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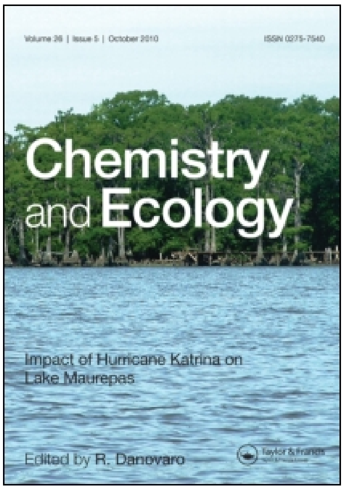

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COMPETITION OF HYDROGEN AND MANGANESE IONS FOR ADSORPTION SITES IN SITKA SPRUCE LITTER

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The competition of hydrogen and manganese ions for adsorption sites in Sitka spruce litter was investigated in a factorial design, simulated acid rain experiment, which involved leaching of litter with simulated throughfall solutions at three pH levels (5.3, 4.3 and 3.3) and three manganese concentrations (0 to $0.2\,\mathrm{mg\,l^{-1}}$) . The throughfall solution at the lowest pH was the most efficient in removing exchangeable manganese from litter. The manganese concentration in the leachates was approximately proportional to the hydrogen ion concentration in the simulated throughfall solution. Under field conditions, throughfall manganese concentration also naturally tends to increase as a consequence of enhanced foliar leaching of manganese in response to increasing precipitation acidity. The manganese concentration in the simulated throughfall also affected manganese concentration in the leachates, however, and contributed to a build-up of exchangeable manganese in litter, thus counteracting to some extent possible adverse effects of excess leaching due to increased throughfall acidity.

Keywords: Picea sitchensis; litter; manganese; acid deposition; 20-day leaching experiment

INTRODUCTION

The removal of exchangeable base cations from forest soils through leaching has been studied extensively in the last two decades. Less attention has been paid to the interaction of transition metals in forest litter with hydrogen ion concentrations in precipitation and throughfall, although the latter largely determine the extent of leaching of these metals (Senesi and Sposito, 1989). The replacing efficiency of hydrogen ions for exchangeable cations in soils was studied by Wiklander and

Anderson (1972) and the inverse reaction, that is the displacement of hydrogen ions by cations, by Wiklander (1975). Manganese, being a mobile element, is unlikely to compete effectively for binding sites in humic substances with other more strongly bound divalent and trivalent cations (Norvell, 1988). Generally, polyvalent ions such as Mn^{2+} might be expected to be more strongly adsorbed on exchange sites than monovalent cations such as H^+. However, in spite of their large hydrated ion radius, hydrogen ions are very effective at displacing ions adsorbed at cation exchange sites, behaving more like trivalent lanthanum in terms of their replacing power (Bohn *et al.*, 1985). It is to be expected, therefore, that acid deposition can deplete the exchangeable manganese from forest litter. Acidification of precipitation has been reported to increase manganese leaching from forest litter in several studies (Abrahamsen *et al.*, 1976; Brown, 1985; Skiba and Cresser, 1986). However, such acidification also is known to enhance foliar leaching of manganese (Skiba *et al.*, 1986) and thus will enhance manganese inputs to forest litter horizons. Thus it might be expected that acidification of precipitation, at least over the mid-term, would enhance both manganese inputs to and outputs from forest litter horizons. So far, in spite of these interactive effects, no factorial type of experiment to investigate the interaction of hydrogen and manganese ions appears to have been conducted.

The aim of the present study was to find the effect of the interaction and competition between hydrogen and manganese ions: a) on manganese concentration in the leachates and b) on exchangeable manganese concentration in forest litter.

MATERIALS AND METHODS

Sites and Sample Collection

Sitka spruce (*Picea sitchensis*) litter was collected from Kirkhill Forest (NJ 852109), 6 km north-west of Aberdeen, at a site bearing podzol soils. The area where sampling took place has a geological parent material of igneous and metamorphosed igneous rocks, especially granodiorite (Geological Survey of Great Britain, 1982). The site was mainly under Sitka spruce cover planted 30–35 yr ago. There was also some beech cover (*Fagus silvatica*) in much less abundance than the

Sitka spruce cover, but not in the immediate vicinity of the sampling site. The ground vegetation mainly consisted of bracken (*Pteridium* sp.) and mosses.

Composite L/F horizons were sampled, transferred to plastic bags and stored in a cold room at $\leqslant 4°C$ in the Department of Plant and Soil Science of the University of Aberdeen, until their use a few days later. Roots from all samples were removed by careful hand sorting, and litter from all bags was mixed thoroughly to form a homogenous mixture. Throughout the experiment litter was maintained and used in the field-moist condition.

Installation and Running of Leaching System

Subsamples of 5 g of litter were weighed and put in leaching tubes. To prevent losses of litter, a small cotton wool plug was put inside the leaching tube below each sample. A thin layer of compacted cotton wool was also placed above the litter, to slow the infiltration rate of water, with the intention of promoting a more even flow distribution of the simulated throughfall additions. The litter percolation through the leaching tubes appeared to be fairly uniform, with no obvious preferred channels. All leaching tubes were clamped vertically. Solution was delivered to the top of the upper cotton wool layer of each leaching tube by means of silicon rubber tubes. These tubes were connected to AutoAnalyser tubes of internal diameter 0.35 mm, capable of delivering 0.1 ml of solution per minute when used with a Technicon II AutoAnalyser peristaltic pump. Leachates were collected in 100-ml conical flasks.

It was decided to apply nine treatments with three replicates for each treatment. The treatments were a combination of pH and manganese concentration in the leaching solution. The pH levels were: 5.3(H^+ 5 $\mu g\,l^-$), 4.3(50 $\mu g\,l^{-1}$) and 3.3(500 $\mu g\,l^{-1}$). The manganese concentrations in the leaching solution were 0, 0.1, and 0.2 mg l^{-1}, based upon recorded values in Sitka spruce throughfall (Skiba *et al.*, 1986). The leaching solution, in all other respects, had a composition appropriate for bulk throughfall under Sitka spruce, composition being based upon the results of Reynolds *et al.* (1989), but with pH adjusted to the above mentioned pH levels. The concentration ratio, on a mol_c basis, of total sulphate to nitrate in the acid used for pH adjustment and in all the final throughfall formulations was two. Table I shows

TABLE I Compositions of initial simulated throughfalls (mg l^{-1}) for the three pH treatments. Treatment pH values were adjusted to the values shown with dilute 2 + 1 (mol_c basis) $H_2SO_4 + HNO_3$

Ion	*pH 5.3*	*pH 4.3*	*pH 3.3*
Na^+	2.82	2.82	2.82
Cl^-	5.48	5.48	5.48
Mg^{2+}	0.43	0.43	0.43
Ca^{2+}	0.82	0.82	0.82
K^+	2.88	2.88	2.88
NH_4^+	0.70	0.70	0.70
H^+	0.005	0.05	0.50
NO_3^-	3.38	4.28	13.5
SO_4^{2-}	5.19	6.63	21.0

the composition of throughfall in mg l^{-1} before manganese (in the form of manganese chloride) was added.

The experiment was run over 20 days, at laboratory temperature (23 ± 3°C), with the simulated rainfall being added at the same time during each day for 10.5 h on each occasion. In total, the amount of simulated rain passed through the litter corresponded to two years of precipitation for the field site (Michopoulos, 1994). Every day over the 20 days of the experiment, pH and manganese concentration were determined in the leachates. Immediately after the twentieth day of leaching, the litter in all leaching tubes was leached with a 1 mol l^{-1} solution of potassium chloride for the determination of exchangeable manganese.

Chemical Analysis

Manganese concentration was determined by flame atomic absorption spectrometry at 279.5 nm using an air-acetylene flame and matrix matched standards.

The leachate pH was measured with a combined, low ionic strength glass-calomel combination electrode and a Jenway PHM 10 pH meter.

Litter moisture content was determined gravimetrically.

RESULTS AND DISCUSSION

Manganese Concentration in Leachates

Analysis of variance was carried out to assess treatment effects for the nine combinations of the factorial design. Although the experiment was a randomised factorial design, a split-plot design analysis of variance was used, because observations were not independent from each other, *i.e.* concentrations of manganese in leachates on the second day were dependent on the leachate concentrations of manganese on the first day, etc. The principle of independence of observations is essential for the application of the analysis of variance for a randomised design (Clarke, 1980). In this case, time was the split-plot factor in all nine treatments of the factorial experiment.

Results are presented in a two-way analysis table for a combination of pH treatment and manganese treatment (Table II). It can be seen that pH highly significantly affected manganese concentration ($p \leqslant 0.001$), the largest value (greatest manganese leaching/least retention of manganese) being given by the pH 3.3 treatment (0.31 mg l^{-1}). Correlations between cation concentrations leached from foliage and rainfall acidity are believed to indicate cation exchange as the mechanism for increased foliar leaching with higher acidity in rain (Wood and Borman, 1975; Parker, 1983).

TABLE II Means of manganese concentrations (mg l^{-1}) in the leachates. Means inside the body of the table are based on 60 determinations

	pH 3.3 treatment	*pH 4.3 treatment*	*pH 5.3 treatment*	*Mn treatment means*
Mn treatment (0 mg l^{-1})	0.27 ± 0.01 **a**	0.18 ± 0.01 **d**	0.15 ± 0.01 **e**	0.20 **a**
Mn treatment (0.1 mg l^{-1})	0.31 ± 0.01 **b**	0.18 ± 0.00 **d**	0.17 ± 0.01 **d**	0.22 **b**
Mn treatment (0.2 mg l^{-1})	0.35 ± 0.01 **c**	0.18 ± 0.01 **d**	0.18 ± 0.01 **d**	0.24 **c**
pH treatment means	0.31 **a**	0.18 **b**	0.17 **c**	

Standard error for comparing two pH treatment or two manganese treatment means : 0.002; LSD at 0.001 significance level : 0.009 for both pH and manganese treatment means.

Standard error for comparing two values inside the body of the table (interaction) : 0.007; LSD at 0.001 significance level : 0.018.

Table II shows that although manganese concentration in the simulated throughfall contributed significantly ($p \leqslant 0.001$) to the concentration of manganese in leachate, its influence apparently was not as strong as the effect of pH treatments. However, it must be remembered that pH is expressed on a log scale, so differences of one unit mean a tenfold increase or decrease in the concentration of hydrogen ions. The authors decided that there was no point in this experiment in using concentrations of manganese in throughfall which were unrealistically high, and well above the usual range (0—0.2 mg l^{-1}) found in throughfall.

Table II also illustrates the interaction between pH and manganese concentration in the simulated throughfall solution treatments. The lowest value (0.15 mg l^{-1}) was attained at the combination of pH 5.3 and no addition (0 mg l^{-1}) manganese whereas the highest (0.35 mg l^{-1}) was at the combination of pH 3.3 and 0.2 mg l^{-1} addition of manganese. It is highly likely that manganese in the throughfall is adsorbed on the exchange sites of the litter, with an almost corresponding amount being instantaneously removed by hydrogen ions. This is important in terms of manganese cycling, because it shows the significance of the combination of high concentrations of manganese and low pH in throughfall in the rapid removal of manganese from the exchange sites of the litter.

Time was a highly significant factor ($p \leqslant 0.001$) in determining manganese concentration in leachates. Figures 1 (A) and 1 (B) show how manganese concentrations in leachates changed over time for different pH and manganese treatments. In both graphs the three lines showing concentrations of manganese in leachates tend to approach a similar manganese concentration during the final stages of leaching. Although the equilibrium manganese concentrations are pH dependent to some extent (Fig. 1, left), the pH 4.3 and 5.3 treatments give similar manganese equilibrium concentrations in drainage water. The results (Fig. 1, right) also appear to suggest that mineralization of the litter was resulting in a manganese concentration in leachate of *c.* 0.2 mg l^{-1} for the zero manganese treatments. For the elevated manganese treatments at 0.2 mg l^{-1}, if the rate of release on manganese by mineralisation remains the same as that for the zero manganese treatments, then the rate of manganese retention from the simulated precipitation input appears to balance almost the rate of manganese

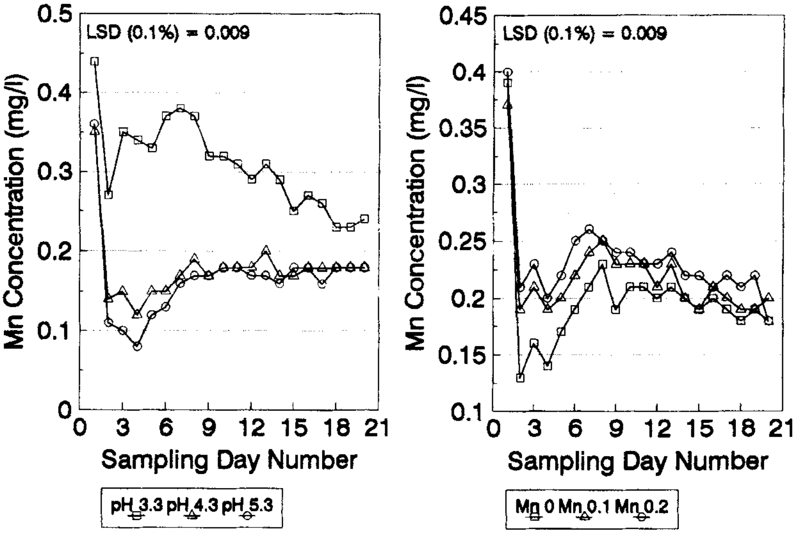

FIGURE 1 Changes, over time, in mean manganese concentration of leachates, over all throughfall manganese treatment concentrations, for the three pH treatments shown (left) and over all pH treatments for the three manganese treatment concentrations (mg l^{-1}) shown (right).

leaching following mineralisation. In spite of this, the highest manganese treatments significantly increased the exchangeable manganese concentration in the litter.

Exchangeable Manganese

The pH 3.3 treatment was the only pH treatment that was highly significant in determining the amount of exchangeable manganese left in litter after the 20 days of leaching (Fig. 2, left). These results agree with those of Senesi *et al.* (1989), who found that organic matter formed stable complexes with manganese at near neutral pH, but complexes were increasingly disrupted by increasingly acidic conditions. Another possible reason for the drastic effect of the pH 3.3 treatment might be a reduction in rate of litter decomposition. This would result in a slower mineralisation rate for organically bound manganese, resulting, in combination with increased manganese leaching, in less exchangeable manganese. It has been found that acid rain

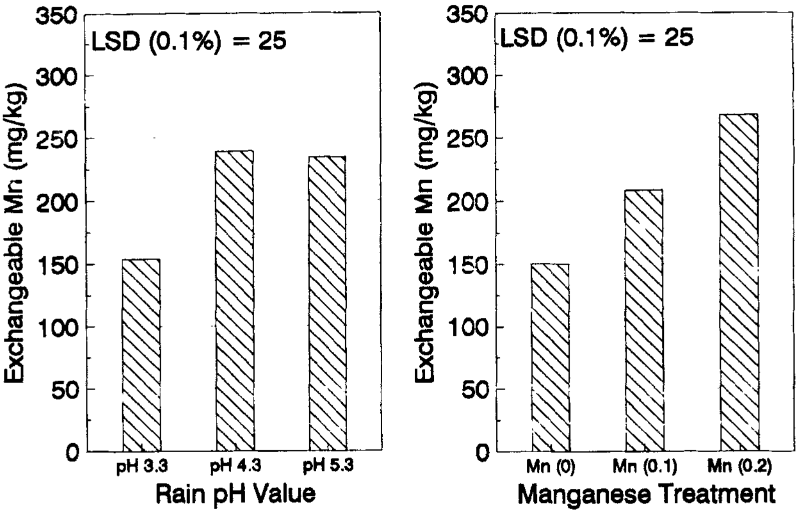

FIGURE 2 Effect of simulated throughfall pH (left) and manganese (right) treatments upon the mean exchangeable manganese concentrations of the litter at the end of the experiment.

can inhibit microbial growth (e.g., Alexander, 1980; Brown, 1985). It would have been of interest to observe changes in exchangeable manganese with time, but that would have involved destructive sampling, something not feasible in this experiment.

Manganese concentration in the simulated throughfall solution significantly ($p \leqslant 0.001$) affected the concentration of exchangeable manganese (Fig. 2, right). Cation exchange was probably the dominant mechanism, since each simulated throughfall input concentration gave a corresponding increase in the exchangeable manganese value. This build-up of exchangeable manganese in forest litter is important in terms of plant nutrition. Although low pH throughfall leaches signficant amounts of manganese from litter, losses in litter exchangeable manganese can be replenished, at least partly, by manganese inputs from enhanced foliar leaching. Senesi and Sposito (1989) argued that although fresh litter material might be depleted initially of a large portion of its native micronutrient content (in particular, manganese), it can re-adsorb metal ions from the surrounding environment and retain them mainly in complexed, acid-stable forms. Such complexation might be the main defensive mechanism of litter against excessive manganese depletion due to acid deposition.

CONCLUSIONS

The pH treatments highly affected significantly manganese concentration in the leachates. Manganese concentration in the leachates was found to be approximately proportional to the hydrogen ion concentration in the simulated throughfall solution. Cation exchange on the litter surfaces is believed to be the primary mechanism involved.

The manganese treatment effects on manganese concentrations in the leachates were also highly significant, although their effect was not as marked as the pH treatment effects, partly because of the smaller, more regular ionic concentration steps for the manganese treatments.

Interaction between manganese concentration in the simulated throughfall solution and pH treatments was found to be highly significant for manganese concentration in leachate. The lowest value of pH and the highest manganese throghfall concentration gave the highest value of manganese in leachates, which indicates reduced manganese adsorption and/or subsequent removal by hydrogen ions.

The pH 3.3 treatment was by far the most efficient in removing exchangeable manganese from litter. However, manganese in the leaching solution contributed to a build-up of exchangeable manganese, thus offering some resistance to leaching due to increased acid conditions. However, it should be remembered that the litter was subjected to the equivalent of 2 years of throughfall over 20 days, so that mineralisation of organically bound manganese would not be taken fully into account in this experiment. It should also be realised that throughfall with a pH of 3.3. would only be experienced at a grossly polluted site.

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