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Effects of simulated acid precipitation on the cycling of manganese under Sitka spruce (*Picea sitchensis*)

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Abstract. Simulated acid rain at pH 3.3, 4.3 and 5.3 has been applied by overhead spraying to reconstructed soil profiles and young Sitka spruce (*Picea sitchensis*) trees in pots to assess the effect of rainfall acidity on the fate and recycling efficiency of Mn from ^{54}Mn-labelled Sitka spruce litter. The concentration of ^{54}Mn in throughfall was significantly increased by acidification of the rain, but ^{54}Mn activity in drainage water remained low and was not significantly affected. The fact that only $< 1.5\%$ of ^{54}Mn was lost in drainage water suggests that forest ecosystems efficiently retain Mn, at least in the short term. The bulk of ^{54}Mn (approximately 60 to 70%) was retained in the litter layer. Compared with rain at pH 4.3, rain at pH 3.3 acidified L/F and H/A horizon soils. The amount of ^{54}Mn found in the different soil horizons was only influenced significantly by rainfall acidity in the E horizon soil, however, where ^{54}Mn activity was increased by the most acid treatment. The activity of ^{54}Mn in Sitka spruce needles did not differ significantly with treatments.

Introduction

The importance of forest litter as a major pathway for Mn transfer from vegetation to soil has been stressed by many workers. Bergvist (1987) examined metal cycling in a spruce forest and found that litterfall and throughfall together recycle more than half of Mn taken up by plants. Mayer and Ulrich (1974) found that Mn in litterfall was 5.1 kg ha^{-1} yr^{-1} in a beech stand compared to 3.1 kg ha^{-1} yr^{-1} and 0.2 kg ha^{-1} yr^{-1} for Mn reaching the forest floor through throughfall and open field input respectively. In comparison with other heavy metals, Mn bound to forest litter is easily leachable (Heinrichs and Mayer 1980).

Acid deposition may enhance Mn leaching (Berg 1986; Hovland et al. 1980). Manganese is lost from litter via cation exchange, since most of the Mn in forest litter is in the exchangeable form (Michopoulos 1995). Manganese leached from litter can migrate down the soil profile to increase its concentration in mineral soil. When soils acidify, mobilised Mn may reach toxic levels for forest plants (Kazda and Zvacek 1989; Raunemaa et al. 1987). Mobilised Mn can end up in drainage waters. In Scotland, undesirable Mn concentrations (> 0.05 mg l^{-1}) were found by Heal (2001) in upland freshwaters. The author attributed the high concentration of

Mn to the low pH and organic nature of the catchment soils she studied. Thus it is important to understand the mobility of Mn bound to forest litter in acid soils or soils receiving rain of low pH. This may be achieved by labelling the litter Mn with a traceable isotope. Although it would be difficult and time-consuming to produce completely uniformly labelled Mn in litter, it is reasonable to use litter equilibrated with ^{54}Mn for tracing pathways, because litter Mn that is labile is so predominantly in the exchangeable form. This radioisotope is particularly suited for studies of the chemistry of Mn, since it is a γ-emitter with a moderate half-life. It has been used to study Mn distribution in plants (Millikan 1951), its interaction with other micronutrients (Toth and Romney 1954), the fate of Mn applied to soils as manganese sulphate (Romney and Toth 1954), and its interactions with clays (Epstein and Pearson 1951). Other workers have used ^{54}Mn to determine the labile Mn pool in soils (Lopez and Graham 1972; Sims et al. 1979; Goldberg and Smith 1984).

It was decided to use a Mn label in the present study to monitor acid deposition effects on the redistribution and cycling of Mn in soils and plants. The aim was to see how efficiently Mn associated with litter was recycled through young trees, and whether the recycling was sufficiently efficient to prevent leaching loss of Mn from the soil profile. To do this it was decided:

- To label Sitka spruce litter with ^{54}Mn and apply the litter to the surface of reconstituted soil profiles in pots with Sitka spruce plants subjected to simulated acid rain.
- To measure the subsequent change over time in the activity of the ^{54}Mn in drainage water and throughfall.
- To measure the distribution of the activity of ^{54}Mn in soil horizons at the end of the experiment
- To measure the activity of ^{54}Mn in the Sitka spruce needles at the end of the experiment.

Materials and methods

Experimental design

The experiment was based upon a completely randomised design, with three treatments (rainfall at three pH levels, 5.3, 4.3, 3.3) and four replicates (one pot with one tree for each replicate) per treatment. Rain was applied via purpose-built nebulisers (Skiba et al. 1987). To avoid errors due to different growth among the trees, the random allocation of treatments was based on the amount of Mn found in the throughfall prior to establishment of the main experiment. Initially the three treatment labels were allocated randomly among the 12 plants. All trees were then washed with a fine spray of 400 ml deionized water over approximately 4 h. The throughfall was collected and analysed for Mn. If the throughfall samples showed any apparently significant treatment effect prior to the true treatment application, the young trees were allocated new random numbers. The water wash and analysis were then repeated until there was no apparent (artificial) treatment effect. In practice, two allocations were necessary. To reduce the variance due to the position in the glasshouse, the pots in sets of treatments were relocated every 15 days so that they occupied all possible positions in the glasshouse during the experimental period.

Soil collection

Sitka spruce litter and mineral soil were collected from Kirkhill Forest, 6 km north west of Aberdeen in Scotland. The geological parent material of this area, according to Geological Survey of Great Britain (1982), is metasedimentary rocks of the Dalradian supergroup and the Aberdeen formation subgroup. It consists largely of metamorphosed arenaceous sediments (i.e. of psammitic and semi-pelitic metasediments).

Four soil layers were sampled individually from the L/F, the H and A (mixed), the E and the B horizons. To collect adequate and representative soil, five pits were used. Litter and mineral horizon soils had roots and plant parts removed by hand, and all samples, except from the L/F horizons, were passed through a 5.3-mm sieve. Litter and mineral horizon soils were each thoroughly mixed, and soils were stored at 4 °C prior to use.

Potting of the trees

Soil "profiles" were reconstituted in 12 pots. The lowest part of the mineral soil had a radius of 75 mm. Filling (by hand) started with 90 mm of soil from the B horizon, followed by 40 mm of soil from the E horizon, and finally 20 mm of the H/A horizon soil. Sitka spruce trees five to six years old and 0.4 to 0.5 m high were collected from a nursery close to Aberdeen. The indigenous soil of the tree roots was gently removed by hand and all trees were transferred to pots after the B horizon soil had been put in the pots. In this way most of the roots had contact with the B horizon soil. The filling with soil was continued until the horizon/profiles reached the required depths. For 15 days each plant was watered with the same quantity of deionized water (ranging from 150 to 200 ml per day) as an overhead spray. Drainage was minimal over this period, but this pre-treatment phase allowed the trees and the soil profiles to consolidate.

Installation and operation of the simulated precipitation system

The rain simulation system consisted of an array of nebulisers, one above each tree. All nebulisers were supplied with compressed air at matched flow rates via a plastic micro-pipette tip (Skiba et al. 1987). The "rain" solution was fed to the nebulisers under gravity through silicon rubber Auto-Analyser capillary tubes of 0.65 mm internal diameter. The tubing was selected on a trial and error basis, to deliver rain to each pot at a rate of 100 ml h^{-1}.

Table 1. Concentrations (mmoles l^{-1}) of major ions in the simulated rain used.

	Treatments pH 5.3	pH 4.3	pH 3.3
Na^+	0.107	0.107	0.107
Cl^-	0.140	0.140	0.140
Mg^{2+}	0.013	0.013	0.013
Ca^{2+}	0.015	0.015	0.015
K^+	0.014	0.014	0.014
NH_4^+	0.048	0.048	0.048
H^+	0.005	0.05	0.50
NO_3^-	0.030	0.045	0.195
SO_4^{2-}	0.030	0.045	0.195

Each of the three treatments was isolated from the others by a vertical transparent heavy duty polyethylene sheet, to avoid potential spray drift problems. Each pot was supported over a plastic funnel held rigidly in a purpose-built, plastic-covered wooden stand and drainage water samples were collected in plastic beakers under the funnels. Throughfall samples were collected via 80-mm diameter plastic beakers under the tree canopy.

During the preliminary watering with deionized water, 200 ml per day was needed to bring the soil to field capacity and provide sufficient throughfall solution for analysis, corresponding to 2110 mm of rain per year. This is rather high for the Aberdeen area, but not for Scotland as a whole. The composition of the artificial rain was taken from data from Reynolds et al. (1989) for Crathes, 20 km west of Aberdeen, and is given in Table 1. The ratio of nitrate and sulphate ions used was 1:2 on a mol_c basis.

Litter labelling with ^{54}Mn and application to soil

Field moist litter (50 g) was shaken for 2 hr in a mechanical shaker with 10 ml of evenly distributed, carrier-free 4.2 kBq ml^{-1} ^{54}Mn (as manganese chloride, $MnCl_2$) and was allowed to equilibrate for two days at room temperature before it was applied to the soil surface in all of the pots in mid October. The litter was spread on the surface as uniformly as possible. This resulted in a layer height of 10 mm. The radius of the top of the litter was 105 mm. After litter spreading, treatment applications started immediately.

Running of the experiment

Treatments started on the 18th of October and ended on the 11th of January. Drainage water was collected on 18 occasions and throughfall on 13, from the second week of November. There were four replicates of drainage water for each treatment. The ^{54}Mn activity was measured in 5 ml from the measured drainage water

Table 2. Selected chemical parameters of the soil used. Cations and CEC are expressed in mmoles_c kg^{-1}. Means and standard errors are based on triplicate determinations.

Horizon	pH	Ca^{2+}	Mg^{2+}	K^+	Na^+	CEC
LF	3.07 ± 0.01	10 ± 28	39.6 ± 4.8	4.8 ± 0.4	14.0 ± 0.3	758 ± 13
H/A	2.45 ± 0.01	31.7 ± 2.3	15.0 ± 0.4	1.16 ± 0.04	3.80 ± 0.47	625 ± 16
E	3.02 ± 0.01	2.9 ± 0.1	0.66 ± 0.08	0.19 ± 0.00	0.16 ± 0.00	42.1 ± 1.1
B	3.68 ± 0.04	2.5 ± 0.3	0.62 ± 0.11	0.19 ± 0.02	0.40 ± 0.02	118 ± 5

amount in each collector. Throughfall volumes were very small, because only small collection beakers, placed randomly under the canopy, were used to minimise disruption of Mn cycling. Therefore the throughfall contents of all beakers for a given treatment were mixed and ^{54}Mn activity was measured using 5 ml of the measured total volume. Thus there was one throughfall replicate for each treatment at each time of sample collection. It was not desirable to collect more throughfall by increasing rainfall amount, because this could have had an excessive effect on the litter Mn cycling processes.

Chemical analysis and measurement of the activity of ^{54}Mn

Soil moisture contents were determined gravimetrically by heating at 105 °C for 24 h. Soil pH (before and after harvest) was measured using a suspension of field moist sample in 0.01 M calcium chloride (1:2.5) with a glass-calomel electrode and pH meter. Exchangeable base cations and cation exchange capacity (CEC) were determined by a leaching technique. Field-moist soil sub-samples (10 g) were leached with 250 ml of 1 M neutral ammonium acetate solution (pH 7). The leachates were collected and analysed for exchangeable base cations. Calcium and Mg^{2+} concentrations were determined by atomic absorption spectrometry and K^+ and Na^+ concentrations by flame emission spectrometry. Selected chemical parameters of the soil used are shown in Table 2. The soil was then leached with 250 ml 80% ethanol to wash out excess NH_4^+, and finally with 250 ml 1 M sodium chloride (NaCl) solution. The concentration of NH_4^+ in the NaCl leachate was determined colorimetrically using a flow injection analyser.

Exchangeable Mn in soil horizons was extracted with 1 M $Mg(NO_3)_2$ at pH 7 (Shuman 1985). Total Mn in litter and tree needles was determined by wet digestion with $H_2SO_4/HClO_4$ (Cresser and Parsons 1979). Total Mn in mineral soils was determined following fusion with lithium metaborate (Potts 1987). Concentrations of exchangeable and total Mn in the soil used are shown in Table 3. When treatment application ceased, the Sitka spruce trees and soils were removed from the pots. Needles were removed, oven dried at 80 °C for three days and ground to pass a 0.2-mm sieve. Sub-samples were analysed for ^{54}Mn activity. Soils from all horizons were dried and weighed. Subsamples of dried soils were also analysed for ^{54}Mn activity. The activity of ^{54}Mn was measured with a Canberra Packard Autogamma 500.

Table 3. Concentrations (mg kg^{-1}) of exchangeable and total Mn in soils used. Means and standard errors inside the body of the table are based on three determinations.

Horizon	Exchangeable Mn	Total Mn
LF	256 ± 4	439 ± 6
H/A	6 ± 0	115 ± 0
E	0.29 ± 0	137 ± 0
B	0.33 ± 0	274 ± 0

Results in drainage water and soil are expressed as percentages of total activity. Results in throughfall are expressed as total counts min^{-1} per sample since the amount of total throughfall was not known. This amount could not have been measured directly without excessive disruption of the Mn cycling. Moreover the throughfall distribution over the pot surface area was not sufficiently uniform to allow scaling upon an area ratio basis. Activity of ^{54}Mn in plant material is expressed in units of counts g^{-1} min^{-1}. Results for soil and plant material are expressed on an oven dry-weight basis.

Statistical analysis

The experiment was a completely randomised design, but the analysis of variance for the percentage of total activity of ^{54}Mn in drainage water was based on a split-plot design. The reason for this was that results in drainage water are not independent from each other, since the ^{54}Mn output at any given time depended on the output at previous times. Time was the split-plot factor in the analysis of variance. The analysis of variance for total counts in throughfall samples was based upon a randomised block design with time as the block factor. It was considered that time should not be a split-plot factor as plants can replenish what they have lost in throughfall through nutrient uptake. All the other analyses of variance for pH and percentages of total activity of ^{54}Mn in the various soil fractions were based on a completely randomised design. In the tables that follow, standard errors of means are shown beside means, and are indicated by the symbol ±.

Multiple mean comparisons were made by using the Bonferoni modified LSD test. The LSD values were computed for the probability level derived from the analysis of variance, i.e. if the means differ at 0.001 probability level, LSD values were computed accordingly. Therefore in subsequent tables means on the same line followed only by different letters differ significantly at the probability level mentioned in the text.

Parametric statistics was used for the statistical analysis. Zar (1996) in a thorough examination of the controversy over whether or not to use parametric statistics argued that the analysis of variance is robust, operating well even with considerable heterogeneity of variances, as long as the numbers of observations per treatment are equal (as in this experiment) or nearly equal. He also argued that the analysis of variance is also robust with respect to the assumption of the underlying population's normality. The validity of the analysis is affected only slightly by even considerable deviations from normality.

Results and discussion

Isotopic equilibria

The total Mn concentration in litter was 439 ± 6 mg kg^{-1} (Table 3). The labile Mn pool constituted 75 to 80% of this (Michopoulos 1995) and the ^{54}Mn absorbed in litter will initially be distributed throughout this pool, rapidly attaining equilibrium with native Mn. It may be assumed in the present study that isotopic exchange also occurs rapidly between Mn in percolating solution and that absorbed on litter or soil over the three months of the experiment. However, totally unequivocal verification of equilibration would have involved soil sampling at different times until it could be shown that the ratio of native to label Mn was constant. This procedure would have involved destructive sampling, which in a glasshouse experiment on a relatively small scale would have entailed significant loss of labelled litter.

Field vs pot experiments

Results from simulated acid rain experiments should be interpreted with caution. Morrison (1983) argued that when dealing with simulated acid rain input effects over a short period of time, interpretation should be based on cation exchange equilibria rather than effects of changes in weathering rates. During the time period of this experiment ^{54}Mn was distributed among various soil fractions. Some of it was bound to organic matter, some of it to clay minerals and iron and manganese oxides surfaces. Over the three months period that the experiment lasted, the rates of organic matter decomposition and mineral soil weathering are probably not fast enough to affect significantly the ^{54}Mn distribution in the soil-plant system. However, exchange reactions are generally rapid in soils and in this respect this experiment offers valuable information.

Some oxidation of organic matter occurs in reconstituted soil profiles. The authors minimised this effect by reconstituting the soil profiles from field moist soil. The partial oxidation of organic matter through air-drying and subsequent rewetting of soils may cause soil reduction and release of Mn in exchangeable and soluble form (Bartlett and James 1980). Smith and Paterson (1995) found that determination of Mn concentration in moist soils minimises changes. Another precautionary measure was to sieve soil through a 5.3-mm sieve instead of the traditional 2 mm in order to reduce soil sites exposed to oxidation and contact between dispersed micro-organisms and fresh organic matter surfaces.

Another difference between natural and reconstitured soils is water flow through macropores and micropores. In natural soils swelling and shrinking of clays greatly affects water flow. Ritchie et al. (1972) have demonstrated that large continuous pores were of major significance in percolation of water through swelling clay soil. Reconstituted soil profiles are more homogenous than natural soil profiles. The absence of structure and the removal of stones reduce variability caused by preferential water flow. In this respect, reconstituted soil profiles offer an “advantage” over natural soils when judging various treatment effects on chemistry of percolating water. However, some variability still exists in pot experiments. The plant roots open channels in soils in which preferential water flow may occur. The alternating temperatures during day and night also affect swelling and shrinkage of clay. The authors believe that re-randomization of the experimental design that took place every 15 days minimised this effect.

Percentages of ^{54}Mn spike found in drainage water

Only ^{54}Mn was determined in this experiment, and not total Mn of concentrations of any other species. For safety reasons determination of total Mn or of other compounds in drainage water, throughfall, soils and plant tissues containing ^{54}Mn, a γ emitter was not possible. Nebulisation of radioactive material into an atomic absorprtion spectrometer is not permissible. The only way to overcome this problem would have been to run a parallel experiment without any radioactive tracer, but this was not plausible in the available glasshouse space.

Treatments did not significantly affect the percentage of total added activity of ^{54}Mn found in drainage water (Table 4). The most probable explanation is that soil horizons and/or roots absorbed most of the radioactive Mn mobilised from the litter, minimising leaching and loss from the pots. Over the three months of the experiment, the total losses of ^{54}Mn in drainage water as percentages of total added activity were 1.03, 0.81, 1.37 for the treatments at pH 3.3, pH 4.3, and pH 5.3 respectively. These small amounts suggest strong absorption by soil of most of the ^{54}Mn leached from the litter. It will be seen later (Table 6) that the soil pH for the B horizon soil at the bottom of the profiles established in the pots had not fallen significantly in response to 3 months of treatment. The higher pH of this lower horizon would favour retention of Mn that was being leached down the profile. These results agree with those of Foster and Nicolson (1986), who found that 90 to 99% of Mn leached from the rooting zone in a maple-birch stand on an acid podzolic soil was retained in the watershed and did not appear in streamwater. Possibly a much longer experiment, in which the deeper mineral soil had acidified significantly, would have facilitated accelerated Mn leaching in response to precipitation acidification.

Activity of ^{54}Mn in throughfall

The lack of knowledge of total throughfall amounts does not allow inferences about the percentage of total added ^{54}Mn mobilised via throughfall. However, the total number of counts can be considered to be associated with a regular representative subsample of throughfall, and the treatment effects can be examined in this light.

Table 4. Means and standard errors of percentages of ^{54}Mn activity in drainage water. Means inside the body of the table are based on four determinations.

Days of collection	pH 3.3 treatment	pH 4.3 treatment	pH 5.3 treatment
1	0.084 ± 0.015	0.112 ± 0.009	0.094 ± 0.016
2	0.030 ± 0.010	0.038 ± 0.013	0.042 ± 0.004
3	0.011 ± 0.005	0.007 ± 0.004	0.018 ± 0.009
4	0.072 ± 0.006	0.100 ± 0.022	0.576 ± 0.145
5	0.049 ± 0.013	0.059 ± 0.011	0.070 ± 0.015
6	0.042 ± 0.025	0.027 ± 0.003	0.047 ± 0.014
7	0.019 ± 0.003	0.033 ± 0.004	0.066 ± 0.018
8	0.013 ± 0.001	0.025 ± 0.011	0.047 ± 0.013
9	0.047 ± 0.017	0.026 ± 0.011	0.030 ± 0.006
10	0.273 ± 0.195	0.072 ± 0.008	0.076 ± 0.020
11	0.107 ± 0.013	0.096 ± 0.004	0.053 ± 0.010
12	0.043 ± 0.027	0.011 ± 0.007	0.034 ± 0.012
13	0.058 ± 0.012	0.046 ± 0.007	0.050 ± 0.004
14	0.042 ± 0.013	0.034 ± 0.009	0.038 ± 0.005
15	0.017 ± 0.006	0.021 ± 0.003	0.040 ± 0.004
16	0.042 ± 0.014	0.039 ± 0.011	0.038 ± 0.007
17	0.034 ± 0.004	0.040 ± 0.011	0.025 ± 0.004
18	0.052 ± 0.007	0.035 ± 0.010	0.024 ± 0.004
Mean values for different pH treatments	0.057	0.045	0.076

Table 5. Means and standard errors of total counts in throughfall samples, based on 13 determinations.

pH 3.3 treatment	pH 4.3 treatment	pH 5.3 treatment
68.4 ± 9.2a	31.8 ± 4.3ab	20.4 ± 1.8b

Treatments affected ($p < 0.05$) the total activity in throughfall samples significantly (Table 5). Root uptake of Mn from the litter is likely to be increased by the acid treatments, as more Mn will pass into the solution phase under the more acid treatments (Michopoulos and Cresser 1996). Once Mn reaches the needles, however, exchange reactions on needle surfaces between H^+ ions and foliar ^{54}Mn will also be enhanced (Tukey 1970). The two mechanisms collectively provide the most probable explanation of the significant effect found.

Treatment effects on pH in soil horizons

Knowledge of soil pH and pH changes is essential in understanding Mn behaviour in soils (Sims and Patrick 1978). The mobility of Mn increases as the soil pH becomes lower. The soil pH was affected by treatments in the litter ($p < 0.001$) and H/A ($p < 0.05$) horizons, which exhibited lower pH values for the pH 3.3 treatment compared with the pH 4.3 treatment (Table 6).

Table 6. Effect of treatment on soil horizon pH values. Means and standard errors are based on four replicate determinations of H^+ concentration.

	Treatments		
Horizon	pH 3.3	pH 4.3	pH 5.3
Litter	2.58 ± 0.02a	2.71 ± 0.01b	2.68 ± 0.03ab
H/A horizon pH	2.42 ± 0.02a	2.51 ± 0.02b	2.48 ± 0.01ab
E horizon pH	3.11 ± 0.04	3.15 ± 0.02	3.19 ± 0.04
B horizon pH	3.73 ± 0.01	3.69 ± 0.01	3.72 ± 0.02

Treatment effects on ^{54}Mn distribution between soil horizons

Apart from pH, redox potential can influence Mn concentration in soils (Sims and Patrick 1978). In this experiment the effect of redox potential on the pH treatments are considered to be random. The reconstructed soil profiles are considered to be aerobic as they were made from coarse textured podzol soils. Wet aerobic soils can become anaerobic in some locations, but it is not very probable that redox potential might have a masking effect on treatments in this experiment. According to Bartlett (1981), measuring redox potentials in aerobic soils is only of qualitative nature and this measurement is worth doing only if comparing different soils or treatments that redox is likely to be important. Sparks (1995) considers that redox measurements are most reliable for flooded soils and sediments.

The percentage of ^{54}Mn found in the litter, H/A and B horizons was not significantly affected by treatments (Table 7). However, the treatments affected ($p < 0.001$) the percentage of added ^{54}Mn found in the E horizon soil (Table 7). Thus it appears that an additional Mn leaching loss from the litter and H/A horizons in response to acid treatments was counterbalanced by enhanced inputs from throughfall as a result of the enhanced ^{54}Mn uptake mentioned above. This could mask any significant differences in leaching rate for Mn. However, Mn was apparently accumulating in the E horizon soil, possibly because of its slightly greater pH compared with the overlying soils.

Recoveries of ^{54}Mn in soils

If the percentages of total added ^{54}Mn activity in each soil layer (Table 7) are added for each treatment, the total recoveries of ^{54}Mn retained in the pots can be found. From the standard errors of each component, the standard error of the totals can be calculated (Miller and Miller 1989) and from these the confidence limits ($p \leqslant 0.05$) for the means (Table 8). Since the standard errors overlap with each other there cannot be any significant difference between the three sums. However, a safe conclusion is that the greatest part of total activity of ^{54}Mn was retained in the soils. From Table 7, approximately 30 to 40% of the original ^{54}Mn applied to forest litter migrated down the soil profile, but very little was lost in drainage water (Table 4). Although Mn is considered to be a mobile trace element, it seems that the forest

Table 7. Effect of treatments on percentages of ^{54}Mn activity in soil horizons. Means and standard errors are based on four replicate determinations.

	Treatments		
Horizon	pH 3.3	pH 4.3	pH 5.3
Litter	73.3 ± 5.3	63.6 ± 5.2	61.1 ± 5.2
H/A horizon	11.5 ± 1.7	9.20 ± 0.90	7.72 ± 1.05
E horizon	12.9 ± 0.53a	8.06 ± 0.21b	8.62 ± 0.57b
B horizon	7.22 ± 0.51	8.04 ± 0.30	7.40 ± 0.29

Table 8. Means and confidence limits at 0.05 significance level for the sum of total activities of ^{54}Mn for each treatment found in all horizon soils.

pH 3.3 treatment	pH 4.3 treatment	pH 5.3 treatment
$93.5 < 105 < 116.5$	$77 < 88.9 < 100$	$73.5 < 84.8 < 96.1$

Table 9. Activity of ^{54}Mn in Sitka spruce needles (counts g^{-1} min^{-1}) Means and standard errors are based on four replicate determinations.

pH 3.3 treatment	pH 4.3 treatment	pH 5.3 treatment
25.84 ± 5.2	17.4 ± 0.7	11.0 ± 0.9

ecosystem retains this mobile nutrient via biogeochemical cycling, at least over the duration of this experiment.

Activity of ^{54}Mn in Sitka spruce needles

Treatments did not significantly affect the activity of ^{54}Mn in the Sitka spruce needles (Table 9). This lack of significance might be due to the season of sampling, which was in the autumn/winter period. In winter plants reduce their metabolic rate and, as a result, the nutrient uptake. Greater mobility of ^{54}Mn from litter in response to acidification of rainfall may result in greater Mn uptake by the trees. This would be countered, however, by greater ^{54}Mn leaching in throughfall. It must be pointed out also that if ^{54}Mn uptake was greater at pH 5.3 because growth was better at this pH, the lack of any significant activity effects as reported in Table 9 could be attributable partly to a dilution effect associated with greater needle growth. Regrettably needle yield data was not collected, so conclusions must remain speculative.

Conclusions

The simulated acid rain treatments did not significantly affect the percentages of added ^{54}Mn found in drainage water, and only a very small percentage of radioactive Mn was leached out of the profile in the drainage water. The bulk was retained in the soils, especially in the litter layer.

The pH 3.3 treatment gave the highest values of ^{54}Mn in throughfall. This extra input to the soil seemed to offset enhanced leaching losses from the litter horizon in response to treatment effects.

The litter and H/A horizons were acidified by the pH 3.3 treatment. However, these changes were not associated with any significant treatment effects on the ^{54}Mn activity in the respective horizons. A significant treatment effect was only seen in enhanced ^{54}Mn activity in the E horizon soil for the most acid treatment.

The activity of ^{54}Mn in Sitka spruce needles did not differ significantly with treatments. Combination of effects of low metabolic rate of plants during winter, a dilution effect as a consequence of better growth at higher pH, and a balance between enhanced uptake and enhanced foliar leaching might explain this observation.

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