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Metal distribution across different pools in the organic layer of a forest under acid deposition and its consequences for the metal dynamics

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Abstract

Acid atmospheric deposition can cause losses of metal nutrients from the organic layer of a soil. The size of these losses depend on the sizes of the different pools in which the metals are present, as these pools differ in mobility. The metal pools in an organic soil layer of a Douglas fir forest in the Netherlands subjected to acid deposition were determined by means of extractions and percolations. Na was mainly dissolved and exchangeably adsorbed, K dissolved, exchangeably adsorbed and present in the soil microbial biomass, Ca exchangeably adsorbed and present in organic precipitates, Mg exchangeably adsorbed and present in the soil biomass, and Mn exchangeably adsorbed and present in inorganic precipitates. The main part of the metals was exchangeably adsorbed. The adsorption affinity increased in the order Na < K < Mg < Mn $\approx$ Ca. The vertical distribution of the metals in the organic layer showed that all metals were continuously lost from the organic layer. The differences between the metals in retention and vertical distribution patterns were in agreement with their differences in deposition rate, pool distribution, and exchange affinity. Since the metals were mainly exchangeably adsorbed, and the acidifying cations dominated the atmospheric deposition, acid deposition and cation exchange must be processes that strongly affect the losses of metals from this organic soil layer.

Introduction

Forests on acid, sandy soils in the centre and southeast of the Netherlands are seriously affected by acid atmospheric deposition (Van Breemen and Verstraten, 1991). The mineral soil layer of these forests is covered by a mor- or moder-like layer of organic material, the so called ectorganic layer (Klinka et al., 1981). This layer contains a major part of the metal nutrients present in these nutrient-poor soils. Acid deposition has a substantial influence on the dynamics of these metals: an important threat is their increased loss from the system (Cronan et al., 1978; James and Riha, 1986; Stuanes, 1980), leading to soil acidification (Verstraten et al., 1990), and nutrient shortages for the vegetation (Roelofs et al., 1985).

Metal dynamics in organic matter has been studied by means of litterbag experiments (e.g. Bockheim et al., 1991; Gosz et al., 1973; Hågvar and Kjøndal, 1981; Staaf and Berg, 1982; Van Wesemael, 1993), and also lysimeter experiments (Cronan, 1980; Joergensen and Meyer, 1990; Lee and Weber, 1982, 1983). Differences in dynamics between the metals have been explained by assuming that the metals were distributed across several different pools: dissolved, exchangeably adsorbed, incorporated in organic compounds, immobilized by the soil biomass and precipitated in inorganic solids (Gosz et al., 1973; Lawrey, 1978; Lousier and Parkinson, 1978; Staaf and Berg, 1982). As these pools differ in mobility, the distribution between these pools must be an important factor influencing the metal dynamics. However, because these pools have not been measured, interpretation remains difficult (Lousier and Parkinson, 1978).

The objective of the present research was to determine the size of these metal pools in the ectorganic horizons of a Dutch Douglas fir forest under acid deposition, and to identify the main processes responsible

Table 1. Amounts of cations deposited on the forest floor in Speuld; average of 3 years (Van Der Maas, 1990)

Cation	Throughfall mmol m^{-2} a^{-1}	Cation	Throughfall mmol m^{-2} a^{-1}
Na	92.9	Mn	2.9
K	48.1	H	7.3
Ca	20.8	NH$_4$	217.9
Mg	16.2		

for the metal dynamics in the ectorganic layer. Batch exchange experiments were carried out to determine water-soluble and exchangeably adsorbed fractions. Furthermore, reconstituted columns of the ectorganic material were percolated with acid and ammonium sulphate removing all mobile metals. With the results obtained the metal dynamics in a litterbag experiment in the same forest were interpreted, as well as the metal concentrations in the ectorganic horizons. The possible role of acid deposition in the metal dynamics was discussed.

Materials and methods

Site description

Experiments were carried out with the ectorganic layer of a forest located near Speuld in the Veluwe region in the central part of the Netherlands;. This forest is a monoculture Douglas fir stand (*Pseudotsuga menziesii* (Mirb.) Franco) without any undergrowth, planted in 1962. The soil is a Haplic Podzol (FAO, 1988), well-drained, acid, and with a sandy texture. The transition between the L and the F horizon is indistinct, and there is no H horizon; the thickness of the ectorganic layer varies between 3 and 8 cm. The transition between the ectorganic layer and the mineral soil is abrupt.

The site was one of the study sites of the Dutch acidification programme (Van Breemen and Verstraten, 1991). The large acidifying deposition on this forest consists mainly of ammonium sulphate (Table 1). Despite the large NH$_4^+$ input, this cation is only moderately present on the exchange complex (Table 2) due to NH$_4^+$ immobilization and nitrification (Tietema et al., 1993). Both these N transformation processes generate

H$^+$, which, as a consequence, is the dominant cation in the organic soil layer.

Experiments

The material for the batch extractions and column percolation experiments was sampled in June 1990 by collecting one square metre of forest floor in several horizons. The two upper horizons (LF1 and F2) were separated on the basis of macromorphological differences in the degree of decomposition. The remainder, which was over 2/3 of the total mass of the ectorganic layer, was divided in an upper part (F31) and a lower part (F32) of approximately the same mass. Large twigs, cones, and roots were removed and each separate horizon was mixed by hand and stored field-moist at 2°C. Dry mass at 70°C and ash content at 500°C were determined on sub-samples of each horizon. Some general characteristics of the horizons are presented in Table 2.

To measure water-soluble and exchangeable cations of this material, aqueous, BaCl$_2$, and HCl extractions were carried out a few days after sampling. Field-moist, organic material equal to 6 g dry mass was weighed into a polyethylene bottle. Demineralized water and a concentrated solution of the salt or the acid were added, in order to obtain a solid : water ratio of 1 : 25. In the BaCl$_2$ extracts the concentration was 0.125 M BaCl$_2$, and in the HCl extracts 7.3 mM HCl. The bottles were shaken for 2 hours and subsequently filtered over a 0.2 μm membrane filter. The pH in the filtrate was determined potentiometrically and metal cations were determined by atomic absorption/emission spectrophotometry.

The sampled material was also used for three percolation experiments of reconstituted columns. For each of these experiments material from the different horizons was stacked in a plexiglass cylinder 12 cm in diameter in such a way that the dry mass per area was the same as that in the field. The horizons were separated by polythene netting (mesh size 2 mm) to allow separate analysis of each horizon at the end of the experiment.The column was mounted on a ceramic suction plate; suction was applied by means of a drainage tube with a length of 1 to 1.5 m suspended from the plate. Simulated rainfall was applied with either a 10^{-2} M HCl or a 10^{-3} M HCl or a 10^{-2} M (NH$_4$)$_2$SO$_4$ (pH 5.38) solution. The flux was 400 cm^3 per day (35 mm day^{-1}) in all experiments. Each experiment was carried out in duplicate. The pH and metal concentrations were determined in the percolates. The

Table 2. Some characteristics of the organic horizons of the Speuld Douglas fir forest as used in the experiments

Horizon	Dry mass	Ash content	CEC_{eff}	Exchangeable NH_4^+
	$kg\ m^{-2}$	$g\ kg^{-1}$ dry mass	$mmol_c\ kg^{-1}$	$mmol\ kg^{-1}$
LF1	0.39	44.3	217	21.6
F2	0.57	55.0	222	20.7
F31	1.22	140	209	10.9
F32	1.05	248	209	9.87

experiments were stopped after 7 [10^{-2} M HCl], 46 [10^{-3} M HCl], and 35 [$(NH_4)_2SO_4$] days respectively. At those dates the pH values of the percolates had become constant - 2.0, 3.0 and 3.86 respectively - and the concentrations of the metal cations had become very small and were continuing to decline. The horizons were then separated and their wet and dry (70°C) mass were determined.

Total amounts of cations in the untreated and in the percolated organic material were determined by digesting 0.25 g of the dried (70°C) and ground (0.5 mm) samples with a 4:1 (v/v) mixture of concentrated HNO_3 and HCl in a microwave oven (Bettinelli et al., 1989). Total K, Na, Ca, Mg and Mn were determined by atomic absorption/emission spectrophotometry.

Losses from the percolated material were calculated as the differences between untreated samples and the percolated samples. Some decomposition of the organic material occurred during the percolation experiments, as indicated by the fact that the mass of the horizons, corrected for the loss of leached elements, decreased. In order to be able to compare the cation contents all results were recalculated to mmol per kilogram original dry mass, i.e. at the time of sampling.

A litterbag experiment was carried out in this forest as described by Tietema (1993). The experiment started in December 1986. Litterbags of 20×20 cm (0.6 mm mesh) containing 5.0 g of air-dried needles shaken from the trees were placed in 5 subplots (6-8 m²). From each of the five subplots one randomly chosen litterbag was collected after 0, 1.5, 3, 6, 9, 12 and 15 months incubation. The contents of the sampled litterbags were dried at 70°C until constant weight was reached to determine the remaining mass. After grinding, total cation (Na, K, Ca, Mg and Mn) concentrations in the contents of each individual litterbag were determined.

The ectorganic horizons contained only a minor amount of ash; therefore, contamination with mineral soil was very limited. As the sandy soil is very poor in exchangeable base cations (CEC of the Ah horizon: 75-100 $mmol_c$ kg^{-1} with a base saturation of < 0.1%; Tiktak et al., 1988), contribution from this source to the cations in the L and F horizons was negligible. Although the mineral part of the soil contains substantial amounts of Na, K and Mg in non-exchangeable form (Tiktak et al., 1988), it was assumed that these were not to be taken into account because they are not dissolved by the HCl / HNO_3 digestion. This assumption was confirmed by the fact that the yield of Na in this digestion did not exceed the yield of Na in the $BaCl_2$ extraction.

Results

Sodium

The total concentrations of Na in the ectorganic horizons were small compared to most other metals (Table 3). Na was the only metal cation with a similar concentration in all ectorganic horizons. In contrast to the other cations the percentage of water-extractable Na was large. The $BaCl_2$, and 7.3 mM HCl extractions completely removed all the Na from the organic material. As it is impossible that Na measured in the $BaCl_2$ and HCl extractions is not measured in the HNO_3/HCl digestion, the values exceeding 100% must be artifacts. Since the total concentrations were determined on a single sample of about 0.25 g, while 6 g was used for the extractions, the total concentrations are less reliable. The percolations also removed almost all Na from the material. Values did not completely reach 100%, as the amount of Na measured in the percolated

Table 3. Total content of metal cations in the organic horizons, and fractions removed by various extractions and percolations (averages of two replicates; values between parentheses are differences between averages and observations)

Cation	Horizon	Total content	Batch extractions			Percolations		
			Aqueous	BaCl$_2$ (0.125 M)	HCl (7.3×10^{-3}M)	HCl (10^{-2}M)	HCl (10^{-3}M)	(NH$_4$)$_2$SO$_4$ (10$^{-3}M^a$)
		mmol kg^{-1}	% removed	% removed	% removed[b]	% removed	% removed	% removed
Na	LF1	5.8	73. (6)	108. (11)	114.	91. [b]	73. (15)	91. (7)
	F2	5.3	59. (3)	107. (0.16)	97.	89. (1.2)	98. (1.6)	78. (1.8)
	F31	4.5	68. (4)	124. (3)	103.	91. (8)	86. (14)	98. (2.3)
	F32	5.1	64. (2.5)	118. (3)	107.	94. (2.1)	94. (6)	98. (2.4)
K	LF1	29.2	18. (0.4)	53. (0.5)	54	78. [b]	74. (1.6)	74. (0.3)
	F2	19.7	11. (0.3)	47. (0.16)	45.	66. (1.2)	63. (1.7)	68. (1.7)
	F31	11.4	9. (0.4)	38. (0.4)	34.	46. (1.6)	34. (7)	44. (0.7)
	F32	10.1	10. (1.1)	28. (0.00)	27.	26. (0.8)	22. (4)	37. (6)
Ca	LF1	100	1.7 (0.01)	62. (0.9)	37.	97. [b]	95. (0.7)	83. (0.6)
	F2	73.1	0.6 (0.03)	82. (1.2)	45.	96. (1.1)	92. (0.3)	83. (1.5)
	F31	40.5	0.4 (0.07)	96. (0.13)	50.	92. (2.3)	67. (7)	68. (0.3)
	F32	37.3	0.9 (0.17)	98. (0.09)	50.	92. (1.8)	62. (3)	63. (1.4)
Mg	LF1	29.5	2.1 (0.02)	67. (0.4)	55.	86. [b]	90. (0.8)	87. (0.1)
	F2	19.7	0.8 (0.04)	76. (1.7)	58.	81. (0.3)	81. (0.3)	79. (1.2)
	F31	12.8	0.7 (0.08)	68. (0.10)	49.	67. (1.8)	62. (2.1)	62. (0.7)
	F32	12.0	1.0 (0.20)	65. (0.20)	47.	63. (1.1)	56. (1.0)	60. (1.3)
Mn	LF1	10.8	1.5 (0.04)	61. (0.4)	48.	91. [b]	94. (0.7)	38. (1.1)
	F2	7.14	0.5 (0.00)	72. (2.5)	47.	96. (0.7)	82. (1.2)	80. (1.0)
	F31	2.42	0.6 (0.00)	88. (0.4)	58.	82. (4)	53. (3)	79. (5)
	F32	2.25	0.7 (0.10)	86. (0.01)	60.	86. (1.9)	44. (0.4)	68. (1.6)

[a] pH Input 5.38, final percolate 3.86.

[b] Only one replicate available.

material is always somewhat above zero. In the litterbags Na had the smallest initial concentration of all cations and after a few months its concentration was even smaller (Fig.1).

Potassium

Total K concentration in the ectorganic horizons decreased with depth from 29.2 mmol kg^{-1} in the LF1 to 10.1 in the F32. The sizes of the water-extractable fractions of K were intermediate between Na and the divalent cations. The fractions extracted with BaCl$_2$ were the smallest of all cations, and decreased with depth; the yields of the extractions with 7.3 mM HCl equalled those with BaCl$_2$. In the three percolations

similar fractions of the total K were removed; in the two upper horizons these slightly exceeded the BaCl$_2$ extraction results, but in the two lower horizons all results were comparable. In the litterbags the K concentration initially decreased rapidly, after which it remained constant (Fig.1).

Calcium

The total Ca concentration in the ectorganic horizons showed a relative decrease with depth similar to the one found for K. Only about 1% of the Ca was water-extractable. Ca was completely extracted with BaCl$_2$ in the two lower horizons, but in the two upper horizons only a part could be extracted. Less Ca could be
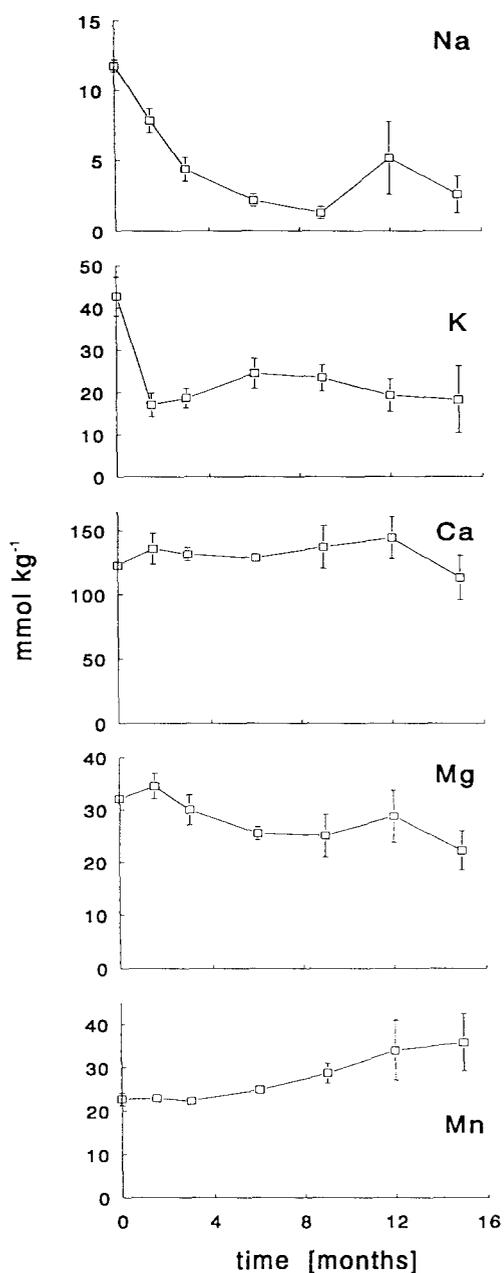
Fig. 1. Changes in metal concentrations in decomposing Douglas fir needles in Speuld, determined by means of litterbags; datapoints are mean of five litterbags; bars indicate standard deviations

well. In the litterbags the Ca concentration remained more or less constant (Fig.1).

Magnesium

The Mg concentration in the ectorganic horizons showed a comparable decrease with depth as K and Ca. Relatively little Mg proved to be water-extractable, being similar to Ca. The $BaCl_2$-extractable fraction was about 70% of the total amount, and did not vary much across the horizons. The 7.3 mM HCl extraction yields were smaller than those with $BaCl_2$. In the percolations as well, a part of the Mg remained in the organic material, the size of which was independent of the percolation medium. The yields of the percolations were comparable to those of the $BaCl_2$ extractions except for the LFl horizon, where they were larger. In the litterbags the Mg concentration decreased slowly with time (Fig.1).

Manganese

Of all measured metal cations Mn showed the most pronounced decrease with depth. Water-extractability of Mn was small and comparable to that of Ca and Mg. $BaCl_2$-extractability was almost complete in the lower horizons, but decreased towards the surface. Amounts of the 7.3 mM HCl extraction were smaller than those of the $BaCl_2$ extraction. In the percolation with 10^{-2} M HCl only a small part was retained in the organic material, whereas in the two other percolations the results varied with horizon and percolation medium. The smallest fraction was extracted in the LF1 horizon in the $(NH_4)_2SO_4$ percolation: only 38% was removed. In contrast to the other cations, the Mn concentration in the litterbags increased with time (Fig. 1). However, the amount of Mn per bag did not increase during field incubation, taking the loss of dry mass into account (Tietema, 1993).

Discussion

Sodium

The high water-extractability of Na in the ectorganic horizons implies that Na was mainly present in the soil solution. The remainder of the Na was exchangeably adsorbed, as Na was completely extracted with $BaCl_2$ and removed in the percolations. Because the adsorption affinity of Na was only weak, as was shown by its

extracted with 7.3 mM HCl than with $BaCl_2$. Percolation with $10^{-2}M$ HCl removed all Ca - even in the two upper horizons. Percolation with 10^{-3} M HCl extracted almost all Ca in the two upper horizons, but less in the two deeper horizons; percolation with $(NH_4)_2SO_4$ resulted in smaller values for the upper horizons as

complete extraction with 7.3 mM HCl, this part of the Na was also rather mobile. The insignificance of other Na pools is consistent with the characteristics of Na: Na salts are highly water-soluble, there are no organic compounds of biological origin known to contain Na (Epstein, 1972), and soil microbial biomass contains an insignificant part of the soil Na (Díaz-Raviña et al., 1993).

The concentration of Na in the litterbag experiment was small after the initial decrease, which is also observed in other litterbag studies (Attiwill, 1968; Gosz et al., 1973; Lousier and Parkinson, 1978; Van Wesemael, 1993). Most authors have assumed that this was the result of a small chemical as well as biological retention of Na in litter. In the present case this assumption was confirmed by the extraction results. The high initial Na content of the litter in the bags may be due to dry deposition of sea salt on the needles or to uptake by the vegetation.

Potassium

Only part of the K in the ectorganic soil layer was BaCl$_2$-extractable. A part of this BaCl$_2$-extractable K was present in the soil solution according to the aqueous extracts, and the rest was exchangeably adsorbed. The adsorption affinity of K was small as shown by the large fraction of the BaCl$_2$-extractable K present in the aqueous and 7.3 mM HCl extracts. The fact that the percolations removed only a part of the organic-soil K, the size of which did not depend on the kind of percolation solution, indicates that the non-exchangeably bound K fraction was not chemically bound, but was present in the soil microbial biomass (Lee and Weber, 1982). This is corroborated by the literature: K salts are very soluble and K is not incorporated non- exchangeably in organic matter, though it is required both by higher plants and micro-organisms (Epstein, 1972). Díaz-Raviña et al. (1993) found in the soils they investigated that a significant part of the K is bound in the soil microbial biomass.

The pattern found in the litterbags of a fast initial decrease followed by a constant level is very typical for K and has been observed in many other field decomposition studies (Attiwill, 1968; Bockheim et al., 1991; Gosz et al., 1973; Hågvar and Kjøndal, 1981; Joergensen and Meyer, 1990; Lousier and Parkinson, 1978; MacLean and Wein, 1978; Van Wesemael, 1993). In the majority of these cases this pattern is ascribed to the uptake of K into the soil microbial biomass, but K adsorption is also mentioned. Taking the extraction

Table 4. pH values in the filtrates of the various extractions

Horizon	Extractions		
	Aqueous (0.125M)	BaCl$_2$	HCl
		(7.3×10^{-3} M)	
LF1	4.95	3.38	2.83
F2	4.66	3.00	2.57
F31	4.04	2.54	2.32
F32	3.97	2.50	2.29

results into account, the dissolved and exchangeably adsorbed parts of the K must be involved in the initial fast decrease of the K in the bags, while the remainder is retained biologically by the soil microbial biomass.

Calcium

The Ca in the ectorganic layer had a large BaCl$_2$–extractable fraction, of which the major part was strongly adsorbed on the exchange complex according to the aqueous and 7.3 mM HCl extractions. As the non-exchangeable part was percolated completely at pH 2, it is unlikely that this part was present in the soil microbial biomass. Comparing the Ca yields in the BaCl$_2$ extractions with those in the percolation with 10^{-3} M HCl (pH 3), shows that in the upper horizons the percolation produced the largest yields, whereas in the lower horizons the BaCl$_2$ extraction produced the largest yields. As the pH of the BaCl$_2$ extractions of the upper horizons was equal to or above 3 (Table 4), while the pH in the lower horizons was below 3, the size of the non-exchangeably bound Ca was negatively correlated with the pH. According to the literature Ca is unessential for micro-organisms, as opposed to higher plants (Epstein, 1972); plants incorporate Ca into Ca pectate in cell walls and into Ca oxalate. Micro-organisms only contain Ca in small concentrations (Anderson and Domsch, 1980; Díaz-Raviña et al., 1993; Hughes, 1972; Lodge, 1987). Precipitates of Ca oxalate have also been observed on the hyphae of fungi (Graustein et al., 1977; Lodge, 1987). Part of the Ca was probably bound non-exchangeably in such organic compounds and dissolved at low pH.

The strong retention of Ca in the litterbags resembled many other studies in which the Ca concentration remained constant or even increased (Attiwill, 1968; Bockheim et al., 1991; Gosz et al., 1973; Hågvar and

Kjøndal, 1981; Joergensen and Meyer, 1990; Lousier and Parkinson, 1978; MacLean and Wein, 1978; Van Wesemael, 1993). Most authors explain this large retention by the fact that Ca forms a structural component of the vegetational tissues and remains immobile as long as these tissues are not decomposed. However, the extraction and percolation results show that Ca can be mobilized without decomposition of the organic material; the strong adsorption of Ca on the exchange complex provides an alternative explanation for its retention.

Magnesium

In the ectorganic soil horizons the $BaCl_2$-extractable part of Mg was large. This part had an intermediate affinity in cation exchange, as the aqueous and 7.3 mM HCl extractions showed. The non-exchangeable Mg was not retained chemically, as the fraction of Mg removed from the organic material in the various percolations did not depend on the kind of percolation solution. Epstein (1972) reported that Mg and K are the only metals that constitute macro nutrients for micro-organisms. Díaz–Raviña et al. (1993) measured significant amounts of soil Mg to be present in the microbial biomass. Organic compounds in plants containing Mg are less abundant than those containing Ca (Epstein, 1972).

The slow decrease of Mg in the litterbags, intermediate between K and Ca, is a common phenomenon according to previous litterbag studies (Attiwill, 1968; Bockheim et al., 1991; Hågvar and Kjøndal, 1981; Joergensen and Meyer, 1990; Lousier and Parkinson, 1978; MacLean and Wein, 1978). Most authors point to the demand for Mg by the soil microbial biomass as a factor determining the retention of Mg in the litter. Acccording to the extractions the pool of exchangeably adsorbed Mg is more important. The gradual decrease of Mg can be explained by its intermediate adsorption affinity.

Manganese

The extractions showed that Mn was mainly exchangeably adsorbed with a strong affinity. As Mn was almost completely removed by percolation with 10^{-2} M HC1, the non-exchangeable part of the Mn was retained chemically, and not in the soil microbial biomass. Mn is a micronutrient and is required in much smaller amounts by plants and micro-organisms than K or Mg; in addition organic compounds containing Mn are

rare (Epstein, 1972). Probably Mn was bound inorganically in the form of solid Mn (hydr)oxides; this can also explain the strong pH dependence of the Mn retention. The Mn results of the percolation with 10^{-3} M HCl (pH 3) showed the same correlation with pH as did the Ca results: the yields in the upper horizons were larger than those of the $BaCl_2$ extractions and the yields in the lower horizons were smaller. According to the even larger Mn retention in the LF1 horizon of the $(NH_4)_2SO_4$ percolation experiment, which horizon received a percolation solution with a pH above 5, Mn retention depended even stronger on pH than the Ca retention. This pH dependency of the Mn retention may be caused by the shifting equilibrium between soluble Mn^{2+} and solid Mn (hydr)oxides. At a constant redox potential level this equilibrium shifts towards solid Mn (hydr)oxides with increasing pH (Stumm and Morgan, 1981). Hågvar and Kjøndal (1981) and Lee and Weber (1983) also found a clear relationship between pH and loss of Mn. In experiments in which they applied simulated rainfall of increasing acidity to litter the Mn losses increased most of all cation losses.

The strong retention of Mn in the litterbags has been observed in many other studies (Bockheim et al., 1991; Gosz et al., 1973; Hågvar and Kjøndal, 1981; Joergensen and Meyer, 1990; Lousier and Parkinson, 1978; Van Wesemael, 1993). Although some of these authors point to the role of solid Mn (hydr)oxides in retaining Mn, the extractions show that adsorption is also important for the Mn retention in the ectorganic layers. Lawrey (1978) also concluded from his litterbag experiments that Mn dynamics must be primarily due to exchange processes.

General discussion

After litter is deposited on the soil, it shifts downwards in the ectorganic layer, as fresh litter is continuously deposited on top of the layer. Therefore, the ectorganic layer constitutes a time series, as vertical mixing of material is almost absent in this acid material. Although the mass of the organic material decreased with depth due to decomposition, the metal concentrations in the material – in mmol kg^{-1} dry mass – did not increase, but also decreased or remained constant with depth. Therefore, these metals were continuously being lost from the ectorganic layer by leaching and uptake by the vegetation. Leaching refers in this case to all export in the water phase (Tietema and Wessel, 1994). Gosz et al. (1973) and Lousier and Parkinson (1978) have made a distinction between nutrient losses that are in

proportion to the total mass loss, and the remaining losses. They consider only the latter part as leached. However, both parts require some transport process, such as leaching and root uptake, to be removed from the layer.

The two lower horizons of the ectorganic layer contain roots, so uptake can take place from these horizons. However, the contribution of the roots in the ectorganic layer to the uptake of nutrients must be small, because according to root measurements in the upper 80 cm of the soil in Speuld (Olsthoorn, 1991) only 7% of the active, fine roots is present in the ectorganic layer, and the remainder is present in the mineral part of the soil. This makes it likely that in the ectorganic part of the soil only a small part of the nutrients is taken up and most is leached to the mineral soil layer.

Although all metals were lost from the ectorganic layer, they clearly differed in retention in the ectorganic layer. A measure for this retention is the ratio between the metal cation concentrations in the organic material and their amounts deposited in throughfall (Table 1). This ratio increased in the order: Na < K < Mg < Mn < Ca, reflecting an increasing retention, which is in agreement with the different metal characteristics: Na, which was poorly retained, was present mainly in the soil solution. K, of which the retention was larger, was partly present in the soil microbial biomass, and partly in the soil solution. The divalent cations, which were retained the most, were mainly exchangeably adsorbed on the exchange complex and only present in minor amounts in the soil solution.

There was also a difference between the vertical distributions of the total metal concentrations: Na had a uniform distribution, while the other metals decreased with depth. Na was mainly present in the dissolved pool and relative to its presence in the ectorganic layer it had the largest deposition of all metals. Therefore, it is likely that the Na in the ectorganic layer reached equilibrium with the Na in throughfall already in the young material in the upper part of the ectorganic layer, resulting in a uniform distribution with depth. As the dissolved pool of the other metals was only relatively small, their approach towards equilibrium must be much slower: the fractions present in the other pools have to move to the dissolved pool first to be available for leaching. This contributes to decreasing concentrations with depth, as the oldest material is located at the bottom of the ectorganic layer. A second factor that contributes to the decreasing vertical distributions is that many conditions deeper in the ectorganic layer favour the dissolution of the metals. In gener-

al, nitrification taking place in this material (Tietema et al., 1993) results in an increasing amount of H^+ ions with depth contributing to the exchange of metal cations. Furthermore, the pH of the ectorganic horizon decreased with depth (Table 3), which diminished the non-exchangeable fractions of Ca and Mn. The CEC_{eff}, also slightly decreased with depth (Table 2). This implies that the pool of exchangeably adsorbed cations must also decrease with depth. However, since the CEC_{eff} is pH dependent (Kalisz and Stone, 1980), the decrease in CEC_{eff} was rather the result of the replacement of metal cations by H^+ ions (pH_{BaCl_2} in Table 3) than the cause for the loss of cations.

The exchangeably adsorbed fractions of the different cations also showed clearly different trends with depth. The exchangeably adsorbed fraction of K decreased, whereas that of Mg remained constant, and those of Ca and Mn increased. This is in agreement with the increasing adsorption affinity of these cations: K < Mg < Mn ≈ Ca.

Thus, the above mentioned differences between metals in retention and vertical distribution can be explained by their differences in pool distribution and exchange affinity. This is in disagreement with another concept stating that the C : nutrient ratio in the material determines whether the amount of a nutrient increases or decreases in decomposing organic matter (Gosz et al., 1973; Staaf and Berg, 1982; Van Wesemael, 1993). The existence of such a critical ratio is explained by the nutritional requirements of the microbial decomposers in the material (Swift et al., 1979). As these results show, this concept is incorrect for these metals, because their retention in the organic material is due not only to storage in the microbial biomass, but also to storage in other pools.

Because the exchangeably adsorbed pools dominated, cation exchange and the composition of the throughfall deposition are the main factors determining the leaching of the metals. This makes the metal dynamics in the ectorganic layer susceptible to acidifying deposition, which exceeds by far the metal cations in throughfall. To gain a quantitative understanding of the role of the acidifying deposition, knowledge of the cation exchange affinities is of primary importance together with data about the deposition, the nitrogen transformations, and the water flow.

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