Original article

Effects of liming and gypsum regimes on chemical characteristics of an acid forest soil and its leachates

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Summary – A dystric cambisol (acid brown soil) with an acid mull humus consisting of Of, A_1 and (B) horizons was used to study changes in soil and leachate chemistry. The natural soil was reconstituted in columns equipped with zero tension lysimeters. $CaCO_3$, $CaCO_3 + MgO$ and $CaSO_4$ treatments were added at rates equivalent to 0.56, 2.8 and 5.6 t ha^{-1} of CaO. Soil pH and exchangeable cations were determined before treatments were applied, and at the end of the 20 month experimental period. Leachates from the columns were analyzed for pH, S, Ca, Mg, Al, K, $N-NO_3$ and $N-NH_4$ at monthly intervals throughout the 20 month period. Liming provoked the greatest increase in the soil pH values. This was limited to the A_1 horizon when using the lowest rate but was also observed in (B) horizon after application of 2.8 and 5.6 t ha^{-1}. Exchangeable calcium values were higher in the upper 6 cm but decreased rapidly in the deeper layers. When gypsum was added, the pH increased significantly but this was restricted to the humus and A_1 horizons; exchangeable calcium was increased significantly down to the (B) horizon. Aluminium saturation decreased in the layers with high exchangeable calcium and higher pH values. For base saturation, patterns similar to calcium were observed throughout the profile. Leachates were enriched with basic cations which increased the pH, especially when the high liming rate was applied and also with the 2.8 and 5.6 t CaO ha^{-1} rates of gypsum. Nitrogen was leached mostly as $N-NO_3$ in the lime treatments and in the control, whereas nitrification was inhibited in the gypsum treatment and nitrogen was predominantly in $N-NH_4$ form.

acid soil / nutrient / leachate / lime / gypsum / forest

Résumé – Effets des formes et doses d'amendements et de gypse sur les caractéristiques chimiques et les percolats d'un sol forestier acide. Un sol brun acide (dystric cambisol, FAO) avec un humus mull composé des horizons Of, A_1 et (B) est utilisé afin d'étudier les modifications chimiques du sol et de ses percolats. Le sol d'origine est reconstitué dans des colonnes associées à des lysimètres sans tensions. Les traitements sous forme $CaCO_3$, $CaCO_3 + MgO$ et $CaSO_4$, $2H_2O$ sont apportés aux doses équivalentes en CaO de 0, 0,56, 2,8 et 5,6 t ha^{-1}. Le pH du sol et les cations échangeables ont été déterminés avant et après application des traitements, et à la fin de la période expérimentale de 20 mois. La plus forte augmentation de la valeur du pH du sol est induite par les amen-

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dements. Elle est limitée à l'horizon A_1 pour la dose faible $(0,56\ t\ ha^{-1})$ mais elle est observée dans l'horizon (B) pour les doses 2,8 et 5,6 t ha^{-1}. La disponibilité en calcium échangeable est élevée sur une profondeur de 6 cm, mais diminue rapidement dans les couches profondes. La valeur du pH est augmentée significativement dans le traitement gypse mais uniquement dans les horizons Of et A_1. L'augmentation en calcium est significative même dans l'horizon (B). La saturation en aluminium a diminué essentiellement dans les couches enrichies en calcium et là où les valeurs du pH sont élevées. Un effet comparable à celui du calcium est observé également pour le taux de saturation le long du profil de sol. Les percolats au travers du sol ont été enrichis en cations basiques parallèlement à une augmentation des valeurs du pH pour la dose la plus élevée d'amendements et avec les doses 2,8 et 5,6 t ha^{-1} pour le gypse. L'azote des percolats est sous forme de $N-NO_3$ pour les traitements amendements et le témoin, alors que la nitrification est inhibée avec le gypse où l'azote est transféré principalement sous forme de $N-NH_4$.

sol acide / élément nutritifs / percolat / amendement / gypse / forêt

INTRODUCTION

Forest soils in the French Ardennes are predominantly dystric cambisols (FAO) (typic dystrochrept, USDA), characterized by a low effective cation exchange capacity, low base saturation and high concentration of exchangeable A_1 throughout the profile (Nys, 1987). These soils are either acid in their natural state or have become so after long periods of silvicultural harvesting. Forest decline has been observed since 1983 in Belgium (Weissen et al, 1988) and has been confirmed in France (Nys, 1989). This phenomenon has been accelerated by natural acidification of organic acids in litter, acid atmospheric deposition, cation uptake and biomass harvest (Andersson and Persson, 1988). High A_1 concentrations in the soil solution affect plant uptake of basic cations, P and root elongation or seedling growth (Hutchinson et al, 1986; Bruce et al, 1989; Asp and Berggren, 1990; Cronan, 1990). In order to alleviate the detrimental effect of these processes, liming is the most common silvicultural practice used for acid forest soils. Crushed limestone is the conventional method of reducing soil acidity but its neutralizing effect and the release of Ca is slow and restricted to the surface layers (Adams, 1984). Furthermore, the immediate economic benefit of liming may be poor when the resulting wood production is low. However, liming may improve the health (Nys, 1989) and biomass of trees in declining forests (Belkacem et al, 1992). Surface applications of gypsum (Farina and Channon 1988; Alva and Sumner, 1990) or dolomite (Munns and Fox, 1977; Adams, 1984; Kamprath and Foy, 1985) can also be used to neutralize acidity, to reduce the exchangeable A_1 and to increase the level of available Ca and Mg in the surface and subsoil. Because of the extensive use of liming material in temperate regions and a paucity of available experimental data under controlled conditions, this paper reports results of a lysimeter-type pot experiment. The objective of this study was to investigate changes in the pH, exchangeable cations and base saturation after the addition of different types and quantities of lime and gypsum, and to examine leachate chemistry throughout the 20 month experimental period.

MATERIALS AND METHODS

Soil characteristics

A dystric cambisol (acid brown soil) with acid mull humus was collected from a deciduous coppice with oak (*Quercus petraea* [Liebl]) standards in the French Ardennes forest. Details of the site are well documented by Nys (1987). The soil profile consists of an Ol, Of organic layer (2 cm), A_1 (0–5 cm), A_1(B) (5–15 cm) and (B)

(15–50 cm) mineral horizons. This soil was developed on silty material overlying the Revinien slates. The texture is silty clay in both A_1 and (B) horizons, with clay contents of 29 and 25%, respectively. Bulk density is low in the surface horizon and increases gradually with depth. Organic carbon is high in the Of and A_1 horizons, but organic N is relatively low, giving a fairly high C/N ratio. The principal components of the clay fraction of the soil are chlorite, vermiculite and mica with some feldspars (Belkacem, 1993). This soil was selected because of its high exchangeable acidity and low base saturation and the major chemical properties are summarized in table I.

Experimental method

The field profile was reconstituted in containers of rigid polyethylene (30 cm deep and 20 cm diameter) using 6 cm of A_1 and 15 cm of (B) with bulk densities of 0.65 and 0.9 kg L^{-1} respectively. The organic layer (Of) was spread on the surface of the A_1 horizon. $CaCO_3$, $CaCO_3$ + MgO and $CaSO_4$, $2H_2O$ treatments were distributed uniformly by hand, in a single application, on the top of the humus without mixing at rates equivalent to 0, 0.56, 2.8 and 5.6 metric tons ha^{-1} of CaO. Four replicates were installed in an open air nursery.

The local rainfall of 800 mm $year^{-1}$ was augmented with additional local rainfall to simulate rainfall of 1 126 mm $year^{-1}$, the annual precipitation at the field site in the Ardennes. The leachates were collected monthly over a period of 20 months from the containers via tubes connected to sampling bottles. Subsequently, the volume of drained water was measured and the solution filtered through a 0.45 μm filter. After 20 months prior to chemical analysis the soil was subdivided into thin layers: A_1 to $A_{1/1}$ (0 to 3 cm), $A_{1/2}$ (3 to 6 cm) and (B) to $B_{1/1}$ (6 to 11 cm), $B_{1/2}$ (11 to 16 cm), $B_{1/3}$ (16 to 21 cm). The organic Of layer was analyzed separately.

Analytical methods

Soil analyses

The soil was analyzed before experimentation and at the end of the 20 month leaching period.

Soil pH was determined both in H_2O and in N KCl, with soil to solution ratios of 1:2.5 for the mineral soil and 1:5 for the organic layer. Exchangeable cations were determined by agitating a 1:20 ratio of soil and a 0.5 N NH_4Cl solution for 16 h (Trüby, 1989; Trüby and Aldinger, 1989). The solution was then centrifuged and filtered. Basic cations (Ca, Mg, K, Al) were measured by emission spectrometry (ICP) and exchangeable acidity (Al^{3+}, H^+) by automatic titration. Total nitrogen was determined by Kjeldahl digestion and organic carbon by the Anne method (Duchaufour, 1977).

Leachate analyses

After pH determination, the leachate samples were analyzed for Al, Ca, Mg, K, S by emission spectrometry and $N-NO_3$, $N-NH_4$ using colorimetric methods (Federer, 1983).

Statistical analyses

For statistical validity of the results, four replicates of the solid phase were analyzed. In the leachate, except for the pH, only replicates at 0, 12 and 20 months were analyzed separately during the experimental period. For both soil and solution data ANOVA was used to assess the treatments for significant effects.

RESULTS

Changes in the untreated soil during the 20 months

Untreated control soil was used to check for changes resulting from the 20 month experimental conditions. Table I shows data on soil pH, organic carbon, exchangeable cations (Al, Ca, Mg, K), exchangeable acidity and base saturation data for the untreated soil before and after the experiment. In the Of horizon pH decreased from 4.7 to 3.8 whereas in the 0–6 cm and 6–21 cm depths it increased. Exchangeable A_1 increased in both the 0–6 and 6–21 cm layers. Organic carbon content of Of and A_1 horizons decreased, indicating a high decomposition rate in the upper soil layers. High nitrifica-

Table I. Chemical properties of the untreated soil before and after the 20 month experimental period.

	Horizon	pH (H_2O)	pH (KCl)	C (%)	H	Al	Ca	Mg ($cmol_c\ kg^{-1}$)	K	EA	ΣEBC	CEC	S/T (%)
Initial values	Of*	4.7[a]	3.8[a]	37.5[a]									
After 20 months	Of*	3.8[b]	3.2[b]	32.9[b]									
Initial values													
0–3 cm	A$_{1/1}$*	3.4[a]	2.9[a]	12.2[a]	3.92[a]	5.68[a]	1.32[a]	0.52[a]	0.46[a]	9.6[a]	2.7[a]	12.3[a]	22[a]
3–6 cm	A$_{1/2}$*	3.4[a]	2.9[a]	12.2[a]	3.92[a]	5.68[a]	1.32[a]	0.52[a]	0.46[a]	9.6[a]	2.7[a]	12.3[a]	22[a]
After 20 months													
0–3 cm	A$_{1/1}$*	3.8[b]	2.9[a]	9.1[b]	1.81[b]	7.75[b]	1.69[b]	0.43[b]	0.48[a]	9.6[a]	3[a]	12.5[a]	24.2[b]
3–6 cm	A$_{1/2}$*	3.7[b]	2.9[a]	9.3[b]	1.85[b]	8.74[c]	1.28[a]	0.36[b]	0.46[a]	10.6[b]	2.5[a]	13.0[a]	19.3[c]
Initial values													
6–11 cm	B$_{1/1}$*	4.2[a]	3.9[a]	2.4[a]	0.00[a]	4.32[a]	0.2[a]	0.16[a]	0.16[a]	4.32[a]	0.8[a]	5.2[a]	15[a]
11–16 cm	B$_{1/2}$*	4.2[a]	3.9[a]	2.4[a]	0.00[a]	4.32[a]	0.2[a]	0.16[a]	0.16[a]	4.32[a]	0.8[a]	5.2[a]	15[a]
16–21 cm	B$_{1/3}$*	4.2[a]	3.9[a]	2.4[a]	0.00[a]	4.32[a]	0.2[a]	0.16[a]	0.16[a]	4.32[a]	0.8[a]	5.2[a]	15[a]
After 20 months													
6–11 cm	B$_{1/1}$*	4.3[a]	3.7[b]	2.4[a]	0.28[b]	6.37[b]	0.17[a]	0.11[b]	0.26[b]	7.0[b]	0.9[a]	7.7[b]	11.2[b]
11–16 cm	B$_{1/2}$*	4.4[ab]	3.8[ab]	2.4[a]	0.11[c]	5.59[c]	0.14[b]	0.10[b]	0.24[b]	6.1[b]	0.8[a]	6.7[b]	11.7[b]
16–21 cm	B$_{1/3}$*	4.5[b]	3.8[ab]	2.2[b]	0.09[c]	5.48[c]	0.17[a]	0.10[b]	0.27[b]	5.9[b]	0.9[a]	6.7[b]	12.6[b]

* Mean values obtained from four replicates. [abc] Values designated by the same letter are not significantly different by Student Newman-Keul's multiple range test ($P < 0.05$). C: organic carbon; EA: exchangeable acidity; ΣEBC: Σ exchangeable base cations; CEC: cation exchange capacity; S/T: base saturation.

tion, deduced from high N-NO$_3$ concentrations in the leachate, was a possible proton source at the beginning of the experiment, and may have resulted in dissociation of aluminium in a polymerized form. This would also explain the increase of exchangeable K in the (B) horizon where protons can remove interlayer potassium from the mica (Fanning et al, 1989). As a result of these increases in both exchangeable A$_l$ and K, the cation exchange capacity (CEC) in the (B) horizon was higher than in the initial soil (table I).

Effect of lime and gypsum on the soil chemistry

pH

Soil pH values were increased greatly in the lime (CaCO$_3$) treatments (table II) especially when MgO was added and additional alkalinity was released. An increase in pH relative to doses of lime treatments was very marked in the Of (pH increased from 3.8 in the control to between 5 and 7.8) and in A$_1$, 0–6 cm depth (pH increased from 3.7 in the control to between 4.2 and 7.0). Below this depth there was no significant difference between the three rates of lime but there was a difference of 1 to 1.4 units between the control and 2.8 or 5.6 t ha^{-1} rates of CaCO$_3$ and CaCO$_3$ + MgO (table II). Gypsum application resulted in a slight, but significant increase in pH values with a maximum of 0.7 units with the 5.6 t ha^{-1} rate (table II). However, except for the organic layers, the effect of gypsum on the pH values was independent of the rate added, in contrast to the lime effect.

Exchangeable cations

Table II shows the effect of lime and gypsum rates on the exchangeable Ca, Mg, Al and K levels throughout the soil profile. Availability of exchangeable calcium in the soil depends on the ability of the treatments to release Ca^{2+} rapidly. The excessive Ca concentration, measured at 0–3 cm depth, is due to the fact that more than 40% of lime and gypsum remained in the system as undissolved particles (Belkacem, 1993). The significant increase in Ca concentration with lime was restricted to the surface layers (0–11 cm), but Ca penetrated deeper (0–21 cm) when gypsum was used (table II). Using the 2.8 t ha^{-1} rate, the increases in CaCO$_3$ were 4.2, 0.4, 0.2 and 0.2 cmol$_c$kg^{-1} in the A$_{1/1}$, B$_{1/1}$, B$_{1/2}$ and B$_{1/3}$ layers respectively; 1.4, 0.2, 0.1 and 0 cmol$_c$kg^{-1} with CaCO$_3$ + MgO and 7.4, 2.3, 1.2 and 1.1 cmol$_c$kg^{-1} with CaSO$_4$ treatment. For most of the soil, the increase in exchangeable Ca and Mg was associated with an increase in total basic cations. In natural soil, Al was the dominant exchangeable cation whereas after lime and gypsum addition it was largely replaced by Ca or Mg. Due to its high solubility, gypsum releases Ca into the soil faster than lime. Al was inversely redistributed in relation to the Ca throughout the profile, with a particularly pronounced depletion at the 0–6 cm depth (table II). With 2.8 t ha^{-1} as a typical example of what occurs, in the A$_{1/1}$ and A$_{1/2}$ layers this decrease was about 7 and 2.5 cmol$_c$kg^{-1} respectively with CaCO$_3$, 6.9 and 2.6 cmol$_c$kg^{-1} with CaCO$_3$ + MgO, and 5.3 and 3.9 cmol$_c$kg^{-1} with CaSO$_4$ treatment. Exchangeable aluminium was related to the pH values: the higher the pH value, the lower the exchangeable Al (table II). With higher rates of gypsum there was a slight decrease in exchangeable magnesium and an increase in exchangeable potassium at 0–11 cm depth, whereas exchangeable Al decreased. With the lower rate the phenomenon was reversed at 0–6 cm depth (table II). With CaCO$_3$ + MgO, the exchangeable magnesium increased significantly in A$_1$ horizon with the 0.56 t ha^{-1} rate. With the 2.8 and 5.6 t ha^{-1} rates exchangeable magnesium increased throughout the soil profile in contrast to cal-

Table II. Effects of $CaCO_3$, $CaCO_3$ + MgO and $CaSO_4$ with 0, 0.56, 2.8 and 5.6 t ha^{-1} CaO on the soil pH (H_2O) mean values and exchangeable cations (standard error, Of: organic layers).

Horizon	pH	Ca	Mg	Al	K	pH	Ca	Mg	Al	K	pH	Ca	Mg	Al	K
		($cmol_c\ kg^{-1}$)					($cmol_c\ kg^{-1}$)					($cmol_c\ kg^{-1}$)			
Control															
Of	3.80														
	0.11														
A$_{1/1}$ (3 cm)	3.76	1.69	0.43	7.75	0.46										
	0.30	*0.09*	*0.04*	*0.53*	*0.04*										
A$_{1/2}$ (6 cm)	3.72	1.28	0.36	8.74	0.46										
	0.23	*0.07*	*0.05*	*0.31*	*0.04*										
B$_{1/1}$ (11 cm)	4.27	0.17	0.11	6.37	0.26										
	0.09	*0.05*	*0.01*	*0.05*	*0.08*										
B$_{1/2}$ (16 cm)	4.44	0.14	0.10	5.59	0.24										
	0.08	*0.02*	*0.01*	*0.32*	*0.05*										
B$_{1/3}$ (21 cm)	4.46	0.17	0.10	5.48	0.27										
	0.06	*0.05*	*0.01*	*0.16*	*0.04*										
CaCO₃		*0.56 t ha⁻¹*					*2.8 t ha⁻¹*					*5.6 t ha⁻¹*			
Of	5.12					6.30					6.57				
	0.36					*0.09*					*0.06*				
A$_{1/1}$ (3 cm)	4.26	8.53	0.49	4.15	0.48	5.50	28.38	0.63	0.72	0.39	5.91	27.78	0.59	0.21	0.43
	0.17	*0.6*	*0.01*	*0.36*	*0.01*	*0.69*	*12.5*	*0.04*	*0.95*	*0.02*	*0.55*	*5.35*	*0.04*	*0.03*	*0.04*
A$_{1/2}$ (6 cm)	3.94	3.35	0.37	7.32	0.44	4.62	6.07	0.35	6.28	0.54	4.40	8.61	0.40	4.60	0.43
	0.21	*0.24*	*0.03*	*0.32*	*0.05*	*0.20*	*1.27*	*0.05*	*0.67*	*0.12*	*0.41*	*2.43*	*0.01*	*1.42*	*0.02*
B$_{1/1}$ (11 cm)	4.28	0.43	0.12	7.04	0.20	5.23	0.55	0.08	6.24	0.25	4.45	0.41	0.07	5.79	0.28
	0.03	*0.09*	*0.01*	*0.2*	*0.05*	*0.06*	*0.2*	*0.01*	*0.36*	*0.01*	*0.11*	*0.1*	*0.01*	*0.17*	*0.03*
B$_{1/2}$ (16 cm)	4.51	0.25	0.11	5.84	0.22	5.44	0.33	0.07	5.76	0.16	5.65	0.38	0.07	5.73	0.26
	0.02	*0.06*	*0.01*	*0.07*	*0.01*	*0.08*	*0.01*	*0.01*	*0.15*	*0.03*	*0.05*	*0.06*	*0.01*	*0.09*	*0.05*
B$_{1/3}$ (21 cm)	4.48	0.25	0.10	5.73	0.27	5.49	0.38	0.07	5.76	0.30	5.86	1.58	0.10	5.74	0.25
	0.08	*0.02*	*0.02*	*0.2*	*0.03*	*0.1*	*0.04*	*0.01*	*0.3*	*0.03*	*0.07*	*0.68*	*0.01*	*0.07*	*0.04*
CaCO₃ + MgO		*0.56 t ha⁻¹*					*2.8 t ha⁻¹*					*5.6 t ha⁻¹*			
Of	5.44					6.86					7.82				
	0.12					*0.10*					*0.11*				
A$_{1/1}$ (3 cm)	5.43	7.37	1.36	4.70	0.40	6.44	13.73	9.83	0.90	0.42	7.03	11.78	17.75	0.51	0.40
	0.21	*0.83*	*0.11*	*0.59*	*0.01*	*0.19*	*6.88*	*0.41*	*0.73*	*0.05*	*0.06*	*3.36*	*2.13*	*0.16*	*0.03*
A$_{1/2}$ (6 cm)	4.94	2.28	0.98	7.88	0.45	5.35	2.72	4.68	6.14	0.46	5.96	8.59	15.49	0.85	0.39
	0.14	*0.27*	*0.04*	*0.36*	*0.05*	*0.15*	*0.58*	*0.65*	*0.17*	*0.03*	*0.26*	*2.16*	*5.39*	*0.73*	*0.01*
B$_{1/1}$ (11 cm)	5.51	0.34	0.16	6.91	0.13	5.71	0.37	0.43	6.46	0.29	4.95	3.26	5.39	3.39	0.17
	0.08	*0.07*	*0.03*	*0.38*	*0.04*	*0.06*	*0.18*	*0.17*	*0.65*	*0.06*	*0.34*	*1.49*	*3.35*	*1.43*	*0.01*
B$_{1/2}$ (16 cm)	5.82	0.23	0.12	6.08	0.20	5.83	0.21	0.26	6.11	0.15	4.81	0.39	0.67	5.64	0.20
	0.06	*0.06*	*0.03*	*0.21*	*0.01*	*0.03*	*0.04*	*0.06*	*0.26*	*0.04*	*0.09*	*0.13*	*0.28*	*0.06*	*0.04*
B$_{1/3}$ (21 cm)	5.85	0.20	0.13	6.04	0.20	5.86	0.21	0.26	6.00	0.14	4,80	0.24	0.44	5.67	0.20
	0.06	*0.02*	*0.02*	*0.22*	*0.06*	*0.02*	*0.02*	*0.02*	*0.13*	*0.05*	*0.05*	*0.04*	*0.1*	*0.07*	*0.01*
CaSO₄		*0.56 t ha⁻¹*					*2.8 t ha⁻¹*					*5.6 t ha⁻¹*			
Of	4.05					0.94					4.52				
	0.02					*0.03*					*0.20*				
A$_{1/1}$ (3 cm)	4.28	5.26	0.53	5.48	0.36	4.34	11.98	0.36	2.48	0.63	4.29	14.50	0.33	1.89	0.61
	0.33	*0.93*	*0.04*	*0.89*	*0.03*	*0.06*	*0.24*	*0.04*	*0.1*	*0.04*	*0.03*	*0.56*	*0.02*	*0.25*	*0.05*
A$_{1/2}$ (6 cm)	4.16	4.23	0.57	7.10	0.36	4.24	8.70	0.30	4.36	0.58	4.19	10.93	0.30	3.35	0.61
	0.40	*0.53*	*0.2*	*0.81*	*0.02*	*0.06*	*0.88*	*0.01*	*0.37*	*0.18*	*0.04*	*0.22*	*0.02*	*0.16*	*0.04*
B$_{1/1}$ (11 cm)	4.41	0.37	0.10	6.82	0.19	4.62	6.54	0.24	4.55	0.53	4.65	1.71	0.10	5.08	0.36
	0.01	*0.15*	*0.01*	*0.11*	*0.01*	*0.02*	*4.54*	*0.1*	*0.82*	*0.2*	*0.02*	*0.07*	*0.01*	*0.1*	*0.04*
B$_{1/2}$ (16 cm)	4.42	0.30	0.10	6.36	0.18	4.63	1.35	0.11	5.02	0.33	4.67	1.69	0.09	4.88	0.31
	0.03	*0.09*	*0*	*0.25*	*0.02*	*0.02*	*0.22*	*0.01*	*0.01*	*0.02*	*0.02*	*0.09*	*0.01*	*0.18*	*0.04*
B$_{1/3}$ (21 cm)	4.45	0.31	0.12	6.21	0.21	4.59	1.25	0.10	5.30	0.32	4.60	1.58	0.10	5.74	0.25
	0.07	*0.06*	*0.01*	*0.15*	*0.02*	*0.02*	*0.08*	*0.01*	*0.3*	*0.05*	*0.01*	*0.68*	*0.01*	*0.07*	*0.04*

cium, with both $CaCO_3$ and $CaCO_3 + MgO$ (table II).

Base saturation

Figure I shows wide variations in base saturation throughout the soil profile between the different treatments. The base saturation was significantly higher at the 3–6 cm depth with increasing Ca and Mg rates (fig 1a). The increase was evaluated to be 16, 33 and 46% respectively for the 0.56, 2.8 and 5.6 t ha^{-1} rates of $CaCO_3$ treatment, 16, 37 and 76% for $CaCO_3 + MgO$ and 22, 47 and 56% for $CaSO_4$. Below a depth of 6 cm the lowest lime rate had no significant effect on the base saturation (fig 1b, c, d). At a depth of 6–11 cm, the largest increase in base saturation was related to the higher rate of lime, and was about 16% with $CaCO_3$ and 64% with $CaCO_3 + MgO$ treatment (fig 1b). Because of the relatively high exchangeable Ca level when gypsum was added, the base saturation was affected significantly, even in deeper layers (fig 1c, d) showing an increase of about 50% with the 2.8 and 5.6 t ha^{-1} rates in comparison with the untreated soil.

Effect of treatments on leachate chemistry

Except for the pH, the following results are from the 2.8 t ha^{-1} treatments only. Similar trends were obtained for 5.6 t ha^{-1} lime rate whereas 0.56 t ha^{-1} rate had no significant effect on the leachate elements (Belkacem, 1993).

pH

The changes in pH values (fig 2a, b, c) display three distinct periods; two with decreasing pH values and the other with increasing pH values corresponding to the warm (May to September) and cold (December to April) seasons, respectively (Belkacem and Nys, 1995). The pH value seems to depend on the nitrification rate, which is high in the warm periods and low in the cold one (fig 4c). On the other hand, liming induced substantial alkalinity and loss of basic cations which raised pH values but the effect was delayed in comparison to gypsum. The leachate pH increased between 0.2 and 0.4 units during the first month when using gypsum but the first increase was only observed after 6 months when lime was added at the high rate (fig 2a, b, c). Rates of 0.56 and 2.8 t ha^{-1} with lime, and the rate of 0.56 t ha^{-1} with gypsum had no significant effect on pH (fig 2a, b, c).

Cation content in the leachate

Calcium concentrations in the leachate were lower with lime than with gypsum due to their different solubilities. The high concentration of Ca and S (fig 3a, b) in the leachate indicates that part of the calcium moved through the soil as $CaSO_4$ salt. $CaCO_3$ released more Ca into the solution than $CaCO_3 + MgO$. However, with the $CaCO_3$ treatment, Ca concentration increased with time (fig 3a), indicating that the effect of lime was delayed in comparison to gypsum. Except for calcium in the gypsum treatment, aluminium remained the dominant cation in the leachate (fig 3a, c). Aluminium concentration stabilized after 11 months and there was no treatment effect (fig 3c). With gypsum, Al concentration increased compared to the other treatments when the percolating solution at 6 cm was measured (Belkacem, 1993). This suggested that Al reached equilibrium under the (B) horizon. European and Asian critical load calculations use the percolating soil solution ratio between (Ca + Mg + K) and Al as the critical parameter, assuming that a limit of (Ca + Mg + K)/Al $\geq$ 1.0 will protect the forest ecosystem from damage (Sverdrup and Warfvinge, 1993). The ratio was much higher with gypsum than with other treatments (fig 3d), due to the high amount
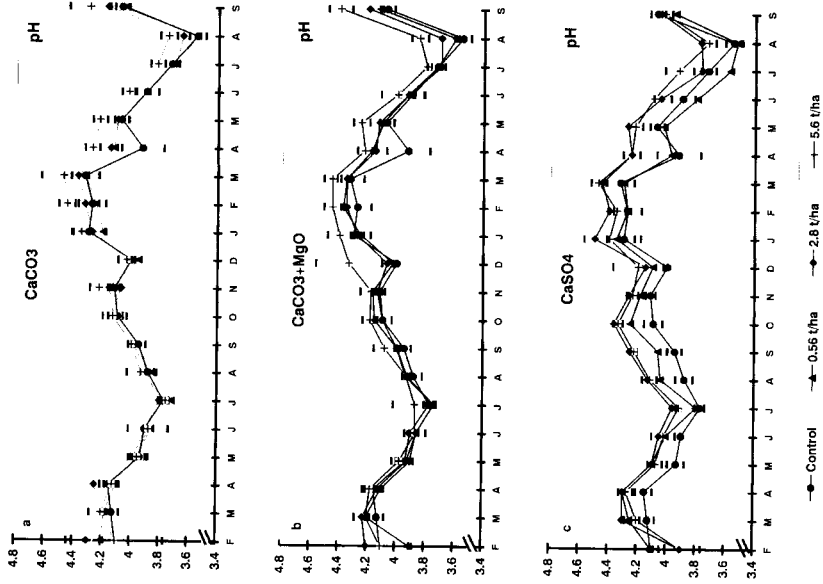
Fig 2. Effects of (**a**) $CaCO_3$, (**b**) $CaCO_3$ + MgO and (**c**) $CaSO_4$ on the pH of the percolating solution with 0, 0.56, 2.8 and 5.6 t ha^{-1} rate (bars designate the standard error only for the control and 5.6 t ha^{-1} rate).
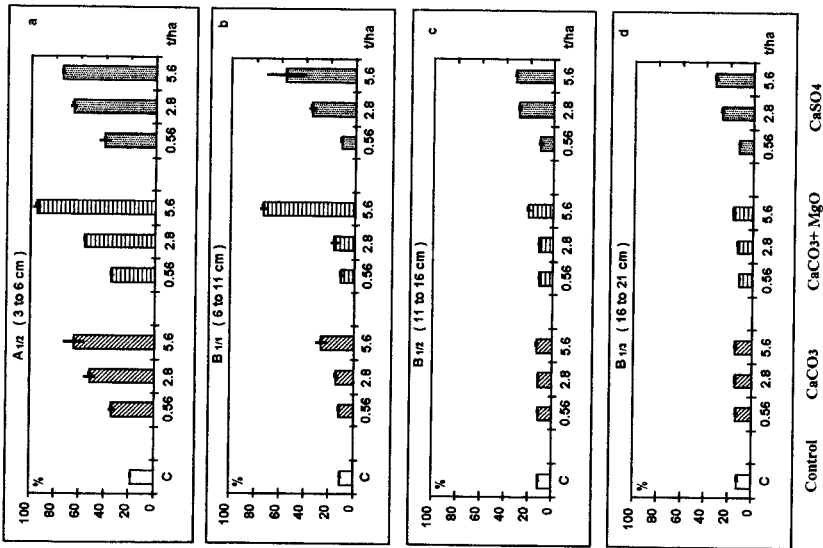

Fig 1. Effects horizon by horizon, of $CaCO_3$, $CaCO_3$ + MgO and $CaSO_4$ with 0, 0.56, 2.8 and 5.6 t ha^{-1} rate for some layers on base saturation (%). (bars = standard error, 1 = control, 2 = 0.56, 3 = 2.8, 4 = 5.6 t ha^{-1}).
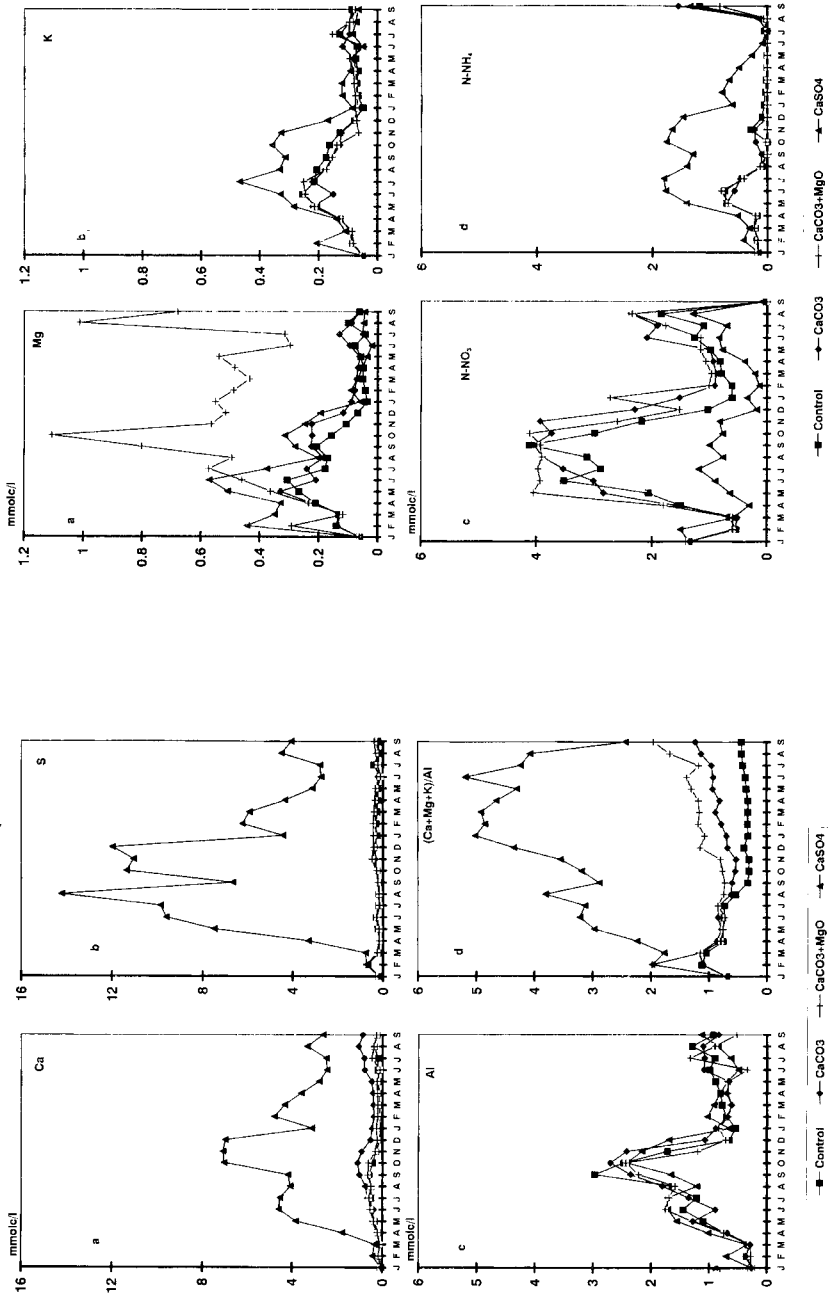
Fig 3. Effects of $CaCO_3$, $CaCO_3$ + MgO and $CaSO_4$ with 2.8 t ha^{-1} rate on (**a**) Ca, (**b**) S, (**c**) Al (mmol$_c$ L^{-1}), and (**d**) (Ca + Mg + K)/Al in the leachate (−21 cm) during the 20 month experimental period.

Fig 4. Effects of $CaCO_3$, $CaCO_3$ + MgO and $CaSO_4$ with 2.8 t ha^{-1} rate on (**a**) Mg, (**b**) K, (**c**) N-NH$_4$, and (**d**) N-NO$_3$ (mmol$_c$ L^{-1}) in the leachate (−21 cm) during the 20 month experimental period.

of Ca released. With lime treatments the ratio also increased but less rapidly than the former treatment whereas in the control the value was still below one (fig 3d). Both magnesium and potassium were leached more strongly with gypsum than in the control because of the high concentration of sulphate anions in the leachate especially at the beginning of the experiment (fig 4a and b); therefore, the exchangeable Mg level was lowered as shown before (table II).

Nitrogen forms in the leachate

The mineralization rate indicated by the nitrogen concentration in the leachate showed a large increase at the beginning of the experiment, but this increase was 50% lower after 20 months (fig 4c, d). Consequently, a significant decrease in organic carbon in the humus layers was observed (table I). The form of nitrogen in the leachate differed depending on the treatments during the experimental period (fig 4c, d). The nitrogen was leached as $N-NO_3$ with the lime and in the control, where the nitrification was much higher (fig 4c). $N-NO_3$ concentration under the 2.8 t ha^{-1} lime rate reached a mean value of 4 $mmol_c$ L^{-1} after 4 months and decreased to 1.5 $mmol_c$ L^{-1}, but then increased again to 2.5 $mmol_c$ L^{-1}. With the gypsum, $N-NO_3$ concentration was 50% lower than that of the $N-NH_4$. The latter form was leached to a greater extent with the gypsum treatment than with the other treatments, including the control (fig 4d).

DISCUSSION

In the solid phase, due to its lower solubility, lime affected calcium availability only in the topsoil, but the pH was increased significantly even in the deeper layers (21 cm). In the short term, application of lime under field conditions rarely affects the subsoil and the most modifications occurred in the upper layers. A delayed effect at low rates of lime application in the subsoil has been reported by several authors (Ulrich and Keuffel, 1970; Adams, 1984; Matzner et al, 1985; Weissen et al, 1994). However, with a high lime application rate and accelerated leaching due to high annual rainfall, an increase in soil pH can be detected to depths greater than 30 cm (Messick et al, 1984). In the $CaCO_3$ + MgO treatment, Mg was leached more easily than Ca (fig 3a) due to the higher solubility of MgO and to its large hydrated radius. Consequently, Mg was retained less well on exchangeable sites (Galindo and Bingham, 1977). Exchangeable Al decreased with all added materials and the decrease was more pronounced with lime treatments than with gypsum. Gypsum application improved exchangeable calcium levels throughout the profile as reflected by an increase of Ca concentration in soil leachate. The presence of excess Ca^{2+} in an acid system is capable of desorbing acid cations (Al^{3+}, H^+) from the exchange sites (McBride and Bloom, 1977). With gypsum, it is probable that there was a Ca–Al exchange and aluminium was then leached and reorganized in deeper layers. In the case of lime treatments, the reduction in exchangeable Al may have resulted in polymerization at high pH values. Alleviation of aluminium toxicity by $CaSO_4$ may be partly due to an increase in formation of a less phytotoxic Al form ($AlSO_4^+$) (Noble et al, 1988).

In the leachate, pH values with gypsum were significantly higher than with lime because of an increase in negative charges resulting from a concomitant specific adsorption of SO_4^{2-} and release of OH^- (Gobran and Nilsson, 1988; Lelong et al, 1989). The apparent stability reached in all the treatments after 11 months indicates that Al was mainly affected by the soil properties in the lower part of the column, and not by the treatments applied to the surface. The increased nitrate content in the leachate and a decrease in exchangeable Al by polymerization in the surface layers, could be the

main source of proton production which contributes to the acidification of the soil leachate and release of Al and K by weathering. An exchange of Al by K may have occurred at low pH due to the specific adsorption of K onto the clay minerals as reported by Chung et al (1994). The leachate enrichment in Ca, Al and Mg cations was attributed to an excess of NO_3^- and SO_4^{2-} anion vectors resulting from high mineralization and added gypsum in conditions without root absorption. With the latter treatment more Mg and K were leached compared with the untreated soil and $CaCO_3$ application. This phenomenon could be considered as a negative effect of the gypsum treatment especially in soil with low K and Mg availability. In the leachate most of the nitrogen in the lime treatments and in the control was in nitrate form, whereas in the $CaSO_4$ treatment the mineralized N was predominantly in ammonium form. This may be related to the change in soil microbial biomass due to high sulphate application or to the NH_4^+ which was rapidly leached by sulphate anion before complete nitrification. It is generally thought that nitrification is very sensitive to high Al concentrations and low pH levels (Brunner and Blaser, 1989), but this hypothesis was not verified in this experiment since nitrification was still high in the untreated soil in spite of low pH values. The high nitrification flush at the beginning of the experiment was related to soil disturbance as reported by Van Praag and Weissen (1973), similar to the effect of clear-cutting applied to forest ecosystems. In addition, the lack of nitrogen absorption by trees has been estimated to be about 100 kg of nitrogen each year in undisturbed temperate forests (Peter et al, 1993).

CONCLUSION

The $CaSO_4$ treatment was therefore more efficient than liming in increasing calcium concentration, base saturation, in reducing exchangeable Al in the subsoil, and NO_3-N loss in the leachate but had little effect on the soil pH. The $CaCO_3$ + MgO treatment had the greatest effect on the pH values, exchangeable Ca, Mg and reducing exchangeable aluminium especially in the A_1 horizon. Further information is required not only to understand the mechanism involved in the change of nitrogen forms as a result of the different treatments, but also the effects on other minor, heavy metals and soil formation processes. It seems that undisturbed forest soils are more resistant to changes in patterns of pH and nitrogen mineralization; therefore, the extrapolation of the results to field conditions must be made with care. From an ecosystem function viewpoint, long-term field experiments must be established to study the effects of lime and gypsum additions to undisturbed forest soil.

ACKNOWLEDGMENTS

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