance components for sites and residuals were 0.16 and 0.14, respectively, and the descriptive correlation was $r = -0.53$. These results suggest that higher local temperatures (MAT) are associated with lower Mn concentrations in the needle litter formed at that site. The mechanism underlying this empirical relationship is unknown. Because of the close relationship between Mn and MAT, a separate backward elimination for Scots pine local litter (Swedish data, 37 sequences) using model 2 without Mn as an explanatory variable resulted in the final estimate for the limit value as $\hat{m} = 89.1 - 2.4MAT$, $p = 0.032$ and $r = -0.29$. This corresponds to a correlation $r = 0.29$ between m^* and \hat{m} (cf $r = 0.32$ in Table 4). Thus, Mn showed a somewhat better fit. Berg et al. (1995), presented a negative relationship for Mn versus MAT for Scots pine needle litter in a climatic gradient ranging from the Barents Sea in the north to the Carpathian Mountains in Poland ($r = -0.44$; $n = 22$; $p < 0.05$). For several pine species along the same gradient ($n = 35$) the relationship was more apparent ($r = -0.63$; $p < 0.001$). There was also, in a similar gradient, a weak negative relationship to MAP. It is thus possible that there may be an effect of MAT on Mn concentration in litter that in turn influences the fraction of organic matter that becomes recalcitrant, leading to regional variation in the formation of recalcitrant organic matter from *Pinus* detritus. Thus there may be counteracting effects of MAT and Mn on the extent of decomposition at a regional scale. The higher MAT is related to low Mn concentration in litter, leaving higher remains whereas at lower MAT a higher Mn concentration would promote a more complete decomposition. Thus, Mn appears to be the dominant factor determining limit values in pine ecosystems (cf. Fig. 5).

The present study is heavily biased on Nordic conditions as 52 of the 56 used sequences were from Sweden and we can only speculate about a more general validity although data from North Africa and North America fit the pattern well. Soil data have not been included in this study and such data, e.g. concentrations of available nutrients may also

influence the limit values. The Nordic climate with an Atlantic influence is a further factor as well as the fact that this mainly boreal area is energy limited as regards e.g. soil processes (Berg and Meentemeyer 2002). Thus, of the climate factors we may expect variation in temperature rather than in precipitation to have a direct influence on soil processes.

Consequences of multicollinearity for the gradients

The number of studied explanatory variables is quite large in the backward elimination for model 2, at least in the initial stages. As the values of the variables are not totally under control, there is a risk that the effect of one variable on the estimate of the limit value is concealed by other variables. In particular, variables with high correlations (Table 2) tend to delete possibilities for each other to give significant effects. A more precise measure for this multicollinearity effect is the variance inflation factor, VIF, calculated as the diagonal element of the inverse of the correlation matrix. The VIF equals the quotient of the variance of a regression coefficient in the multiple regression model to the variance of the coefficient in the hypothetically simplified model using only the particular coefficient. In a perfectly designed experiment, VIF attains the lower limit 1 but mostly in observational studies the VIF is much larger. A common recommendation is that VIF should be at most 10 (Graybill and Iyer 1994).

The first line of Table 5 corresponds to the initial version of model 2 with all explanatory variables for all 56 sequences and is found from the correlations in the upper part of Table 2. The largest VIFs are those for N and P. To some extent, this is explained by the large correlation coefficient, 0.88 of N and P in Table 2.

A large VIF implies a higher risk of eliminating the explanatory variable, although this can be compensated by a wide range in (Fig. 3), or a strong effect of the variable. The first step in the backward elimination in model 2 resulted in the removal of N (Table 5). The VIFs in the successive simplifications of model 2 before the final model was reached (Table 3) are given on the remaining lines of Table 5. As a whole, the VIFs attain acceptable levels quite soon, indicating that most of the explanatory variables are not suffering from multicollinearity. As N

Table 5 Variance inflation factors (VIF) for the analysis of explanatory variables preceding the results in Table 3, ‘Gradient all stands’

MAT	MAP	WatSol	Lignin	N	P	K	Ca	Mg	Mn
4.8	1.4	4.4	6.7	8.8	15.2	6.0	5.2	3.2	5.0
4.6	1.4	4.4	6.0	–	4.3	4.8	4.6	2.9	3.7
1.9	1.1	4.4	6.0	–	3.5	4.5	–	2.5	3.3
1.9	1.1	4.0	5.0	–	–	1.9	–	1.9	2.9
1.7	1.1	3.7	4.0	–	–	1.9	–	–	2.7
1.4	1.1	1.5	–	–	–	1.4	–	–	1.9
1.3	1.1	–	–	–	–	1.2	–	–	1.6
1.3	–	–	–	–	–	1.2	–	–	1.6

MAT	MAP	Lignin	N	Ca	Mn
4.5	1.4	1.7	1.5	4.4	2.4
1.7	1.0	1.6	1.2	–	2.4
1.4	1.0	–	1.2	–	1.5
1.3	–	–	1.2	–	1.5
–	–	–	1.1	–	1.1

The run using all variables (top) and causal variables only (bottom)

was eliminated in the first step with $VIF = 8.8$, that variable can be unfavoured. However, as can be seen in the lower part of Table 5 for the reduced model starting with the causal variables only, N has a quite favourable situation with VIF at most 1.5 in the successive steps. The reason for N not being included in the final model should therefore be that the range in Fig. 3 is too limited or that N has no essential relationship with the limit value.

The VIFs calculated for the correlations below the diagonal in Table 2 are given in Table 6. These values correspond to the analysis for the ‘Gradient Swedish local brown Scots pine needle litter’ (37 sequences). The resulting models after the eliminations are given in Table 4. Except for WatSol and lignin the multicollinearity is limited, cf. the correlation coefficient -0.92 below the diagonal in Table 2. The other subsets of sequences show similar patterns for the multicollinearity with high VIFs only in the very first steps of the backward elimination.

The variable MAT was never kept in the final models (Tables 3 and 4), although its VIF values were not high (Tables 5 and 6). However, in many of the runs MAT was one of the last variables removed

Table 6 Variance inflation factors (VIF) for the analysis of explanatory variables preceding the results in Table 4, ‘Gradient Swedish stands, local brown Scots pine litter only’

MAT	MAP	WatSol	Lignin	N	P	K	Ca	Mg	Mn
1.5	2.4	10.5	11.5	1.9	2.0	4.1	3.3	1.6	2.6
1.5	2.4	10.3	11.0	–	1.9	4.1	3.0	1.6	2.4
1.4	2.3	10.0	10.8	–	–	2.9	2.8	1.6	2.0
1.4	2.1	1.8	–	–	–	2.9	2.0	1.5	1.8
1.3	1.7	1.1	–	–	–	–	1.6	1.5	1.5
1.2	–	1.1	–	–	–	–	1.5	1.2	1.5
1.2	–	1.1	–	–	–	–	1.4	–	1.4
1.1	–	1.0	–	–	–	–	–	–	1.2
1.1	–	–	–	–	–	–	–	–	1.1

MAT	MAP	Lignin	N	Ca	Mn
1.3	1.4	1.3	1.8	2.4	1.6
1.3	1.4	1.3	–	1.8	1.5
1.2	–	1.2	–	1.5	1.5
1.2	–	–	–	1.3	1.3
1.2	–	–	–	1.3	1.3
1.1	–	–	–	–	1.1

The run using all variables (top) and causal variables only (bottom)

from the model. Thus we may conclude that MAT was not unfavoured by the multicollinearity.

In earlier studies (e.g. Berg et al. 1996; Berg 2000a) N was highly significantly and negatively related to limit values and causal relationships are well established (Hatakka 2001; Nömmik and Vahtras 1982; Piccolo and Spaccini 1999). When we ran model 2 using the causal explanatory variables (Table 5), namely MAT, MAP, lignin, N, Ca, and Mn we found that N was the last to be eliminated. In both cases Mn was selected, being the most influential explanatory variable.

Limit value data from one single Scots pine stand (site no 4)

For this stand with 25 sequences of local and experimental litter the climate variables did not change, although there were variations in weather over the 20-year period during which the decomposition studies were performed. The levels of the limit values estimated by model 1 ranged between 66 and 100%. Further, the soil conditions were constant, which allowed us to focus on the litter-chemistry

Table 7 Estimates and standard errors of regression coefficients and variance components in the final versions of model 2, where $\hat{\sigma}_b^2$ and $\hat{\sigma}_e^2$ are for batches and residuals, respectively.Descriptive correlation coefficient r of the direct estimates of m^* in model 1 and regression estimates of \hat{m} in model 2

Final version of model 2	$\hat{\sigma}_b^2$	$\hat{\sigma}_e^2$	r
Site 4, local and experimental litter, 25 sequences			
All variables and causal variables only—three final variables			
$\hat{m} = 104.7 \quad -2.2N \quad -5.0Ca \quad +19.2Mn$	0	82.4	0.75
$s.e. = 15.4 \quad 1.0 \quad 2.1 \quad 4.5$	–	25.4	
Causal variables only—same result as for all variables			
Site 4, local litter, 17 sequences			
All variables – no final variable			
$\hat{m} = 86.6$	0	91.1	0
$s.e. = 2.3$	–	32.2	
Causal variables only—same result as for all variables			

Site 4 data, in all 25 incubations with 4 pine litter types. All available eight substrate-chemistry variables were tested in one run, WatSol, lignin, N, P, K, Ca, Mg, and Mn. In a second run only recognized causal variables based on causal relationships were used, namely lignin, N, Ca and Mn. Unit for \hat{m} is %

factors. Including all eight litter-chemistry factors the stepwise regression selected Mn ($p = 0.0003$), Ca ($p = 0.023$), and N ($p = 0.043$) (Table 7). These three variables were also selected among the four recognized causal litter-chemistry factors (N, Ca, Mn, lignin). When running data from this stand using only the local litter of different batches and excluding the experimental ones (17 sequences) no litter-chemistry variable became significant.

The multicollinearity as measured by the VIFs was not severe when all 25 sequences were studied. After the first two removals, P and WatSol, the maximum VIF was 6.0. When only the recognized causal variables were included, the maximum VIF in the initial step was 4.2. For the 17 sequences with local Scots pine only, the VIFs were very high at the initial step, in particular for WatSol and lignin. The VIFs decreased considerably after some removals. For the restricted analysis with recognized causal variables only, the VIFs were at most 3.3. The main reasons for not obtaining any significant litter-chemistry variables in this case can probably be attributed to limited ranges in explanatory variables are too homogeneous.

Nutrient concentrations in initial litter versus limit values

The positive relationship between the initial concentration of Mn and the limit value, mostly reached

within 10 years' decomposition for pine needles, is obviously empirical, as is the relationship between N and limit values found in earlier studies combining several litter species (e.g. Berg and McLaugherty 2008; Berg et al. 1996; Berg 2000a). However, for both nutrients there are strong general causal relationships between Mn or N and the microbial degradation of lignin (and lignified tissue) that could explain these empirical relationships (e.g. Eriksson et al. 1990; Hatakka 2001).

For example, the significant ($p = 0.043$) negative relationship between limit values and initial litter N concentrations at site 4 (25 sequences) when experimental litter was included (Table 7) agrees with earlier observations and may be explained by the suppressing effects of N on the ligninase production of the white rots (Eriksson et al. 1990) and/or the chemical reaction of N with organic groups in litter (Nömmik and Vahtras 1982). Piccolo and Spaccini (1999) suggested that such reactions with N compounds result in the formation of hydrophobic compounds that would decrease degradation rates. However, in the present study N was not related to limit values of brown, local litter decomposed at its site of origin, not even when including experimental N-rich litter. Thus, N may simply have a lower influence on limit values than Mn in the specific case of decomposition of local pine needle litter, possibly because the range of initial litter N concentrations

was relatively narrow among substrates (Figs. 3 and 4). In contrast, the negative relationship between N and limit values observed by Berg (2000a) using 106 limit values was based on 21 different litter species/types with a wide range in initial N concentrations (2.9 to 30.7 mg g⁻¹).

The most efficient degraders of lignin and humic acids are wood-rotting or litter-decomposing white-rot fungi (Hintikka 1970; Hatakka 2001). Most of these fungi produce MnP or other peroxidases (Hatakka 1994; Hofrichter 2002). Especially in litter, white-rot is believed to be associated with species producing MnP (Steffen 2003) for the breakdown of humic acids and the formation of fulvic acids (Hintikka 1970). Many species which have been found to produce MnP degrade lignin as well as humic acids (Steffen et al. 2000, 2002; Hatakka 2001), which has been shown in numerous experiments and with the help of synthetic, radioactively labeled lignin or humic acids (Hatakka et al. 1983; Steffen et al. 2000, 2002). Manganese peroxidase has been shown to degrade lignin (Hofrichter et al. 1999a, b, 2001) or humic acids in vitro (Hofrichter and Fritsche 1997; Hofrichter et al. 1998). On the level of litter decomposition Berg et al. (2007) found that for late decomposition stages (lignified tissue) litter Mn concentration was positively related to annual mass loss of the litter.

Higher initial concentrations of Mn resulted in a higher limit value, i.e. less remaining organic matter, which is in agreement with earlier empirical findings (e.g. Berg et al. 1996) based on a data base with litter of several species. The positive relationship between the limit value and the initial concentration of Mn may be a consequence of higher Mn concentrations enabling decomposition.

The formation of a very slowly decomposing fraction may occur when litter approaches its limit value because the remaining Mn at this stage is bound in a form that is relatively unavailable to the decomposer microorganisms. The positive relationship between the limit value and the initial concentration of Mn may be a consequence of that higher Mn concentrations enable decomposition to proceed further before a recalcitrant fraction is developed. The dynamics of total Mn in decomposing foliar litter is variable over litter types (Berg and Cortina 1995; Berg and McLaugherty 2008). However, the dynamics of Mn availability is unknown, but may be related to the initial concentration.

Considering the ranges (Fig. 4) for ‘Gradient all Swedish, local brown Scots pine litter’ (Table 4), initial Mn had a concentration range that was c. four times wider than that of N for the same litter. Thus, the wider range of Mn concentrations may have accounted for its stronger influence compared to N, the range of which was relatively narrow. However, for the study at one site (no. 4), the range factors for Mn and N were similar to those in the gradient with local Scots pine litter (15.0 vs. 19.1 and 3.8 vs. 4.6, resp.). In spite of this no significant effect was seen for Mn when just one site was studied (Table 7). Thus the effect may be related to other factors than ranges in concentration.

The resulting model (Table 3) for ‘All variables’ when all 56 sequences are studied differs from that for local litter only with 46 sequences. In addition to Mn, the first case included K as an explanatory variable, whereas Ca and Mg occurred in the second case. To some extent, this can be explained from Fig. 3 where the range of K becomes much smaller when the experimental litters (filled circles) are removed. The ranges of Ca and Mg are essentially unchanged indicating higher potential to be included in the final model as the chances for K were reduced. The same issue applies to the models in Table 3, where K was included in the final model for 52 sequences but not in the one for 37 sequences (cf. Fig. 4). The weaker significance in the test of Mn in the latter case ($p = 0.019$ vs. $p < 0.0001$) is partly a result of the reduced range of Mn as illustrated in Fig. 4.

So far we have not found any causal relationship in the literature that can explain the empirical relationship between decomposition and K or Mg. When selected (which occurred only when experimental litter was included), these nutrients had weaker significances than Mn. For local brown needle litter only, Mn was the sole significant predictor of limit values.

The backward elimination for site 4 selected Ca as a factor in addition to N and Mn. For brown local litter the Ca range factor was 3.1 and 3.5 for site 4 and the gradient with local pine litter, respectively. However, when including experimental litter it increases to above 28 at site 4. By including experimental litter we increased the range factor for Ca by a factor of 10 as compared to the gradient with local litter, perhaps contributing to its significance at site 4 (Table 7). However, in the analysis using all

data ($n = 56$; Table 3), Ca was not selected, in spite of the same range in concentration. In contrast to the negative effect of Ca in the final models for pine litter, Berg (2000b) found a significant and positive relationship for limit values and Ca concentration for Norway spruce litter and Davey et al. (2007) for a relationship to leaf litter of common oak. Thus, we cannot exclude that an effect of Ca may differ among tree species as indicated by Berg et al. (2007).

Conclusions

We found that for locally collected pine needle litter the Mn concentration has a dominant and positive influence on the limit value, and indeed was the single main factor governing the estimated stable or very slowly decomposing residual amounts of locally collected pine litter. There was a negative relationship between litter Mn concentration and MAT, thus the limit value may in fact decrease with increasing MAT, leaving a higher fraction of recalcitrant pine litter at sites with higher MAT. This was supported by regression analysis without Mn, which resulted in a negative relationship between the limit value and MAT.

For pine litter, its Mn concentration can predict the fraction of extremely slowly decomposing fraction of litter, a fraction that resembles humus. Thus, litter Mn concentration may be used to estimate the accumulation of humus and carbon sequestration from pine litter. To our knowledge, Mn has received little attention in decomposition studies to date. Given its significance in this synthesis, the role of Mn in influencing variation in the late stages of decomposition among ecosystems and among litters of genera other than *Pinus* deserves further attention.

Acknowledgments This work was carried out when Björn Berg was a guest scientist at the Department of Forest Ecology, University of Helsinki, Helsinki, Finland and Dipartimento Biologia Strutturale e Funzionale, Università Federico II, Napoli, Italy. The work by Prof R. C. Björn Berg has been financed by the program “Incentivazione alla mobilità di studiosi stranieri e italiani residenti all’ estero”. We are most grateful to two anonymous referees for very constructive comments.

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