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Litter decomposition rate is dependent on litter Mn concentrations

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Abstract A statistically significant linear relationship was found between annual mass loss of foliar litter in the late stages of decomposition and Mn concentration in the litter. We used existing decomposition data on needle and leaf decomposition of Scots pine (*Pinus sylvestris* L.), lodgepole pine (*Pinus contorta* var. *contorta*), Norway spruce (*Picea abies* (L.) Kars.), silver birch (*Betula pendula* L.), and grey alder (*Alnus incana* L.) from Sweden and Aleppo pine (*Pinus halepensis* Mill.) from Libya, to represent boreal, temperate, and Mediterranean climates. The later the decomposition stage as indicated by higher sulfuric-acid lignin concentrations, the better were the linear relationships between litter mass loss and Mn concentrations. We conclude that Mn concentrations in litter have an influence on litter mass-loss rates in very late decomposition stages (up to 5 years), provided that the litter has high enough Mn concentration. The relationship may be dependent on species as the relationship is stronger with species that take up high enough amounts of Mn.

Keywords Decomposition · Lignin · Manganese · Plant litter

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Introduction

For a given site and climate, one should expect litter mass-loss rate to be related primarily to chemical and physical properties of the litter. Such relationships have been demonstrated in many studies (Fogel and Cromack 1977; McClaugherty et al. 1985; Upadhyay and Singh 1985). As litter decay progresses through time, the constituents regulating mass-loss rate can change (Berg and Staaf 1980). During early stages of decay, concentrations of e.g. N and P (Berg and McClaugherty 2003) control decay rates whereas lignin concentration exerts the dominant control in the later stages. Climate can control the rate at which these decay phases (Berg and Staaf 1980; Berg and Matzner 1997) proceed. Thus in one

climatic regime the early, nutrient-controlled phase, could persist while in other regimes this phase could pass quickly. The climatic effect on early stages of litter decay at regional levels has been clearly demonstrated for Scots pine (*Pinus sylvestris* L.) (Berg et al. 1993a, b). However, in a different study using Scots pine litter, it was found that for later stages of decay climate has little influence on litter mass-loss rates over a region ranging from the Arctic Circle (66° N) to northern Germany (53° N) (Johansson et al. 1995). This suggests that for late stages substrate quality can be the main controlling factor for decomposition rates over sites with very varying climate.

It has been suggested that in late stages the very slow degradation of lignin is rate-retarding. A reason for this is that litter lignin concentration has been negatively related to annual mass loss of litter. A partial explanation for the resistance of lignin to degradation has become clearer in recent years. The 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), produced by the majority of all wood-degrading basidiomycetes which cause white-rot as well as various soil-litter colonizing saprotrophic fungi. Among the ligninolytic enzymes MnP is probably the most widely spread peroxidase produced by these fungi (Hofrichter 2002). Manganese peroxidase is a glycosylated heme protein which is secreted by the fungi into their environment. It oxidizes Mn^{2+} ions, which are found in plant residues, wood and soil, to highly reactive Mn^{3+} ions. These ions in turn are stabilized by organic acids also produced by these fungi. Organic acids such as oxalate or malate, are chelating Mn^{3+} ions and prolonging their life time until they attack the phenolic structure of lignin or humic acids.

Positive relationships between decomposition rates of plant litter and the Mn concentration in litter were seen for decomposing needle litter of Norway spruce (*Picea abies* (L.) Karst.) (Berg et al. 2001) and the connection between lignin degradation and Mn as a limiting resource was reasonable to expect in that case. It is also reasonable to expect that an effect of Mn is not limited to one litter species, although it so far has not been reported for any other litter species.

The objective of this research was to determine a relationship between litter mass loss in the later stages of decomposition as determined by sulfuric-acid lignin concentrations in the litter and litter Mn concentrations. Available data from field mass-loss studies of lodgepole pine (*Pinus contorta* var. *contorta*), Scots pine (*Pinus silvestris* L.), Norway spruce, silver birch (*Betula pendula* L.), and grey alder (*Alnus incana* L.) from Sweden and Aleppo pine (*Pinus halepensis* Mill.) from Libya were used and related.

Materials and methods

Experimental sites and design

All sites at which decomposition studies were carried out had monoculture stands of Norway spruce, Scots pine, Aleppo pine, or lodgepole pine. Vegetation, soils, geographic and climatic characteristics for all sites are summarized in reports (Berg et al. 1991a, 1997a, Faituri 2001). Some a priori restrictions were applied to the site characteristics and at each site the stand used for decomposition studies measured at least ca. 30×30 m (Berg et al. 1993b). The sites were located throughout Sweden with locations ranging from ca. 56° N to ca. 66° N and all litter species were incubated within a region with AET ranging from 425 to 545 mm. The two stands for Aleppo pine were located in northern Libya at 32°49′ N; 21°51′ E at altitudes of 300 and 600 m. Elevation of all sites and associated climatic data are listed in Table 1.

The experimental design was very similar at all sites. Preparation and handling procedures for litter bags and litter samples were standardized as were all subsequent analyses.

Needle and leaf collection, storage, sample preparation and analysis

In each study or each single experiment, one set (ca. 200–400 litter bags) containing leaf litter of Norway spruce, Scots pine, lodgepole pine, grey

Table 1 List of sites in Sweden and Libya used in this investigation, geographic location, tree species, altitude and some climate data

Site name	No.	Lat/long	Alt. (m)	Ann mean precip (mm)	Ann mean temp. (°C)	Tree sp.
Skällarimsheden	106	66°32′ N; 20°11′ E	280	490	– 0.5	Scots pine
Ätnakobbo	109	66°22′ N; 20°02′ E	405	469	– 1.7	Norway spruce
Harads	2	66°08′ N; 20°53′ E	58	650	1.3	Scots pine
Manjärv	3:1	65°47′ N; 20°37′ E	135	516	0.2	Scots pine
Manjärv	3:2	65°47′ N; 20°37′ E	135	516	0.2	Scots pine
Manjärv	3:3	65°47′ N; 20°37′ E	135	516	0.2	Scots pine
Norrliden	4:23	64°21′ N; 19°46′ E	260	595	1.2	Scots pine
Västbyn	108:1	63°13′ N; 14°28′ E	325	460	2.1	Scots pine
Västbyn	108:2	63°13′ N; 14°28′ E	325	460	2.1	Norway spruce
Jädraås	6:51	60°49′ N; 16°01′ E	185	609	3.8	Scots pine
Anundberget	18:2	60°38′ N; 13°37′ E	400	450	2.0	Scots pine
Anundberget	18:1	60°38′ N; 13°37′ E	400	450	2.0	Lodgepole pine
Nyhusen	19:2	60°35′ N; 13°34′ E	435	450	1.8	Scots pine
Nyhusen	19:1	60°35′ N; 13°34′ E	435	450	1.8	Lodgepole pine
Kappsjön	17:2	60°33′ N; 13°44′ E	375	450	2.8	Scots pine
Kappsjön	17:1	60°33′ N; 13°44′ E	375	450	2.8	Lodgepole pine
Stråsan	5	60°55′ N; 16°01′ E	350	745	3.1	Norway spruce
Hässlen	111:2	60°16′ N; 16°15′ E	185	425	4.2	Norway spruce
Hässlen	111:3	60°16′ N; 16°15′ E	185	425	4.2	Silver birch
Tomta	103:1	59°49′ N; 16°33′ E	63	550	5.1	Scots pine
Tomta	103:2	59°49′ N; 16°33′ E	63	550	5.1	Norway spruce
Grythyttan	20:1	59°44′ N; 14°33′ E	220	475	5.4	Scots pine
Grythyttan	20:2	59°44′ N; 14°33′ E	220	475	5.4	Lodgepole pine
Kungs-Husby	102:1	59°31′ N; 17°16′ E	30	470	5.2	Scots pine
Kungs-Husby	102:2	59°31′ N; 17°16′ E	30	470	5.2	Norway spruce
Dimbo	100:1	59°07′ N; 15°44′ E	70	560	5.5	Scots pine
Dimbo	100:2	59°07′ N; 15°44′ E	70	560	5.5	Norway spruce
Grensholm	101:1	58°33′ N; 15°51′ E	58	520	6.1	Scots pine
Grensholm	101:2	58°33′ N; 15°51′ E	58	520	6.1	Norway spruce
Remningstorp	105:1	58°28′ N; 13°39′ E	128	530	5.6	Scots pine
Remningstorp	105:2	58°28′ N; 13°39′ E	128	530	5.6	Norway spruce
Tveten	104:1	58°06′ N; 13°17′ E	170	675	5.5	Scots pine
Tveten	104:2	58°06′ N; 13°17′ E	170	675	5.5	Norway spruce
Sänksjön	107	58°04′ N; 14°08′ E	245	595	5.1	Scots pine
Tönnersjöheden	113:1	56°42′ N; 13°05′ E	80	870	7.2	Norway spruce
Tönnersjöheden	113:2	56°42′ N; 13°05′ E	80	870	7.2	Silver birch
Mästocka	10:1	56°36′ N; 13°15′ E	135	1070	6.8	Scots pine
Mästocka	10:2	56°36′ N; 13°15′ E	135	1070	6.8	Norway spruce
Farabol	114	56°26′ N; 14°35′ E	140	660	5.7	Norway spruce
Shahat[a]		32°49′ N, 21°51′ E	600	200–600	16–18	Aleppo pine
Shahat[a]		32°49′ N, 21°51′ E	300	200–600	16–18	Aleppo pine

Site data is taken from Berg et al. (1997a) and from Faituri (2001). The site numbers and names used occur in other publications

[a] For annual average temperature and annual precipitation only data on ranges were found

alder or silver birch were incubated at sites over Sweden. The litter from each stand in two climatic transects (Scots pine and Norway spruce) (Table 1) was collected in the autumn. At site Jädraås experimental needle litter of lodgepole pine and leaf litter of grey alder as well as silver birch was incubated. At this site we also used 'local' litter collected and incubated at the site. The local litter of Aleppo pine was incubated in monoculture stands.

Litter was collected by gently shaking the limbs of the trees at time of litter fall and collecting the needles on spread-out tarpaulins. Green needles were removed by hand.

Litter was air-dried and stored dry at room temperature. Before weighing, the needles were equilibrated to a constant moisture level (5–8 ± 0.5%) by drying them at room temperature for ca. 1 month. Litterbags, measuring 8 × 8 cm, with an 1-cm wide edge around were made of polyester net with a mesh size of about 1.0 × 0.5 mm. We placed 0.6 – 1.0 g of needles in each litter bag. The bags were placed on the litter (L) layer in 20 or 25 randomly located 1 × 1 m measurement spots within each plot. In each such spot, 10–14 bags were fastened to the ground by 10–15 cm long metal pegs of stainless steel using the edge of the bags. Retrieval of litter bags took place one to six times annually for up to 5 years. On each occasion, one litterbag was collected from each of the 20 or 25 spots.

Determination of mass loss

After collection and drying, the litterbag samples of each type were cleaned by removing plant remains, such as mosses, grass, and shrub materials. Dry mass loss was determined by drying the samples to a constant mass at 85°C. Mass loss was averaged for each set of sampled bags and mass-loss rates were calculated on an annual basis. For annual mass-loss in the 2nd through the 5th years we used the average remaining amount after the preceding year as a basis for calculating the decomposition.

Lignin analysis

The amount of water-soluble substances was determined and removed by sonicating the ground samples three times and weighing the samples after filtration and drying. The ethanol-soluble substances were removed. The analyses for sulfuric-acid (Klason) lignin and soluble substances were carried out according to Bethge et al. (1971) (see also Berg et al. 1982) on composite samples.

Nutrients

The milled samples were analyzed for total contents of the elements N and Mn and in some cases total ash.

All local litter (except for that from site Stråsan) was analyzed as follows: After a wet oxidation in H_2SO_4, total N was analyzed using a semi-micro Kjeldahl procedure (Nihlgård 1972). Manganese was determined by atomic absorbtion spectrometry (Perkin-Elmer 603) against acid standard (Pawluk 1967). Local litter from site Stråsan and that incubated at site Jädraås were analyzed as follows; Nitrogen was determined by combustion (Elemental Analyzer NA 1500; Carlo Erba, Strumentazione, I-20090 Rodano, Milan, Italy). For the analysis of Mn, samples were digested for 2 days in a 2.5:1 (v/v) mixture of nitric and perchloric acid and analyzed using plasma atomic emission spectrometry ICP-AES (Jobin YVON JY-70 Plus 16–18, rue du Canal, F-91163, Longjumean, France). In all cases ash concentration was determined by combustion at 550°C for 2 h.

Data on litter chemical composition, litter mass loss, chemical changes as well as restrictions placed on the data

In this paper, we have used data on litter originating from different experiments and only litter that has decomposed to the late stages (Berg and McClaugherty 2003; Berg and Matzner 1997). In this context the late stage was identified as that reached by litter decomposing for more than a year. Decomposition data were taken from Berg et al. (1991b, 2000), Faituri (2001), Berg and Ekbohm (1991) and Berg and Lundmark (1987). Data from site Stråsan were published by Berg and Tamm (1991).

As we used annual mass-loss values to compare mass loss with climatic and substrate-quality variables we set restrictions on sampling time and allowed only data from litter sampled at intervals of 365 days ± 15 days to be used.

All litter investigated was analyzed for sulfuric-acid lignin. As litter decomposes lignin concentrations increase normally in proportion to the accumulated mass loss. We have used this property to separate classes of litter as indexed by lignin concentration; the higher the lignin concentration the more decomposed is the litter.

Statistical analysis

We used linear regression analysis and to compare the coefficient of determination among sets with different numbers of samples we have used the adjusted R^2 (R^2_{adj}). It has been shown by Ekbohm and Rydin (1990) that mean square error and R^2_{adj} are equivalent as criteria of goodness of fit. We have used the formula $R^2_{adj} = 1 - (1 - r^2)(n - 1)/(n - p)$ where p equals 2 for straight lines.

Terminology

We have analyzed for sulfuric-acid lignin but in the text of the paper we use the word lignin for the sake of simplicity.

Results

The available data

We used a set of decomposition data from Norway spruce, Scots pine, lodgepole pine, Aleppo pine, silver birch, and grey alder. All data were taken from litter that clearly was in a late stage of decomposition, i.e. data for litter for the 2nd, 3rd, 4th and 5th years of decomposition. In all we had 136 values of which 32 were for Scots pine, 75 of Norway spruce, 16 of lodgepole pine, 4 of Aleppo pine, 6 of silver birch, and 3 of grey alder. We used the concentrations of nutrients and lignin at the start of each 1-year period. The concentrations of Mn in litter at the start of each period ranged from 0.04 to 7.69 mg g^{-1} and for lignin from 277 to 509 mg g^{-1}, thus with range factors of 192 and 1.8, respectively.

Most of the litter had Mn concentrations below 2 mg g^{-1} (Fig. 1) and included mainly litter of pine species, birch and alder. Most of the litter with Mn concentrations above 2 mg g^{-1} was Norway spruce.

Relationships using all available data

In a first step we regressed all the annual mass loss values to the litter lignin concentration which resulted in a negative linear relationship ($R^2 = 0.210$; $P < 0.001$). We may thus see that for all litter combined, a negative relationship was seen between lignin concentrations and litter mass loss. In a second step we regressed all annual mass-loss values to litter Mn concentration at the start of each year. All available data ($n = 136$) gave a positive linear relationship ($R^2 = 0.151$; $P < 0.001$; Fig. 1; Table 2). We may note that the data did not have a normal distribution as the main part was located below an Mn concentration of 2.0 mg g^{-1}. A logarithmic transformation gave R^2 values of 0.201 and 0.150, respectively, for lignin and Mn concentrations, both highly significant

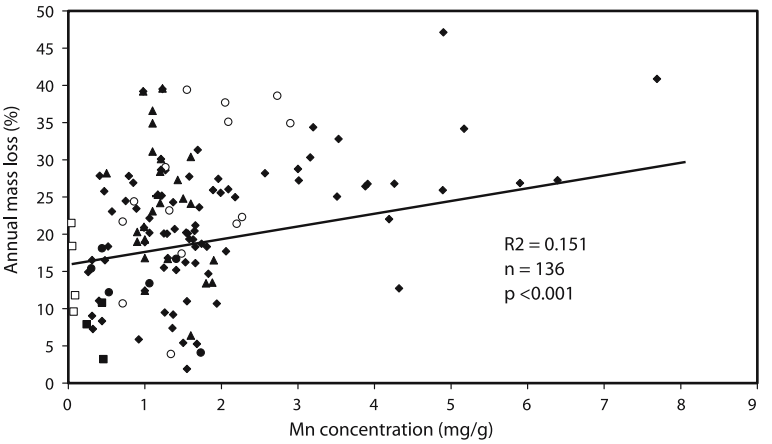

Fig. 1 Relationship between annual mass loss in late stages of decomposition of Norway spruce, lodgepole pine, Scots and Aleppo pine, silver birch, grey alder foliage litter and its Mn concentration at the start of each year. Data from 40 sites in Sweden and two sites in northern Libya. (◆) Norway spruce, (▲) Scots pine, (○) lodgepole pine, (□) Aleppo pine (●) silver birch, (■) grey alder

Table 2 Relationships between annual mass loss and concentration of manganese and lignin in decomposing litter in the late stage. Regressions were made using a progressively more narrow interval in lignin concentrations

Lignin conc. range (mg g^{-1})	Mn			Lignin			*n*	Mn conc. range (mg g^{-1})
	R^2	R^2_{adj}	$P <$	R^2	R^2_{adj}	$P <$		
All available data								
277–509	0.151	0.145	0.001	0.206	0.200	0.001	136	0.04–7.69
> 350	0.182	0.175	0.001	0.138	0.130	0.001	115	0.04–7.69
> 400	0.215	0.206	0.001	0.059	0.049	0.05	94	0.24–7.69
> 450	0.360	0.349	0.001	0.005	–	ns	62	0.24–7.69
> 475	0.457	0.441	0.001	0.002	–	ns	35	0.24–7.69
Norway spruce data only								
> 475	0.671	0.653	0.001	0.059	0.001	ns	20	0.31–7.69
Data for Scots pine, lodgepole pine, grey alder, and silver birch								
> 475	0.115	0.031	ns	0.011	–	ns	15	0.24–1.90

As the lignin concentrations increase with increasing accumulated mass loss, lignin concentrations index the decomposition level of the litter

($P < 0.001$). The relationship improved when Mn and lignin concentrations were combined in a multiple regression ($R^2 = 0.349$; $P < 0.001$).

Relationships using different species

We subdivided the data set and investigated the three dominant litter species (Norway spruce, lodgepole pine and Scots pine) separately.

Norway spruce needle litter

Using Norway spruce needle litter only, we regressed lignin concentration versus litter mass loss, which gave a negative linear relationship with $R^2 = 0.121$; $P < 0.01$). In a logarithmic transformation we obtained an R^2 of 0.149 ($P < 0.001$). We then regressed concentrations of Mn against litter mass loss ($R^2 = 0.294$; $n = 74$; $P < 0.001$) (Fig. 2) with an Mn concentration range of 0.24–7.69 mg g^{-1}, a range factor of 32. As data did not have a normal distribution we made a logarithmic transformation which gave a highly significant relationship ($R^2 = 0.198$; $n = 74$; $P < 0.001$). A multiple linear regression with both Mn and lignin resulted in an R^2 value of 0.423 ($n = 74$; $P < 0.001$).

Lodgepole pine litter

A smaller data set for lodgepole pine needle litter was investigated. Litter mass loss and lignin concentrations were negatively correlated ($R^2 = 0.491$; $P < 0.01$). A linear regression between Mn concentration (range 0.71–2.7 mg g^{-1}, range factor 3.8) and annual litter mass loss was not significant ($R^2 = 0.290$, $n = 10$) (Table 3). Lignin and Mn combined in a linear regression improved the R^2 to 0.726 ($P < 0.01$). The two stands where this litter was incubated were very similar and both had monocultures of lodgepole pine. We included six values from an experiment in which lodgepole pine needles had been incubated in a stand with Scots pine (site Jädraås; Table 1). These new relationships (n=16) were significant. For Mn R^2 was 0.281 ($P < 0.05$) and for Mn and lignin combined, R^2 was 0.455 ($P < 0.01$) (Table 3).

Scots pine needle litter

When using all data for Scots pine a highly significant and negative relationship to lignin concentrations was found ($R^2 = 0.436$; $n = 32$; $P < 0.001$). A regression between mass loss and Mn concentrations with a range of 0.5–1.9 mg g^{-1} gave no relationship ($R^2 = 0.087$; $n = 32$; ns).

All species combined but different concentration intervals for lignin and for Mn

As decomposition proceeds the lignin concentrations increase in a very regular way (Berg et al. 1997; Berg and McClaugherty 2003) and the

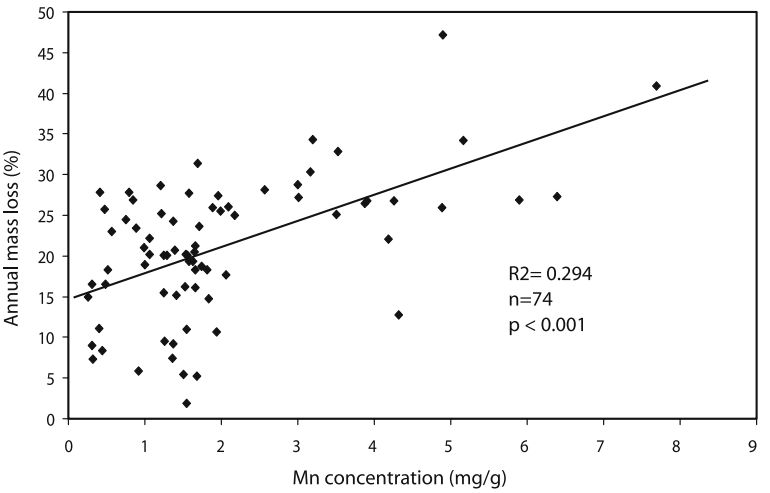

Fig. 2 Relationship between annual mass loss of Norway spruce needle litter in late stages of decomposition and litter Mn concentration

Table 3 Relationships between annual litter mass loss and litter Mn and lignin concentrations at the start of each year

	R^2	R^2_{adj}	n	$P <$
Lodgepole pine (two similar sites)				
Mn	0.290	–	10	n.s.
Lignin	0.491	0.427	10	0.05
Mn + lignin	0.726	0.692	10	0.01
All lodgepole pine data (three sites)				
Mn	0.281	0.230	16	0.05
Lignin	0.424	0.383	16	0.01
Mn + lignin	0.455	0.416	16	0.01

Two data sets were investigated: (i) lodgepole pine needle litter from two nearby and very similar sites (Anundberget and Kappsjön, n = 10, Table 1) and (ii) litter incubated at the two above sites plus litter incubated at site Jädraås (n = 16). The Mn concentration range was 0.71–2.9 mg g^{-1}

increasing lignin level thus reflects the stage of decomposition. Using the whole data set we identified different intervals for lignin concentration, stepwise removing the lower ones. This means that the higher concentrations we selected also indicated further decomposed litter material. The reason behind this stepwise selection was simply that an increasing part of the mass loss would be due to lignin degradation. Further, we considered the possibility that the population of fungi may be increasingly a lignolytic one as decomposition proceeded. With one exception, our data originated from climatic transects across Sweden, with a temperature range from – 0.7 to 7.8°C and precipitation ranging from 410 to 1070 mm (AET 371 to 520 mm). It has been shown (Scots pine) that the effects of climate on decomposition rate decrease as litter becomes more decomposed (Johansson et al. 1995). For Norway spruce needle litter in the same climate transect, Berg et al. (2000) did not see any effect of climate on decomposition rate, not even for newly shed litter (1st year decomposition).

All data, with lignin concentrations ranging from 277 to 509 mg g^{-1} gave a significant relationship (R^2 = 0.206; P < 0.001) as did Mn concentrations (R^2 = 0.151; P < 0.001) (Table 2). By stepwise selecting data in an interval with higher and narrower lignin concentrations we progressively obtained a data set representing a more decomposed litter. We may see (Table 2) that the narrower the lignin concentration interval was, the more the relationship to Mn improved (R^2_{adj} increased). At a lignin concentration interval of 475–509 mg g^{-1} the R^2 value for the relationship between litter mass loss and Mn concentrations was 0.457 whereas the relationship for the influence of lignin was insignificant due to the narrow concentration range. This

reduced data set (n = 35) encompassed 9 values for Scots pine, 1 for lodgepole pine, 20 for Norway spruce, 3 for grey alder and 2 for silver birch. We divided this data set (n = 35) into two main groups, one for Norway spruce litter (Mn concentration range from 0.31 to 7.69 mg g^{-1}) and one for the other litter types combined with an Mn concentration range from 0.24 to 1.9 mg g^{-1}. For Norway spruce needle litter the relationship between Mn concentration and annual mass loss became an R^2 of 0.671 (R^2_{adj} = 0.653) with n = 20 and for the other, combined litter types 0.109 (R^2_{adj} = 0.028; n = 15; ns). For this reduced data set with lignin concentrations > 475 mg g^{-1} we may see that all data basically fit to the linear relationship. The main difference between the groups appears to be that the Norway spruce litter had a wider concentration interval with a range factor of 24.8 whereas that for the other litter types was considerably more narrow with a range factor of 7.9. (Fig. 3)

We made a subdivision of the whole data set (n = 136) and investigated the litter with Mn concentrations below and above 2 mg g^{-1} separately. Using an Mn concentration interval of 0.04–2.0 mg g^{-1} we could not find any relationship between litter Mn concentration and litter mass loss in spite of range factor of 50. When investigating data with Mn concentrations below 2 mg g^{-1} for relationships between lignin concentration and litter mass loss we obtained a highly significant relationship (R^2 = 0.410; n = 81; P < 0.001). For the concentration range above 2 mg g^{-1} with a range factor of ca. 5.5 (n = 27) we found no relationship.

Discussion

The most efficient degraders of lignin and humic acids are wood-rotting or litter-decomposing fungi which produce white-rot in wood or litter (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) and the decolorization is due to the breakdown of humic acids and the formation of light colored fulvic acids (Hintikka 1970). Many species which have been found to produce MnP are degrading 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 itself has been shown to be able to degrade lignin (Wariishi et al. 1991; Hofrichter et al. 1999a, 1999b, 2001) or humic acids in vitro (Hofrichter and Fritsche 1997, Hofrichter et al. 1998).

We used the different concentration intervals for lignin for different reasons. The further the litter is decomposed the higher the lignin concentration. In fact lignin concentration increases linearly relative to accumulated litter mass loss until it reaches a rather constant level somewhere around or above 50% (e.g. Berg and McClaugherty 2003). By selecting a stepwise narrower interval for lignin concentrations we also analyzed rate-limiting factors in more far-decom-

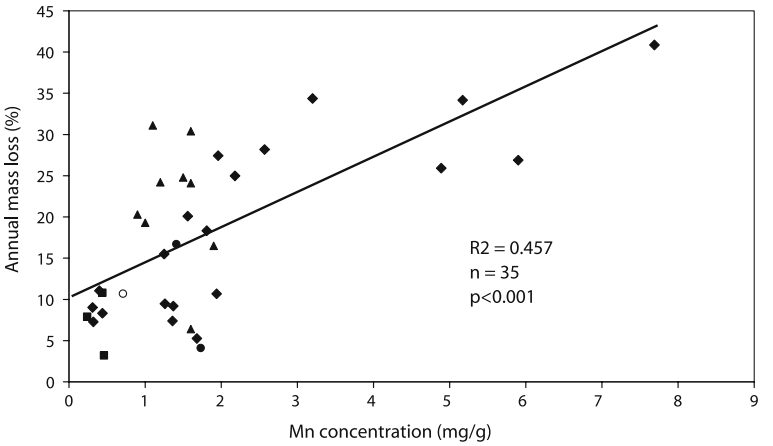

Fig. 3 Relationship between annual mass loss of foliar litter in late stages of decomposition and foliar litter Mn concentrations. The data set was limited to decomposition stages with lignin concentrations above 475 mg g^{-1} including values (◆) for Norway spruce, (▲) Scots pine, (○) lodgepole pine, (●) silver birch, (■) grey alder (cf. Table 3).

posed litter and we can investigate when in the decomposition process the Mn concentration may become important. During this approach we also found that narrowing the interval for lignin concentration the Mn concentration interval remained about the same. This indicates that the further the decomposition had proceeded the better was the relationship to litter Mn concentrations (Table 2).

The significant relationships between annual mass loss and Mn concentration are dependent on both litter species and Mn concentration intervals. Thus for Norway spruce and lodgepole pine litter the Mn concentration intervals were 0.26–7.69 mg g^{-1} and 0.71–2.9 mg g^{-1}, respectively, both with significant relationships. No significant relationship was found for Scots pine needles (concentration range from 0.5 to 1.9 mg g^{-1}), which also was found for more decomposed litter.

We may speculate about a concept found for pure cultures of fungi with MnP. Results obtained from decomposition experiments carried out in the laboratory using pure cultures of the wood decomposer *Pleurotus ostreatus* demonstrated that the loss of dry mass was significantly higher in straw cultures containing 1–10 mM Mn compared to controls (Baldrian et al. 2005). The degradation of straw and its phenolic compounds was also considerably faster in the presence of Mn. Though MnP and H_2O_2 levels have been reported low in these systems containing Mn it cannot be clearly correlated with substantial degradation of lignin (Eichlerova et al. 2000). In fact, the availability of Mn as well as H_2O_2 is probably the most important factor in the degradation process. Only one-third of the total Mn was actually available to fungi in straw cultures (Baldrian et al. 2005). With Mn levels of 10–50 μg g^{-1} for example in birchwood or straw, as little as 3μg g^{-1} would be available and poses thus a limitation to MnP efficiency. A liberation of Mn or higher amounts of available Mn could therefore considerably increase the degradation of litter.

We can of course not directly transfer an observation in a pure laboratory culture to ones made in natural soil systems. Still, we may speculate that if a certain fraction of the Mn bound in litter is biologically available there may be a critical concentration of Mn that is readily available to the microbial community in the litter. Such a possibility may explain the lack of relationship at the Mn levels (below 2 mg g^{-1}) and may mean that a degrading population less dependent on Mn is more active or dominates the decomposition

Conclusions

Manganese concentrations in litter may influence litter mass-loss rates in very late decomposition stages, provided that the litter has high enough Mn concentration. The relationship may be dependent on species as the tree species must have the ability to take up high amounts of Mn.

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