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Calcium content of liming material and its effect on sulphur release in a coniferous forest soil

INGER VALEUR[1,*], STEFAN ANDERSSON[2] & S. INGVAR NILSSON[2]
[1]*Department of Ecology and Environmental Research, PO Box 7072;* [2]*Department of Soil Sciences, PO Box 7014, Swedish University of Agricultural Sciences S–750 07 Uppsala, Sweden (*Corresponding author present address: Department of Ecology, Plant Ecology, University of Lund, Ecology Building, S–223 62 LUND, Sweden)*

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Abstract. Soil columns with O + A (Experiment I) or O horizons (Experiment II) from a Haplic Podsol were incubated at 15 °C for 368 and 29 + 106 days, respectively. Three types of liming material differing in Ca^{2+} content, i.e. calcium carbonate ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and magnesium carbonate ($MgCO_3$), were mixed into the O horizons in equimolar amounts corresponding to 6000 kg of $CaCO_3$ per ha. In the limed treatments of Experiment I, the leaching of dissolved organic carbon (DOC) and the net sulphur mineralization (estimated as accumulated SO_4^{2-} leaching corrected for changes in the soil pools of adsorbed and water extractable SO_4^{2-}) increased with decreasing Ca^{2+} content of the lime and increasing degree of lime dissolution. In relation to the control treatment, only the $MgCO_3$ treatment resulted in a significantly higher net sulphur mineralization. In Experiment I the net sulphur mineralization was 4.06, 1.68, 0.57, and 2.14 mg S in the $MgCO_3$, $CaMg(CO_3)_2$, $CaCO_3$ and control treatment, respectively. The accumulated SO_4^{2-} leaching in Experiment II during the first 29 days was 1.70, 0.74 and 0.48 mg S in the $MgCO_3$, $CaMg(CO_3)_2$ and control treatment, respectively. In the two experiments there were consistently significant positive correlations between leached amounts of SO_4^{2-} and DOC. It was concluded that net sulphur mineralization was strongly connected to the solubilization of the organic matter (DOC formation) and that pH and/or Ca^{2+} ions affected the net sulphur mineralization through their effects on organic matter solubility.

Introduction

The anion concentration in the soil solution is a crucial factor affecting soil acidifying processes (Seip 1980). Factors increasing concentrations of SO_4^{2-} and other anions in the soil solution will also increase the concentration of base cations which are lost from the soil through leaching. The SO_4^{2-} concentration in the soil solution will increase in response to changes in S input in the form of "acid rain", as well as to sulphur mineralization or SO_4^{2-} desorption.

Even though 50% of the organically bound S in soils is assumed to be inactive in turnover processes, there is still a large pool available for SO_4^{2-} release, and the contribution from the mineralization of organic sulphur can be of great importance (Eriksen et al. 1995a, b). This is of particular interest in soils only weathered to a low or moderate extent, where SO_4^{2-} adsorption/desorption processes are of less importance compared with strongly weathered soils (Rochelle et al. 1987).

In addition to efforts aimed at reducing emission levels of S, attempts have been made to improve the chemical status of forest soils by introducing different types of alkalizing substances such as $CaCO_3$ (calcium carbonate), $CaMg(CO_3)_2$ (dolomite) and wood ash. In response to an increase in pH, the organic matter becomes more negatively charged and hydrated, and therefore more water soluble and available for microbial and biochemical attack (Brunner & Blaser 1989) which in turn increases the mineralization rate of mineral nutrients such as S, P and N (Marschner & Wilczynski 1991; Bååth et al. 1995; Eriksen et al. 1995a, b). A sufficient rise in pH will also convert the organic matter-stabilizing Al^{3+} to $Al(OH)_3$ precipitates, thus further increasing the solubility of the organic matter. In addition to the rise in pH, the properties of the cations in the liming material itself will also affect the humic substances. A large proportion of Ca^{2+} ions may stabilize the organic matter (Römkens et al. 1996) and thus decrease the amount of dissolved organic carbon (DOC). It is not entirely clear how or by what mechanism a change in these factors will affect the net sulphur mineralization.

Several studies have been made on the initial effects of liming on net sulphur mineralization (Freney & Stevenson 1967; Williams 1967; Korentajer et al. 1983; Haynes & Swift 1988; Marschner 1993) where the effect of lime seems to be to enhance mineralization. The apparent increase in net sulphur mineralization observed in short-term experiments has been partly attributed to chemical hydrolysis of organic matter at high pH. However, in a study of sterilized and nonsterilized soil Marschner (1993) found that the small effect of chemical hydrolysis was very brief ($<$ 2 weeks), and the following net SO_4^{2-} release was ascribed to microbial mineralization processes, including the enzymatic hydrolysis (biochemical mineralization) of organic ester sulphates. In long-term liming experiments the effect of liming upon net sulphur mineralization is not very clear and there are conflicting results in the literature (Marschner 1993; Valeur & Nilsson 1993; Valeur et al. unpublished). One of the differences between the above cited studies was the presence or not of an A-horizon. Studies including both a limed O horizon and an A (or E) horizon initially unaffected by the liming, resulted in a higher net sulphur mineralization in the limed treatments compared to control treatments whereas the reverse result indicating a lime-induced S net immobilization was found when only an O horizon was used (Valeur & Nilsson 1993; Valeur et al. unpublished). The solubility of the highly humified organic matter in an A horizon may be very sensitive to changes in pH or dominating cation (Skyllberg & Magnusson 1995). If the net sulphur mineralization was positively related to the amount of dissolved organic matter it would then also mean that an A (or E) horizon may have a significant influence on the net sulphur mineralization in the upper part of podsolised forest soils.

The main questions to be asked in this paper are:

1. How is the solubility of organic matter affected by Ca^{2+} or Mg^{2+} either originating from the added liming materials or added as neutral salts?
2. Is there any connection between organic matter solubility and net sulphur mineralization? An additional question is:
3. How will the presence of an initially unlimed A horizon affect the net sulphur mineralization pattern.

Material and methods

Study site

The Hasslöv forest liming field experiment is situated 10 km from the west coast of Sweden (56°24′ N, 13°00′ E, 190 m above sea level). The annual mean temperature is 6.5 °C, and the mean annual precipitation is 1100 mm. The vegetation consists of a planted 50-year-old Norway spruce stand (Picea abies Karst.). The soil is a Haplic Podsol (FAO 1988) on a sandy loam moraine.

We conducted two different laboratory experiments to address the questions stated above. In Experiment I, samples from five soil horizons, i.e., Oi (surface litter), Oe, Oa, A1 and A2, were collected in August 1990 just outside the field plots. A typical E horizon could not be distinguished, as the strongly weathered soil material was coated with humic matter. The field-moist soil was brought to the laboratory and sieved through a 5-mm screen. Samples were stored for 23 days in a refrigerator at +3 °C.

The incubation columns were constructed from PVC tubes with a length of 16 cm and a diameter of 6.7 cm. They were equipped with a bottom plate furnished with a drainpipe (3 mm diameter) connected to a vacuum system. A plastic filter plate (approx. pore diameter 15 μm) was placed 10 mm above the bottom plate.

Portions of sieved Oi (3.22 g dw), Oe (9.66 g dw), Oa (3.22 g dw), A1 (30.78 g dw) and A2 horizon material (153.87 g dw), were placed in this order in each column. The initial moisture content (per gram dry weight) was

230% in Oi, 289% in Oe, 221% in Oa, 56% in A1 and 35% in A2. At the end of the experiment the corresponding moisture content was 58, 213, 210, 101 and 58% respectively.

The columns were kept at a constant temperature (15 °C). There were four replicates for each of three lime treatments and a control, making a total of 16 columns. The lime treatments were calcium carbonate ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and magnesium carbonate ($MgCO_3$). Lime was added to the O horizons by mixing, in proportion to the soil horizon weights. The same molar amount of carbonate was added to each column, corresponding to a calcium carbonate treatment of 6000 kg per ha which was equivalent to 21.1 mmol CO_3-C/column. The water content in the columns was adjusted each week by adding distilled water in amounts corresponding to the soil evaporation (approximately 2 ml/day).

The columns were irrigated before each collection event with 50 ml HCl (pH 4.3). The total amount of HCl solution added per column was 0.82 L which corresponded to 0.04 mmol H^+. After about 5 min. approximately 50 ml of soil solution was collected by suction and immediately passed through a 0.45-μm millipore filter (Millipore HA 0.45 HAWPO4700), which had been rinsed beforehand with 50 ml distilled water to remove contaminating DOC. Samples from the columns were collected every second week during the first half of the experiment and once a month during the second half (after 180 days). pH measurements in the leachates were made on the same day as the leachate collection. Water samples for analyses of SO_4^{2-} and NO_3^- and total dissolved S were kept frozen until analyzed. Initially this was also the case for water samples intended for DOC analysis. We eventually checked the effect of freezing on the DOC concentrations and found a small decrease of about 1% as an average for all treatments. Thereafter we decided to store the samples for a maximum of one week in a refrigerator (+3 °C) before analysis. After sample collection the moisture content in all columns was adjusted to the same level with distilled water.

In Experiment II the A horizon was excluded. Samples from the O horizon (Oe + Oa) (no surface litter included), were collected in November 1996 from four control plots in the Hasslöv experimental area. The same column type as above was used and portions of fresh O-horizon material (19.32 g dry weight) were placed on top of 40 g (dry weight) ignited and acid-washed quartz sand which was used to establish capillary contact with the humus material. The addition of lime to the columns was performed in the same way as above. Calcium carbonate was excluded in this experiment, resulting in a total of 12 columns. At the start of the experiment the water content in the O horizon was 335% by dry weight. During the experiment the average water content of the whole column including the quartz sand was 115% by dry weight. This average water content was further examined using two identical extra soil columns and was found to correspond to 300% by dry weight for the O horizon and 25% for the quartz sand. The experiment was run for a total duration of 135 days. At percolation event 4, 50 ml $MgCl_2$ or $CaCl_2$, (0.114 M) was added to the columns (5.7 mmol Ca or Mg per column). Two columns from each treatment were treated with $CaCl_2$ and the remaining two columns with $MgCl_2$. Thereafter the columns were irrigated with distilled water. The purpose of the salt additions was to specifically study the effects of the Ca^{2+} and Mg^{2+} ions on the DOC level (organic matter stabilization), when no additional carbonate was added together with the cations.

Analytical methods

Dry weight was obtained after drying approximately 5 g of soil material for 24 h at 105 °C. Soil pH (pH_{H2O}) was measured after 2 h extraction with distilled water (weight proportion 2:7), followed by 24 h sedimentation at room temperature. $pH_{(H2O)}$ was measured electrometrically with a combination electrode. Total C, N and S in the solid soil material were determined using a Leco CNS analyzer. CO_3-C was determined on previously ashed soil material (550 °C) with a dry combustion procedure at 1000 °C using a Carlo-Erba CN analyzer.

Analyses for water extractable and $Ca(H_2PO_4)_2{*}H_2O$ extractable SO_4^{2-} were done at the start and at the end of the experiment. Both O and A horizons were extracted with water, whereas only the A horizons were extracted with $Ca(H_2PO_4)_2{*}H_2O$ as we did not expect any adsorbed SO_4^{2-} in the O horizons (see Discussion and Maynard et al. (1987)).

Adsorbed SO_4^{2-} in the mineral soil horizons (A1 and A2) was estimated by subtracting water extractable SO_4^{2-} from $Ca(H_2PO_4)_2{*}H_2O$ extractable SO_4^{2-}. The $Ca(H_2PO_4)_2{*}H_2O$ had a concentration of 0.01 M with regard to P and the weight proportion for all extractions was 1:20. The extracts were passed through OOK filter paper and then through 0.45-μm millipore filter paper (Millipore HA 0.45 HAWPO4700).

Total dissolved S, Ca^{2+} and Mg^{2+} in the leachates were analyzed by ICP. Anions in leachates and soil extracts, i.e. SO_4^{2-} and NO_3^-, were analysed on an ion chromatograph equipped with a Dionex column. The dissolved organic S (DOS) content in the leachates was calculated as the difference between total S and SO_4^{2-}-S. DOC analyses were performed on a Shimadzu TOC-500 analyser after Millipore filtration. The samples were purged with HCl before DOC analysis to remove dissolved inorganic carbon.

Calculations

(a) The amount of C lost through microbial respiration (ΔC_{net}) was estimated from the carbon budget as: [Total C loss] – [CO_3-C loss from added lime] – [C loss in leachates as DOC]. This indirect estimate of the microbial respiration (ΔC_{net}) was used because we failed to get reliable data for the limed treatments of the CO_2 release measured by gas chromatography.

(b) Amounts of dissolved components in the leachates at each collection event (mg per soil column) were obtained by multiplying mutually connected concentrations and volumes. These amounts were then summed to obtain the accumulated leaching for the whole experimental period.

(c) Net SO_4^{2-} release (i.e. the estimate of net sulphur mineralization) was obtained as: [Leached SO_4^{2-}] – Δ[Adsorbed SO_4^{2-}] – Δ[Water extractable SO_4^{2-}], where Δ[Adsorbed SO_4^{2-}] was the net change in adsorbed SO_4^{2-} in the A horizons during the course of the experiment, (the initial value minus the final value). Δ[Water extractable SO_4^{2-}] in the O and A horizons was obtained in an analogous manner.

(d) Differences between treatments were analyzed by one-way ANOVA and LSD (least significant difference) calculations. Statistical significance was set at $p < 0.05$. Relationships between individual variables were also tested by calculating correlation coefficients.

Results

Experiment I

Some general chemical information about the soil is presented in Table 1. The soil was strongly acidic and had a low C/N ratio compared with other Swedish podzolized forest soils (Persson & Wirén 1995). The C/S ratio was within the range of values typically reported for podzolised forest soils (David et al. 1995).

By the end of Experiment I, a pronounced increase in $pH_{(H2O)}$ had occurred throughout the O horizon (Oe + Oa) in all lime treatments (Tables 1 and 2). At these pH values most of the aluminium should have precipitated as $Al(OH_3)$. Also, a slightly higher pH value was noted in the A1 and A2 horizons in the $CaMg(CO_3)_2$ and $MgCO_3$ treatments compared to the control treatment (Table 2). Thus the organic topsoil was strongly influenced by the lime, whereas the mineral soil layers were only slightly affected.

During the first part of the experiment, leachate pH was highest in the control (Figure 1(a)). After Day 225, however, it began to decrease in the

Table 1. General information about the soil in Experiment I and II, based on chemical analyses at the start of the experiments.

Horizon	$pH_{(H2O)}$	C/N	C/S
Oi		25	262
Oe + Oa	4.3	24	199
A1	4.4	21	160
A2	4.7	20	157

Table 2. $pH_{(H2O)}$ in different soil horizons at the end of Experiment I in the control, $CaCO_3$, $CaMg(CO_3)_2$ and $MgCO_3$ treatments. In each column, values with different letters are statistically different ($p < 0.05$). The O horizon includes Oe + Oa.

Treatment	O horizon	A1 horizon	A2 horizon
Control	4.2^d	4.0^b	4.0^c
$CaCO_3$	7.7^b	4.2^b	4.1^{bc}
$CaMg(CO_3)_2$	7.0^c	4.5^a	4.2^b
$MgCO_3$	8.4^a	4.5^a	4.4^a

control, and by the end of the experiment the control value was the lowest one (Figure 1(a)). In all limed treatments there was an obvious decrease in leachate pH which reached a minimum value around Day 50. On Day 193, the leachate pH began to differ between the lime treatments, and by the end of the experiment the highest pH values occurred in the $MgCO_3$ treatment, followed by the $CaMg(CO_3)_2$ and $CaCO_3$ treatments (Figure 1(a)). This order was the same as that of the relative degree of lime dissolution (Table 3).

A high nitrification rate was indicated by the temporal development of the NO_3^- concentrations in the leachates (Figure 2). There were no significant differences in NO_3^- concentration among the limed treatments. Initially, the control treatment had a considerably lower concentration than the limed treatments, and the concentrations in all treatments mirrored the pH values (Figures 2 and 1(a)), which was a further indication of an ongoing nitrification process. By the end of the experiment the nitrification rate seemed to have increased in the control to a level similar to that in the limed treatments. (Figure 2). During the main part of the experiment, the DOC concentration in the control leachates was considerably higher than that of the limed treatments and showed a much more fluctuating pattern, but by the end of the experiment the concentration had approached the same level as the lime treat-

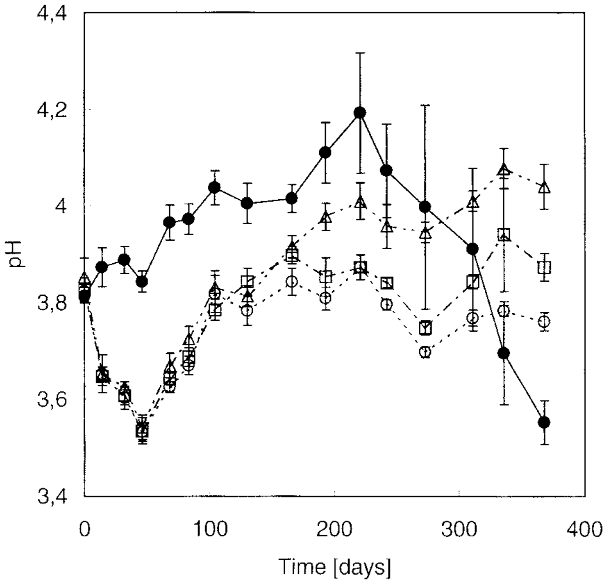

Figure 1a. pH in the leachates during the course of Experiment I. Error bars = 2 SD. ——●—— Control – –□– – Dolomite – –○– – Calcium carbonate – –Δ– – Magnesium carbonate.

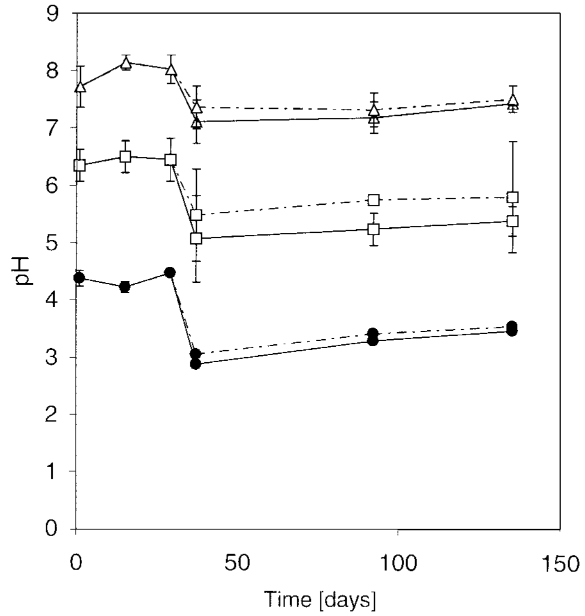

Figure 1b. pH in the leachates during the course of Experiment II. Error bars = 2 SD. ——●—— Control+Ca ——□—— Dolomite+Ca —Δ— Magnesium carbonate+Ca – –●– – Control+Mg – –□– – Dolomite+Mg – –Δ– – Magnesium carbonate+Mg.

Table 3. Carbon balance at the end of Experiment I expressed as mg C per column in the control, $CaCO_3$, $CaMg(CO_3)_2$ and $MgCO_3$ treatments. ΔCtot includes CO_3-C and DOC. ΔCnet is the estimated CO_2 respiration. In each column, values with different letters are statistically different ($p < 0.05$).

	ΔCtot	ΔCnet	CO_3–C
	[mg]		% C dissolved of initially added amount
Control	879^b	822^a	
$CaCO_3$	1552^a	1483^b	15
$CaMg(CO_3)_2$	1635^a	1480^b	49
$MgCO_3$	1736^a	1416^b	93

ments, and the latter treatments appeared in the order $MgCO_3 > CaMg(CO_3)_2 > CaCO_3$ (Figure 3a).

The estimated CO_2 respiration or carbon mineralization (ΔC_{net}) indicated that the biological activity was significantly higher in all limed treatments compared to control treatment (Table 3). The amount of carbonate-C left in the soil at the end of the incubation experiment differed depending on lime type, as a result of apparent differences in dissolution rate, i.e. $CaCO_3 > CaMg(CO_3)_2 > MgCO_3$ (Table 3). There was no clear relationship between ΔC_{net} and net sulphur mineralization.

The SO_4^{2-} concentration in the leachates decreased in all treatments during the first 90–100 days. After Day 220, there was an increase in the $MgCO_3$ treatment (Figure 4). Practically the whole amount of the initially adsorbed SO_4^{2-} was desorbed from the A horizons during the experimental time (Table 4). The change in water extractable SO_4^{2-}, accounted for 4 to 24% of the total SO_4^{2-} release depending on treatment. The largest depletion in water extractable SO_4^{2-} was found in the $CaCO_3$ treatment. In the O horizon, a net increase was actually found in the control treatment and to a smaller extent also in the $MgCO_3$ treatment (data not shown).

The net release of SO_4^{2-} (net sulphur mineralization) for the whole experimental period was highest in the $MgCO_3$ treatment and lowest in the $CaCO_3$ treatment, with values for the control and the $CaMg(CO_3)_2$ treatments being intermediate ($CaMg(CO_3)_2 <$ control) (Table 4; Figure 4). Accumulated amounts of leached DOC, DOS and SO_4^{2-} in the lime treatments tended to decrease with increasing initial Ca^{2+} content of the lime, and to increase with the total amount of dissolved lime by the end of the experiment (Tables 3 and 4). The Ca^{2+} and Mg^{2+} concentrations in the leachates, clearly reflected

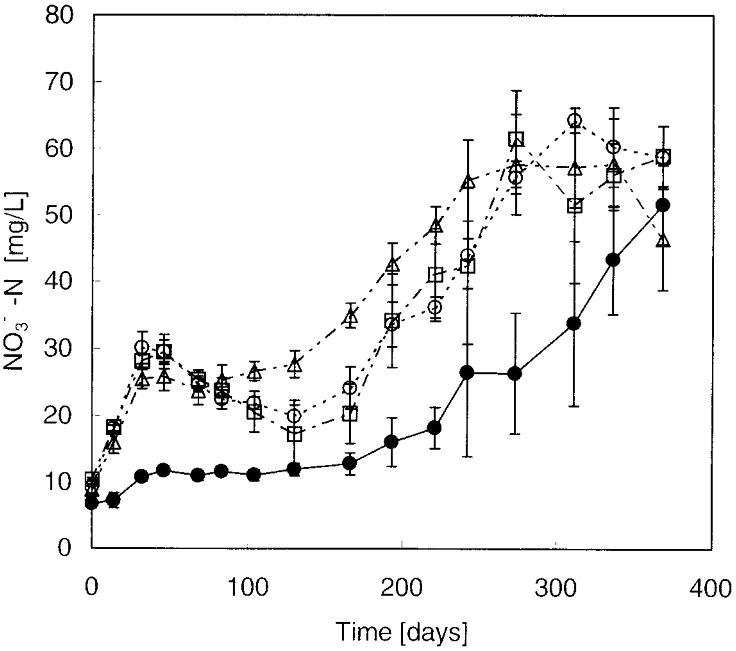

Figure 2. NO_3^- (mg N/L) in the leachates during the course of Experiment I. Error bars = 2 SD. ——●—— Control – –□– – Dolomite – –○– – Calcium carbonate – –△– – Magnesium carbonate.

the Ca^{2+} and Mg^{2+} contents of the lime. The transport time of the Ca^{2+} and Mg^{2+} ions through the soil horizons was indicated by the temporal changes in leachate concentrations (Figures 5 and 6). In spite of the seemingly higher dissolution rate of $CaMg(CO_3)_2$ (Table 3), there was no increase of the Ca^{2+} ions in the leachate water of this treatment until after Day 150 which was much later than for the $CaCO_3$ treatment (Figure 5 and Table 3).

From Day 193 to the end of the experiment (Day 368), positive correlations between pH and SO_4^{2-} (limed treatments) and pH and log DOC (both control treatment and limed treatments) were found (Table 5). For the experimental period between Day 14 and Day 368 there was a positive correlation between the accumulated SO_4^{2-} leaching and the accumulated DOC leaching both in the control treatment and in the limed treatments, although the correlation for the control treatment was barely significant ($p < 0.065$). Similar positive relationships were also found for accumulated DOC leaching versus accumulated DOS leaching (Table 5). In the two latter correlations the first two weeks were excluded, as there were indications of a net leaching of initially water soluble + adsorbed SO_4^{2-} during this period (Figure 4).

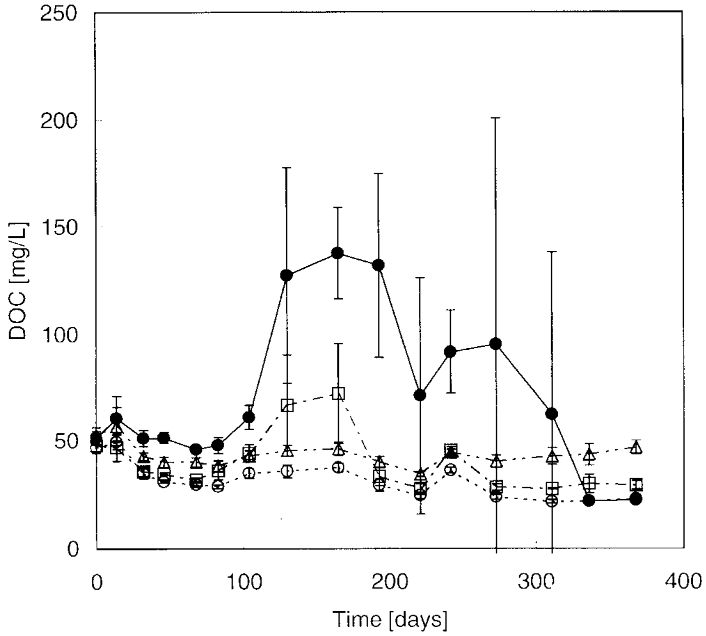

Figure 3a. DOC (mg C/L) in the leachates during the course of Experiment I. Error bars = 2 SD. ——●—— Control – –□– – Dolomite – –○– – Calcium carbonate – –Δ– – Magnesium carbonate.

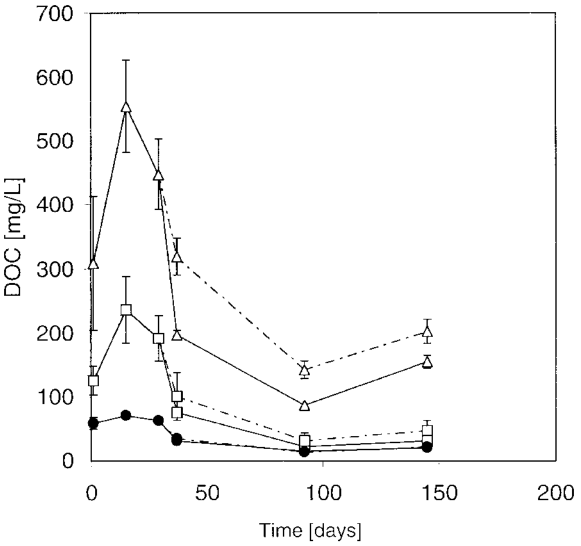

Figure 3b. DOC (mg C/L) in the leachates during the course of Experiment II. Error bars = 2 SD. ——●—— Control+Ca ——□—— Dolomite+Ca ——Δ—— Magnesium carbonate+Ca – –●– – Control+Mg – –□– – Dolomite+Mg – –Δ– – Magnesium carbonate + Mg.

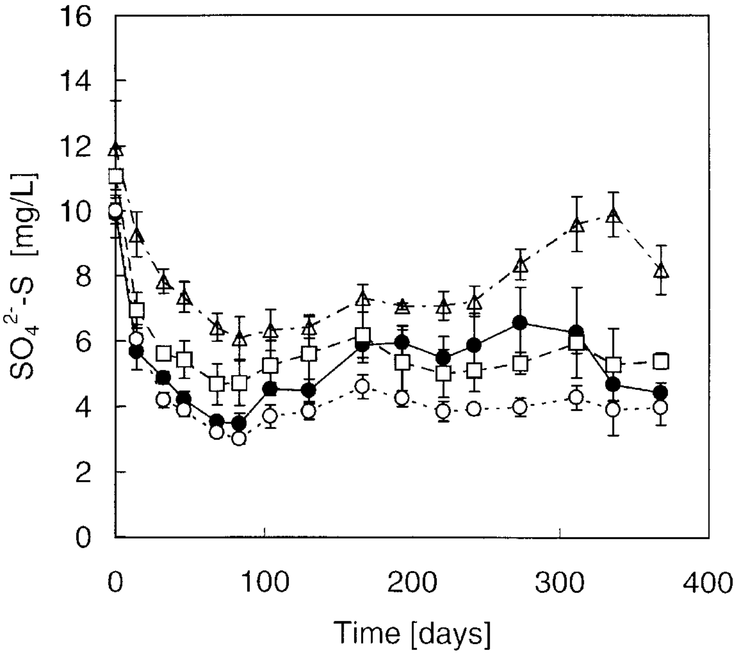

Figure 4. SO_4^{2-} (mg S/L) in the leachates during the course of Experiment I. Error bars = 2 SD. ——●—— Control – –□– – Dolomite – –○– – Calcium carbonate – –Δ– – Magnesium carbonate

Experiment II

As expected, the pH values in the leachates of the lime treatments were higher than in Experiment I, as untreated acid mineral soil (A horizon material) was not included in this experiment (Figures 1(a) and (b)). pH was already significantly different at the start of the experiment in the order control < $CaMg(CO_3)_2$ < $MgCO_3$ (Figure 1(b)). At percolation event 4, there was a decline in pH in all treatments due to the additions of $CaCl_2$ or $MgCl_2$ (Figure 1(b)). There were also significant differences between the treatments with respect to the accumulated amounts of leached SO_4^{2-} (Table 4). These amounts decreased in the order $MgCO_3$ > $CaMg(CO_3)_2$ > control. Note that no corrections were made for changes in the water extractable or $Ca(H_2PO_4)_2$ extractable SO_4^{2-} pools (see Discussion). The accumulated amount of leached DOC decreased significantly in the same order as SO_4^{2-}. There was a significantly lower DOC/SO_4^{2-} ratio in the control compared to the limed treatments mainly as a result of the considerably higher DOC leaching in the limed treatments (Table 4). For the leachates including the control treatment, there were significant correlations (Days 0–29) between accumulated DOC and both

Table 4. Net release of SO_4^{2}, Δ[Adsorbed SO_4^{2-}], Δ[Water extractable SO_4^{2-}] and DOS (all in mg S/column) and DOC (mg C/column). Net release of SO_4^{2-} = [Leached SO_4^{2-}] – Δ[Adsorbed SO_4^{2-}] – Δ[Water extractable SO_4^{2-}] (see text). Also shown are the accumulated DOC/DOS and DOC/ SO_4^{2-}-S ratios (w/w). The data of Experiment I are shown for the whole period (368 days) and for the first 32 days for comparison with Experiment II (29 days). Values with different letters are statistically different ($p < 0.05$).

	Horizons	Net release of SO_4^{2-}	Δ Ads. SO_4^{2-}	ΔWater extract SO_4^{2-}	DOS	DOC	DOC/ DOS	DOC/ SO_4^{2-}-S
		mg S				mg C		
Experiment I								
Days 1–368								
Control	O+A	2.14^{a}	2.07^{a}	0.19^{a}	0.67^{b}	57.7^{a}	86.7^{a}	24.5^{a}
$CaCO_3$	O+A	0.57^{b}	2.00^{a}	0.82^{b}	0.66^{b}	24.5^{c}	37.4^{b}	17.2^{b}
$CaMg(CO_3)_2$	O+A	1.68^{a}	2.05^{a}	0.70^{b}	0.79^{a}	30^{bc}	38.5^{b}	12.8^{b}
$MgCO_3$	O+A	4.06^{c}	1.97^{a}	0.37^{a}	0.79^{a}	35.7^{b}	45.2^{b}	8.06^{b}
Days 1–32								
Control	O+A	1.12^{*}			0.23	9.17	41.4	8.3
$CaCO_3$	O+A	1.02^{*}			0.16	6.85	43.0	6.7
$CaMg(CO_3)_2$	O+A	1.24^{*}			0.23	6.98	31.0	5.6
$MgCO_3$	O+A	1.57^{*}			0.19	8.39	44.2	5.3
Experiment II								
Days 1–29								
Control	O	0.48^{a*}			0.05^{a}	8.83^{a}	221^{a}	18.2^{a}
$CaMg(CO_3)_2$	O	0.74^{b*}			0.13^{a}	24.7^{b}	207^{a}	33.1^{b}
$MgCO_3$	O	1.70^{c*}			0.38^{b}	54.3^{c}	156^{a}	31.7^{b}

* Not corrected for changes in SO_4^{2-} adsorption or water extractable SO_4^{2-}

accumulated SO_4^{2-} and DOS (Table 5). There was also an obvious positive covariation between leachate pH and DOC (Figures 1(b) and 3(b); Table 5). Leachate pH and SO_4^{2-} showed a similar (exponential) positive relationship (Table 5).

At percolation event 4, DOC became significantly lower in the $MgCO_3$ treatment after $CaCl_2$ addition, than after $MgCl_2$ addition (Figure 3(b)). The addition of either $CaCl_2$ or $MgCl_{2,}$ lowered the leachate pH (Figure 1(b)) but there was no significant difference between the two salt additions in

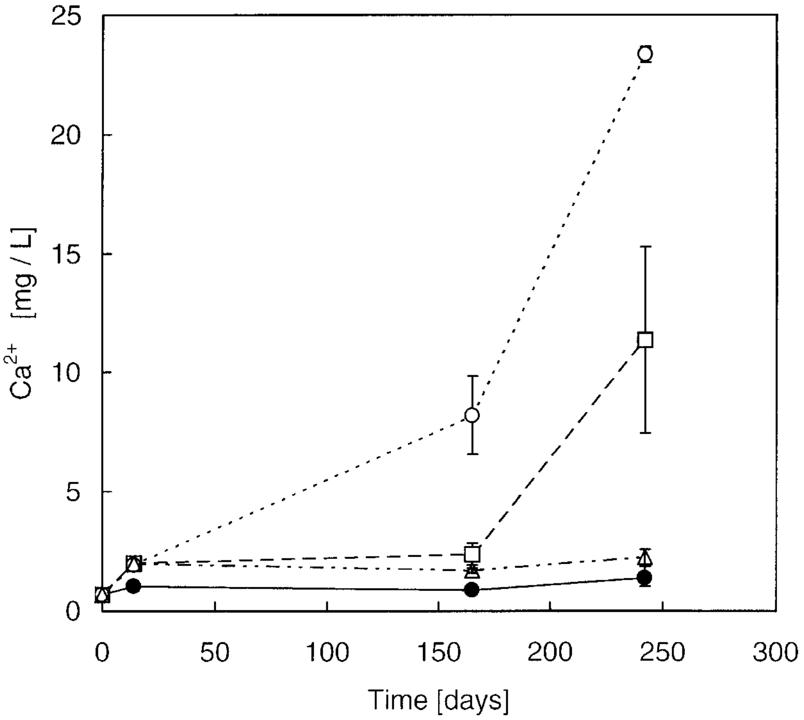

Figure 5. The Ca^{2+} concentration (mg/L) in the leachates on Day 14, 165 and 242 in Experiment I. Error bars = 2 SD. ——●—— Control – –□– – Dolomite – –○– – Calcium carbonate – –Δ– – Magnesium carbonate.

this respect. Similar to the relations prior to the salts additions, there was a positive but weaker, correlation between DOC and leachate pH ($r^2 = 0.58$, $p < 0.001$). Unfortunately, problems with disturbing Cl^- ions made the SO_4^{2-} analyses unreliable.

Discussion

Net SO_4^{2-} release as an estimate of net sulphur mineralization

Previous investigations have shown that the amount of adsorbed SO_4^{2-} in O horizons is negligible (Maynard et al. 1987; Valeur & Nilsson 1993). Therefore, only changes in the water extractable SO_4^{2-} pool were determined in the O horizons of Experiment I, while changes in the $Ca(H_2PO_4)_2$ extractable SO_4^{2-} pool were determined in the A horizons. We are confident that net SO_4^{2-} release according to our definition, should provide a good estimate of

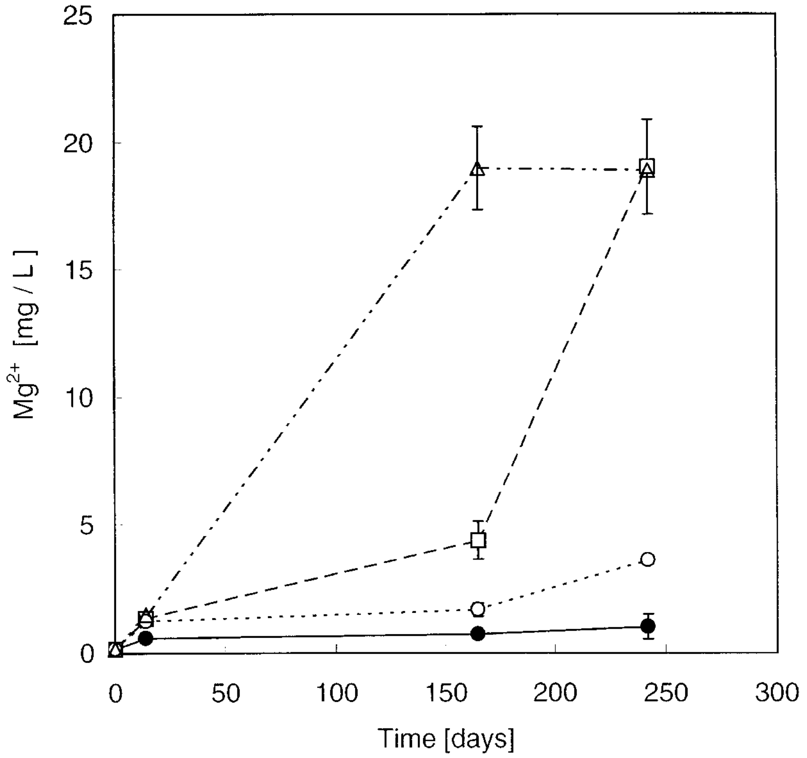

Figure 6. The Mg^{2+} concentration (mg/L) in the leachates on Day 14, 165 and 242 in Experiment I. Error bars = 2 SD. ——●—— Control – –□– – Dolomite – –○– – Calcium carbonate – –Δ– – Magnesium carbonate

the relative differences among the treatments in net sulphur mineralization. In Experiment II, where only the O horizon was included we made no correction for changes in the water extractable SO_4^{2-} pool. There was qualitative agreement between the two experiments in that both net SO_4^{2-} release and SO_4^{2-} leaching in Experiment I, and SO_4^{2-} leaching in Experiment II were highest in the $MgCO_3$ treatment (Table 4; Figure 4).

SO_4^{2-} desorption

An increase in pH in the mineral A horizon should decrease the number of positively charged sites available for SO_4^{2-} adsorption (e.g. Courchesne & Hendershot 1989). The total number of potential adsorption sites should be rather small, however, as the A horizon consisted of strongly weathered soil material which was coated with humic matter and was likely to have a low content of Al and Fe oxides (Karltun & Gustafsson 1993). Theoretically, a pH

Table 5. Correlations (R^2) between DOC, DOS, SO_4^{2-} and pH in the leachates of Experiment I and Experiment II. $p < 0.001$ if not otherwise stated. ns = not statistically significant.

Experiment I

Treatments	Control	Limed	Accumulated amount Control	Accumulated amount Limed
Days	193–368	193–368	14–368	14–368
SO_4^{2-} – DOC	–	–	0.87 ($p < 0.065$)	0.88
DOC – DOS	–	–	0.95 ($p < 0.05$)	0.66 ($p < 0.01$)
logDOC – pH	0.75	0.53		
SO_4^{2-} – pH	ns	0.45		

Experiment II

Treatments	Control + Limed	Accumulated amount Control + Limed
Days	1–29	1–29
SO_4^{2-}– DOC	–	0.97
DOC – DOS	–	0.89
DOC – pH	0.91	
SO_4^{2-} – pH	0.78	

induced SO_4^{2-} desorption would be expected in two of the limed treatments in Experiment I ($CaMg(CO_3)_2$ and $MgCO_3$) as the A horizon pH in those treatments became slightly higher than that of the control treatment by the end of the experiment (Table 2). However, the initial amount of adsorbed SO_4^2 (determined before the liming materials were added) was completely desorbed in all treatments by the end of the experiment (Table 4). According to Charlet et al (1993) and others, SO_4^{2-} adsorption could be explained by electrostatic bonding as outersphere surface complexes. The adsorption would therefore depend on the concentrations of other anions in the soil solution. Since Cl^- was repeatedly added in equal amounts to all treatments, as HCl, (corresponding to a Cl^- concentration of 50 μM, i.e., 1.77 mg Cl/L), Cl^-/ SO_4^{2-} exchange may to some extent have contributed to the treatment independence of SO_4^{2-} desorption. However, competition between DOC and

SO_4^{2-} should have been a quantitatively more important desorption process, because of a much higher selectivity for DOC than for Cl^- or SO_4^{2-} (Gobran & Nilsson 1988; Karltun & Gustafsson 1993; Guggenberger 1994).

Biological activity and net sulphate release

Biological activity (CO_2 respiration) in Experiment I was estimated by calculating the loss of total carbon (ΔC_{net}) during the experimental period, corrected for the measured DOC leaching and carbonate-C losses (Table 3). Provided that this is a reasonable estimate of the CO_2 respiration, it would mean that the initial effect of liming was an increase in the soil biological activity, which was not directly related to the net sulphur mineralization (Tables 3 and 4). Fitzgerald and Strickland (1987) discussed the concept of organic S mobilization as defined in Strickland et al. (1984). They referred to enzymatic processes leading to defragmentation of large, stable organic molecules to smaller, more reactive ones that subsequently became mineralized. Rather than this mobilization being an immediate result of microbial metabolism, it is catalysed by pre-existing depolymerases and sulphohydrolases in the soil. Under such circumstances the solubility of organic S compounds could be an equally important factor for the net sulphur mineralization as the current biological activity.

Relationships between SO_4^{2-}, DOC and pH in the leachates

The positive correlations between accumulated DOC and SO_4^{2-} in both the control treatments and the lime treatments in Experiment I and II (Table 5) may suggest that the net SO_4^{2-} release was at least partly induced by an increased enzymatic hydrolysis of ester sulphates when the organic matter was dissolved, as was discussed above. However, in Experiment I the accumulated DOC/DOS ratio as well as the accumulated DOC/SO_4^{2-} ratio were considerably higher in the control treatment than in the lime treatments (Table 4), the difference in the DOC/DOS ratio possibly indicating a lime induced change in the quality of the dissolved organic matter.

In both Experiment I and II, the pattern of DOC release seemed to be in accordance with theories on the humus-stabilising effect of the Ca^{2+}ion (Römkens et al. 1996). However, a lower percentage of Ca^{2+} in the liming material worked essentially in the same direction as the increase in soil pH (O horizon) or leachate pH, which made it difficult to evaluate the separate influences of pH and Ca^{2+} ions on the release of DOC. However, in experiment II, Ca^{2+}ions added to the $MgCO_3$ treatment decreased the DOC concentration significantly more than the addition of the same amount of Mg^{2+} ions (chloride salts), while the decrease in pH was the same regardless of which salt was added (Figures 1(b) and 3(b)). There was no difference between the cation additions in the $CaMg(CO_3)_2$ treatment with respect to DOC, probably because Ca^{2+} released from the previously added dolomite lime was already in excess and had a stabilising effect on the organic matter.

In Experiment I, the lower pH in the leachates from the limed treatments compared to the control treatment during the main part of the experiment (Figure 1a) was probably established by cation exchange of Ca^{2+} and Mg^{2+} (originating from the liming materials) for H^+ and Al ions in the underlying acid A horizon. Excess cation leaching from the O horizon was probably induced by nitrification, followed by NO_3^- leaching (Figure 2). Due to these processes, a differentiation of leachate pH which mirrored the pH in the O horizons of the respective treatments was delayed and did not begin to appear until just before Day 200 (Table 2; Figure 1(a)). After Day 200, pH and DOC concentration in the control leachates decreased markedly (Figures 1(a) and 3(a)), while there was an equally marked increase in the NO_3^- concentration (Figure 2) and the three variables eventually reached approximately the same levels as those found in the lime treatments. These trends indicated a decline in DOC which was primarily induced by protons originating from the nitrification process. However, the NO_3^- peak and pH minimum in the limed treatments around Day 50 did not affect the DOC concentrations (Figures 1(a), 2 and 3(a)). Not unexpectedly, pH thus seemed to be a relatively more important factor for the DOC concentration at low Ca^{2+} (and Mg^{2+}) concentrations than at high concentrations (Figures 5 and 6).

Neither leachate pH, nor pH in the O horizon by the end of Experiment I could provide a consistent picture of the liming effect on net sulphur mineralization (Figure 1a; Tables 2, 4 and 5). There were more consistent relationships between SO_4^{2-} and DOC in the leachates compared to SO_4^{2-} and pH, in that the positive SO_4^{2-} – DOC relationship found in the control treatment of experiment I pointed in the same direction as that of the other treatments in Experiment I and Experiment II (Table 5).

In conclusion, the net SO_4^{2-} release (net sulphur mineralization) seemed to be connected to the production of dissolved organic matter. pH and/or Ca^{2+} ions affected the net SO_4^{2-} release indirectly, through their effects on the organic matter solubility. From this study it seems likely that factors regulating the dissolution of organic material are important for the net sulphur mineralization. However, further investigations are needed to elucidate the role of different organic matter-stabilising factors in a range of different soils, and the connections between these factors and the net sulphur mineralization.

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