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Response of a Scots pine (*Pinus sylvestris*) stand to application of phosphorus, potassium, magnesium and lime. 2. Soil solution composition

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Abstract

In a previous paper the effects of liming and P, K and Mg fertilization on the extractable and total nutrient concentrations in the forest floor and mineral soil of a Scots pine stand were discussed. The present paper regards the influence of P, K and Mg addition (as one treatment) and liming on solute concentrations at depths of 30 cm, i.e. in the root zone (monitored September 1989 - April 1992) and 100-150 cm, i.e. below the root zone (April 1991). The latter are compared with previous results. Liming increased NO_3 concentrations at both depths. At 30 cm this effect of liming gradually vanished during the monitoring period, concurrently with a declining soil solution pH, while an increasing effect of PKMg on NO_3 developed. Probably it took several years for the nitrifying microflora to adapt to an improved nutrient availability, while the effect of liming was instantaneous. These data show that besides liming, fertilization may increase NO_3 leaching. NH_4 was not affected by any treatment. The applied K and Mg compounds were easily soluble, and their soil solution concentrations were increased at both depths in the PKMg-amended plots. Probably slow-release fertilizers would allow for a more efficient incorporation of K and Mg into the system's biomass. Reducing effects of liming on soluble Al were weak (30 cm) or absent (100-150 cm). Al at 30 cm did not reach concentrations known to be harmful to Scots pine, but Ca:Al ratios were critical in the unlimed plots. No evidence is found for an enhanced cation leaching caused by an increased formation of nitric acid in the limed plots.

Keywords: forest fertilization, leaching, liming, Pinus sylvestris, root zone, soil solution chemistry

Introduction

The soil solution is the carrier for transport in the soil system (Bolt and Bruggenwert, 1978). Therefore, the dissolved nutrient pool has a major effect on the uptake rate of plant roots (Mengel and Kirkby, 1987; Nye and Tinker, 1977) but also on nutrient leaching (Matzner et al., 1983; Vitousek et al., 1979). Necessarily, to have any effect on plants, fertilization and liming treatments should influence nutrient concentrations in the soil solution, but preferably not to such an extent that leaching is enhanced. The balance between increased uptake and leaching depends on the added amounts and the timing of the application. In agriculture, to optimize nutrient uptake and minimize leaching, split applications have become common practice, and the potential to adjust fertilizer additions more closely to crop demand is still increasing. Fertilization and liming in forestry are applied far less frequently, because they are more laborious than in agriculture (Leek, 1990) and the trees can profit from one application for many years. Inevitably, if fertilization is aimed at an increased nutrient availability for more than one season, nutrients are likely to leach in regions with a precipitation excess, especially during the dormant season, thus making it difficult to manipulate the balance between uptake and leaching. A possible tool to minimize leaching is the use of slow-release fertilizers, which will improve the incorporation of nutrients in the ecosystem biomass (Anon., 1990) and minimize losses during the vegetative period.

Liming is rarely aimed at increasing Ca availability but mostly at improving chemical and structural soil conditions. However, it may affect the concentrations of many elements in the soil solution by raising the pH, which affects chemical equilibria and microbial activity, and by exchange processes. Since the added amounts are usually very large compared to fertilization, liming may have a profound influence on the uptake and leaching of nutrients other than Ca.

In a Scots pine forest a fertilization experiment was carried out (Arnold & van Diest, 1993a), in which the effects of fertilizer and lime applications on the soil solution composition were investigated. Soil moisture in and below the root zone was analyzed to assess the effects on nutrient availability and on possible leaching, respectively.

Materials and methods

The experimental area is situated near Harderwijk, the Netherlands. The soil is a coarse sandy fluvioglacial deposit covered by a fine drift sand layer of varying depth (10-40 cm) with a weak podzolic soil formation and a litter layer that is distinct from the underlying mineral soil. The water table is at ca. 9 m. The site was planted with Scots pine (*Pinus sylvestris* L.) in 1960.

Initial soil data are presented in Table 1. P, K, Mg and lime were applied to 22 × 25-m plots in a 2^4 factorial complete randomized block design with 3 replicates. These treatments are denoted as P, K, Mg and Ca, respectively (Table 2). For more details, see Arnold & van Diest (1993a).

Sampling

Root zone. Starting in September 1989, soil moisture sampling was carried out in the Control-, Ca- and PKMg plots. Since 22 February 1991, also the PKCaMg plots were sampled, resulting in a 2^2 experiment derived from the 2^4 experiment. For sampling, per plot 4 ceramic high-flow tension cups (Soil Moisture Equipment Corporation) were installed 6 months in advance at a 30-cm depth, i.e. in the rooting zone. The cups had first been rinsed with dilute HCl and demi water. At a 30-cm

Table 1. Initial element concentrations in the forest floor, and in the 0-25 and 25-50 cm mineral soil segments.

Element	Soil layer		
	forest floor ($g\ kg^{-1}$)	0-25 cm ($mg\ kg^{-1}$)	25-50 cm ($mg\ kg^{-1}$)
DON[a]	–	4.6	2.3
NO_3	–	0.0	0.0
NH_4	–	4.0	1.1
K	–	5.8	2.1
Mg	–	1.7	0.6
pH	–	4.24	4.56
N total	15.7	454	263
P total	0.62	102	142
K total	0.80	632	728
Ca total	1.20	69	74
Mg total	0.33	29	38
Zn total	–	8	10

[a] Dissolved organic nitrogen.

depth, sand of variable texture and low in organic matter is found. For installation a hole was drilled with a gouge at a 45° angle, just above the required depth. The place for the cup was prepared by forcing a PVC tube into the bottom end of the hole, so that the centre of the cup would be 30 cm below the mineral soil surface. A ceramic cup was firmly pressed into this slightly undersized cavity. Next, the soil material was packed back into the hole, restoring the original stratification. The cup was connected with a spaghetti-tube that was plugged into a bottle, which was brought to a suction pressure of ca. 15 KPa (0.15 bar). The bottles were buried under the litter layer to avoid light exposure and warming, and they were changed every 2 or 3 weeks.

Leaching. In order to assess the influence of liming and fertilization on the leaching

Table 2. Amounts and compositions of fertilizers and lime applied in the factorial experiment and at the 3000 kg lime level of the liming experiment.

Nutrient	Amount ($kg\ ha^{-1}$)	Fertilizer	Date of first application
P	25	Rock phosphate	autumn 1985
	25	Triple superphosphate	autumn 1985
K	100[a]	Potassium sulphate	spring 1986
Mg	100[a]	Kieserite	spring 1986
Ca	1200	Calcium carbonate[b] (powder, 3000 kg)	autumn 1985

[a] K and Mg applications were split, with additional applications made in the springs of 1987 and 1988, to a total of 100 kg ha^{-1} each. [b] Contained 3.6% $MgCO_3$ (1% Mg).

of several elements, in April and May 1991 the soil solution of the 100-150 cm layer mineral soil in the above-mentioned 2^2 experiment was sampled. In April, little annual differences in soil water storage are found, making this the best sampling time for comparing different years (Van Grinsven, 1988). In a neighbouring pine stand, De Visser (1991) found that the fine root biomass and fine root density had reached very low values below a 60 cm depth. Hence, elements at a 100-150 cm depth are unlikely to be recovered by root uptake. Nine points per plot were sampled in a regular grid. First, a hole was drilled with an auger to a 100 cm depth. Into this hole a PVC tube was inserted to prevent collapse and contamination by surface-soil material. Next, the 100-150 cm layer was sampled with a smaller auger. In April, 2 experimental blocks were sampled and 1 block at the beginning of May. The soil samples were kept frozen in plastic bags until further handling. The soil solution was collected by centrifugation at 7000 r.p.m. for 15 min using a method similar to that described by Reynolds (1984), and stored frozen until analysis.

Analyses and statistics

Analysis of N species and K were measured in an automated continuous-flow system as described previously (Arnold & van Diest, 1993a). In all subsoil solution samples and in some 30 cm samples (depending on available labour and the amount of solution left after routine analysis) Al, Ca and Mg were measured with an ICP. Occasionally, Mg in the 30 cm soil solution was measured by flame AES. Cl^- was measured with a coulometer. Cl^- is relatively inert with respect to surface exchange (especially if SO_4^{2-} is present) and chemical reactions, and is rather constant in precipitation. Therefore, its concentration fluctuates with, and thus reflects the soil's moisture content. Consequently, element:Cl ratios are more independent of soil moisture content than element concentrations, and these ratios can therefore be used as an index of the amounts of nutrients present in the soil zone extracted by the cup (c.f. Tietema and Verstraten, 1992). However, such estimates are rather rough and were therefore used only for comparisons between treatments.

For statistical analysis SAS software (SAS Institute Inc., 1990) was used. The data were not normally distributed, for which reason medians rather than means were calculated per sampling date and per plot for both sampling depths. The medians were analyzed with the SAS Glm procedure for a correct handling of missing data. A probability level of 5% was denoted as significant. For the 30 cm soil solution data obtained before January 1991, means were separated using the Ryan-Einot-Gabriel-Wagner F test as supplied in the SAS Glm procedure. This test is fully compatible with the overall Anova F test (c.f. SAS manual: GLM Procedure). Hence, it will only indicate pairwise significant differences at P values $\leq P$ from the overall F test, in contrast with some other multiple comparison tests, like Duncan's multiple range test. For data obtained later, the 2^2 design allowed a more efficient statistical analysis and more often treatment effects appeared to be significant. Still, on many individual sampling dates no significant treatment effects occurred. However, time-plots may show (insignificant) differences that persist for a certain period of time, which qualitatively proves that the treatments did have an influence in that period.

Results and discussion

Soil solution composition at 30 cm depth

pH. The pH was variable throughout the season, but did not show any general trend in time, except for the Ca treatment, where a gradual decrease was observed in 1989 and 1990 (Fig. 1). Before January 1991, only for two dates significantly higher pH values for the lime treatment were found; afterwards it frequently occurred that Ca raised, and PKMg reduced the pH significantly. In summer, the pH at the PKMg treatment frequently made a sharp drop. However, these values were based on only one or a few observations, always including those from one sampling cup that extracted relatively large amounts of soil water. The solution pH values were in the same range as the pH-$CaCl_2$ values (Arnold & van Diest, 1993a).

NO_3. Generally, the NO_3 concentrations and amounts showed an increasing trend during the sampling period. Only for the Ca treatment a decreasing trend was seen since the end of 1990 (Fig. 2). Each year, peak concentrations occurred in the autumn and winter. This indicates that ammonification and nitrification proceed when plant uptake is reduced during the dormant season, which is likely to cause N leach-

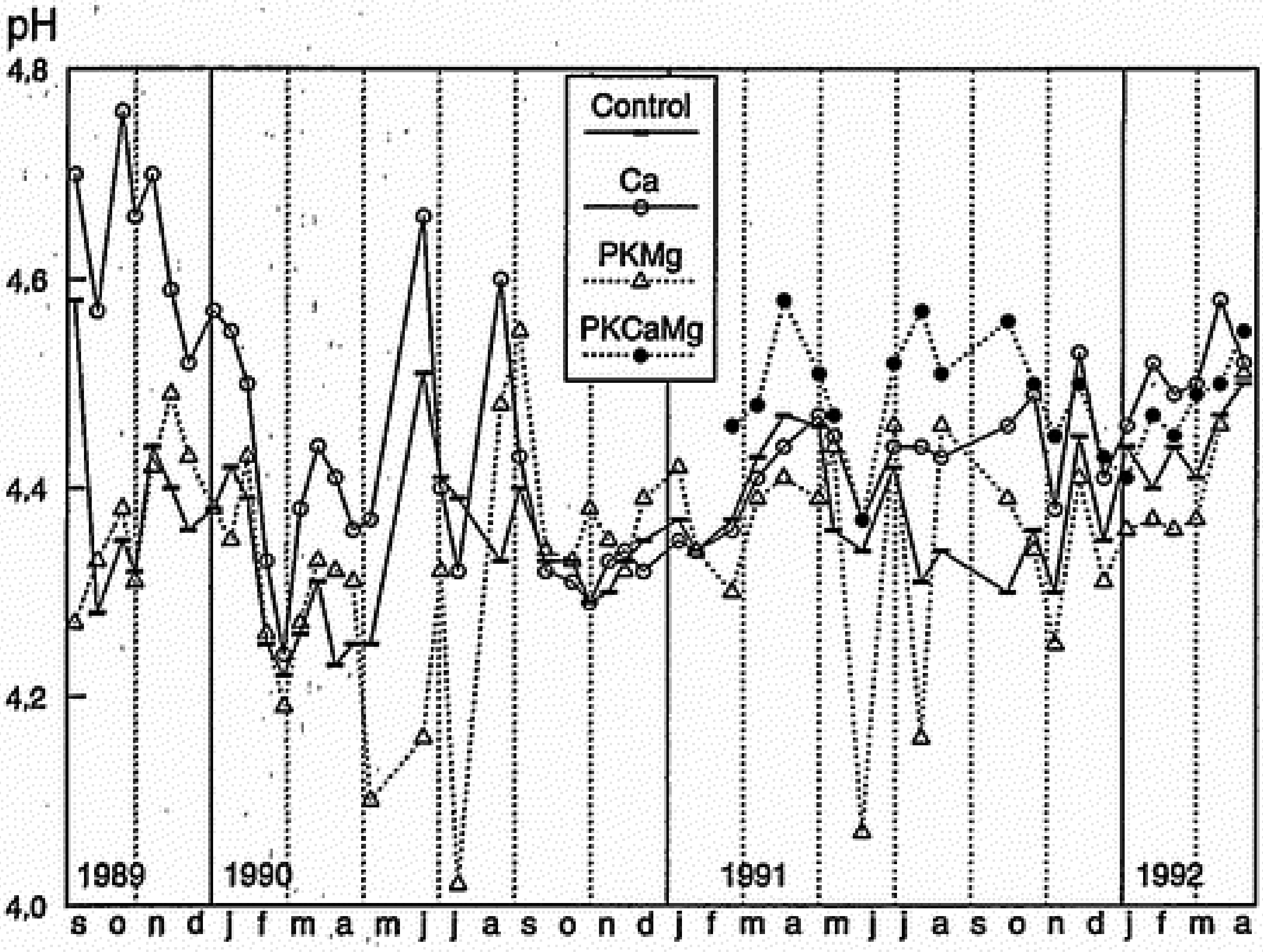

Fig. 1. pH values in the soil solution at 30 cm.

ing to below the root zone. In the vegetative period microbial processes in the topsoil may be inhibited by drought while nutrient uptake from deeper soil layers may still proceed, causing lower NO_3 concentrations. During the sampling period the NO_3 peak concentrations grew higher each year and moved to an earlier date. The increasing peak concentrations may be due to a storm and subsequent thinning that occurred on 25 January and in summer 1990, respectively. Vitousek et al. (1979) pointed out that tree harvesting may lead to increased NO_3 concentrations in the soil solution, if the soil processes that prevent NO_3 accumulation and transport are saturated. When mineralization is stimulated in canopy gaps and at the same time less NH_4 is taken up by roots, more substrate is made available to nitrification, and NO_3 may accumulate. In a situation of a precipitation excess and reduced root uptake, NO_3 is likely to be subjected to leaching since NO_3 retention is governed by biological uptake and not by abiotic chemical processes (Johnson et al., 1986). Vitousek et al. (1979) reported increased lysimeter NO_3 concentrations at least 1 year after making trenches in three different forests. In the present research, after May 1990 NO_3 concentrations quickly rose to much higher values than in 1989.

The most pronounced effects of liming on NO_3 were visible in the 1990/91-autumn/winter peaks in concentrations and amounts, but these effects diminished subsequently (Fig. 2). Although liming increased soil solution NO_3 from the start of the measurement period on, the ecosystem disturbance in 1991 seemed to enhance this effect. The subsequent decline of the liming effect may have been caused by a naturally wearing off of the disturbance effect in combination with the gradual pH decrease at the limed plots (Fig. 1). Mid 1991 for the first time significantly increased NO_3 concentrations were observed in the PKMg plots. This enhancing effect of PKMg on NO_3 suggests that the nitrifying microflora developed an ability to profit from an improved nutrient availability. In a large number of acid forest soils Kriebitzsch (1978) found fairly good correlations between availability indices of P and K+Ca and net NO_3 production, which showed that non-nitrifying soils had a low nutrient availability. However, this does not necessarily mean that supplying nutrients will directly raise nitrification. Sahrawat et al. (1985) found little effect of P addition on in-vitro ammonification and nitrification, and adding P and lime had the same stimulating effect on mineralization as adding lime only. A soil microflora adapted to poor conditions may not have the potential to develop or increase nitrification as a response to a higher nutrient availability, or only do so after a lag-phase. Probably, the sampling period in the present experiment included the end of such a lag-phase.

In several acid forest soils in Germany, Davis (1990) found NO_3 concentrations that at a 20-40-cm depth ranged from undetectable to ca. 500 mmol m^{-3}. Compared to this value, the NO_3 concentrations in the present research are high, but in the same range as, or lower than those observed by many other workers in western Europe (e.g. Van Breemen et al., 1987; Kreutzer et al, 1991; Marschner et al., 1991). In the Netherlands large quantities of atmospheric N are deposited, so that high NO_3 concentrations can be expected. The rapid increase in NO_3 concentrations after a relatively small disturbance as windfelling (see above) also indicates a high N status (Gundersen & Rasmussen, 1990). The term 'nitrogen saturation' is often used for such situations, but it is not yet consistently defined (Skeffington, 1990; Tietema, 1992; Wright et al., 1991).

NH_4. NH_4 was usually present in low concentrations relative to NO_3 (Fig. 3). Treatment effects were inconsistent and rarely significant. The peak concentrations of NH_4 in both summer seasons coincided with dry periods, when only few cups could be sampled. These peaks may be due to increased mineralization during periods with high temperatures, but more likely they are due to water readily running though the dry soil during summer showers. The NH_4 concentrations are in the same range as those found by Davis (1990) in Germany and New Zealand.

K and Mg. The concentrations of K (Fig. 4) and Mg (Fig. 5) were persistently increased due to fertilization up to the last sampling date, which was ca. 4 years after the final PKMg application (Table 2). K was applied in a soluble form and seemed to be readily washed out of the forest floor (Arnold & van Diest, 1993a). Therefore, it is likely that in the long run increased K in the soil solution was caused by K recycling (c.f. Arnold & van Diest, 1993b), e.g. canopy leaching and K release from needle litter. Because Mg was better retained in the forest floor (Arnold & van Diest, 1993a), both a direct fertilization effect and a turnover effect may have played a role in sustaining an increased Mg availability.

Al and Ca. The Al concentrations measured in the growing season of 1991 were lowered by liming and increased by PKMg (Table 3), but only at 1/7/91 these effects were significant. Van Grinsven et al. (1989), using a simulation model, predicted that additions of K and Mg (as sulphates) in a December-month would cause dramatically increased Al concentrations in the soil solution at 40 cm in the following year.

Table 3. Concentrations of Ca and Al in the soil solution at a 30 cm depth at 3 dates in 1991. The effects of liming on Ca were highly significant. Cl ratio = concentration / Cl × 1000.

Element	Treatment	mmol m^{-3} at 3 dates			Cl ratio at 3 dates		
		14/5	1/7	8/8	14/5	1/7	8/8
Ca	Control	35	21	26	46	142	105
	PKMg	85	54	99	110	164	177
	Ca	592	416	296	951	1944	1123
	PKCaMg	354	493	375	422	973	1072
Al	Control	274	183	189	404	995	808
	PKMg	521	373	546	594	956	638
	Ca	172	149	98	337	749	290
	PKCaMg	289	234	225	230	401	348
Ca/Al	Control	0.1	0.1	0.1			
	PKMg	0.2	0.2	0.3			
	Ca	5.7	4.1	5.5			
	PKCaMg	2.2	3.1	3.9			

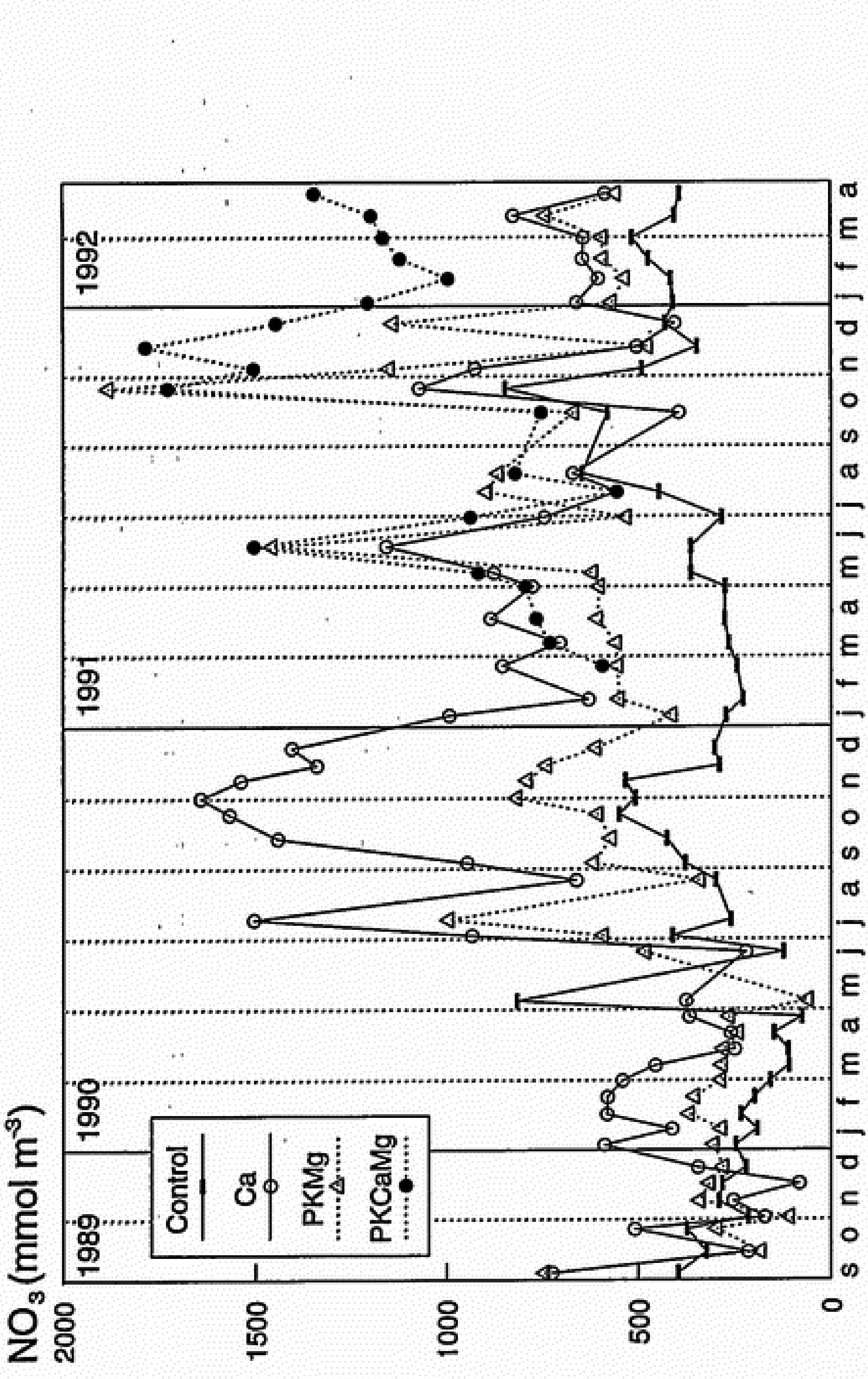

Fig. 2. *top.* NO$_3$ in the soil solution at 30 cm: concentrations.

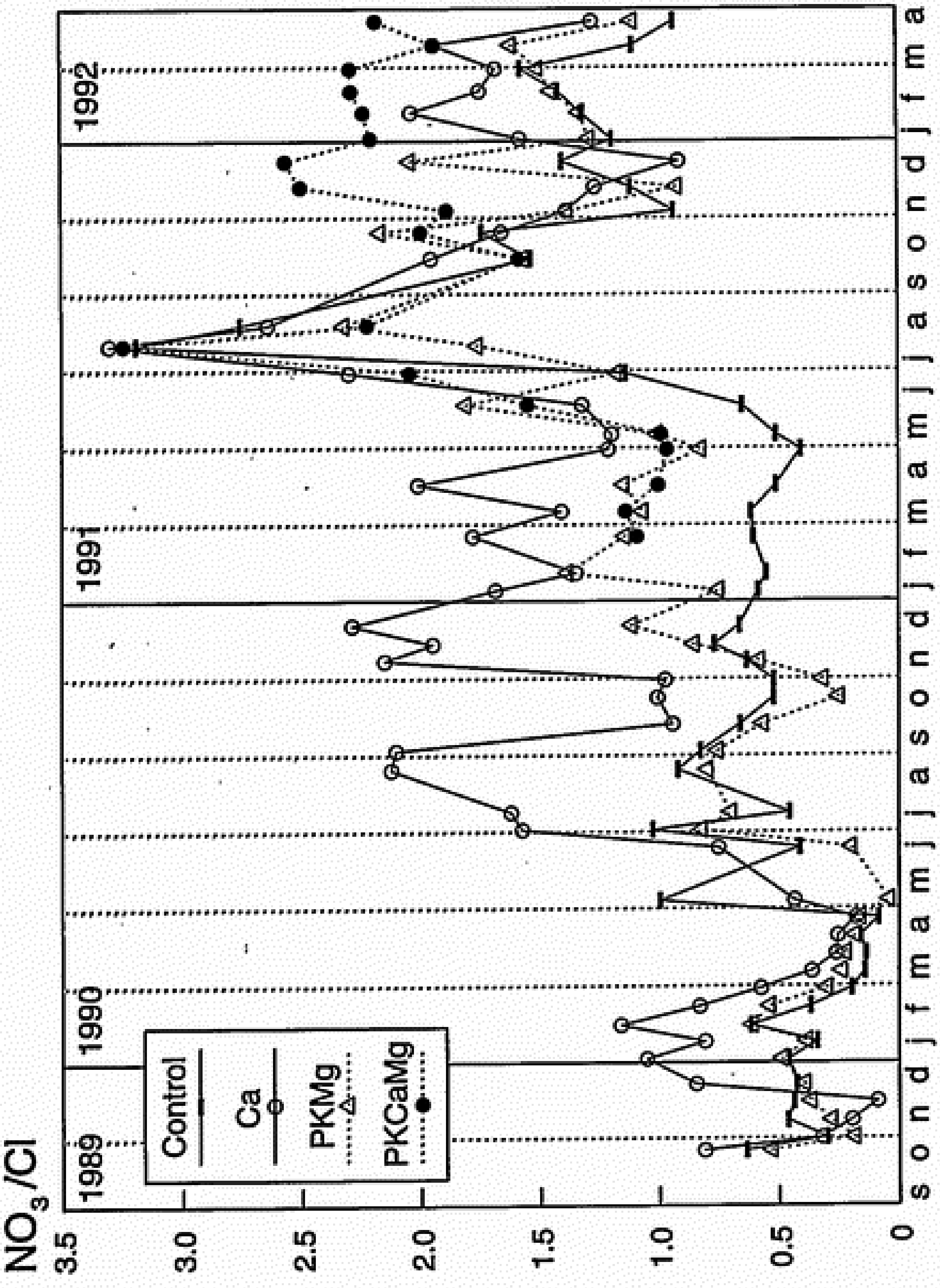

Fig. 2. *bottom*. NO_3 in the soil solution at 30 cm: estimated indices of amounts.

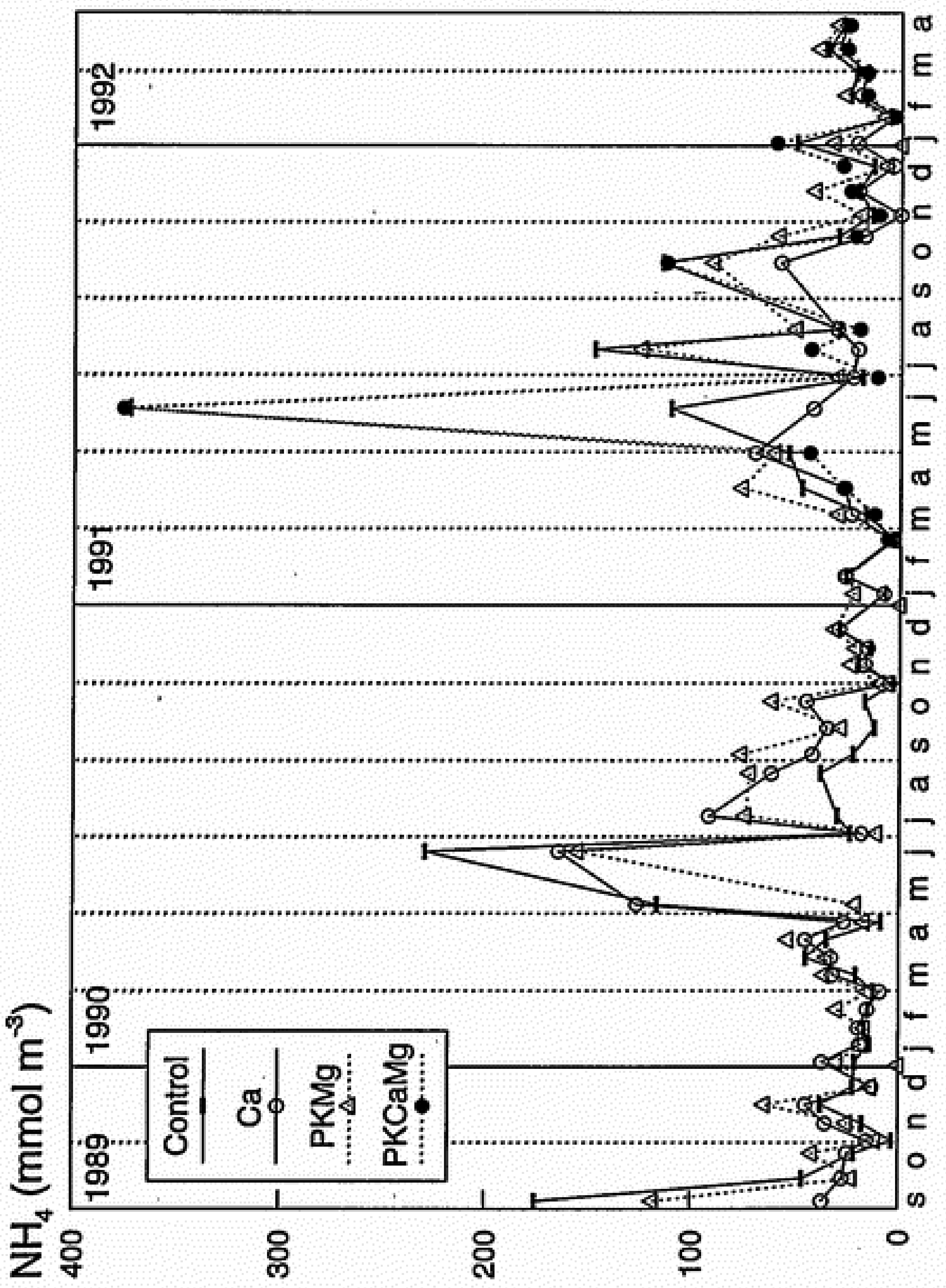

Fig. 3. *top.* NH$_4$ in the soil solution at 30 cm: concentrations.

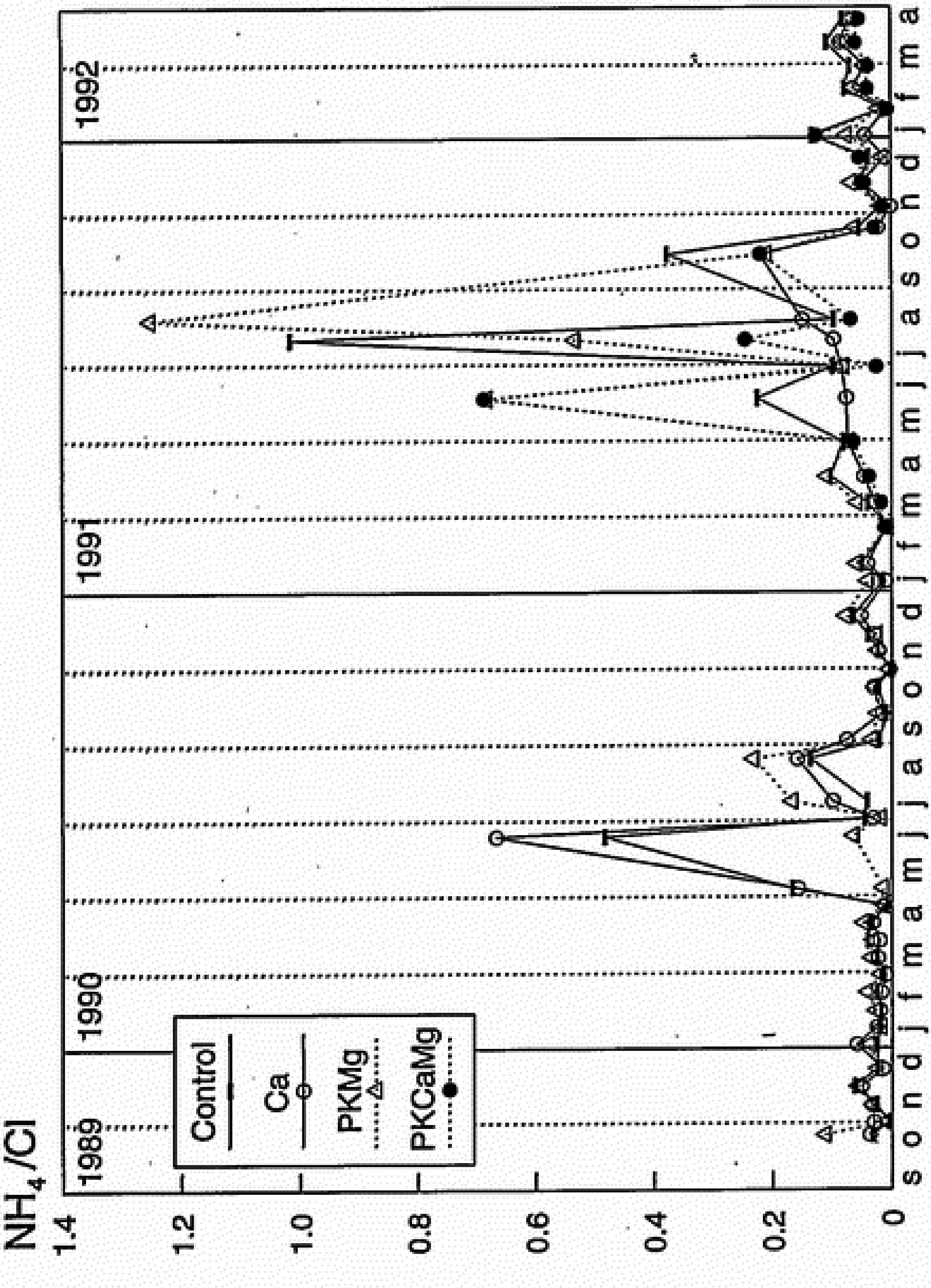

Fig. 3. *bottom*. NH_4 in the soil solution at 30 cm: estimated indices of amounts.

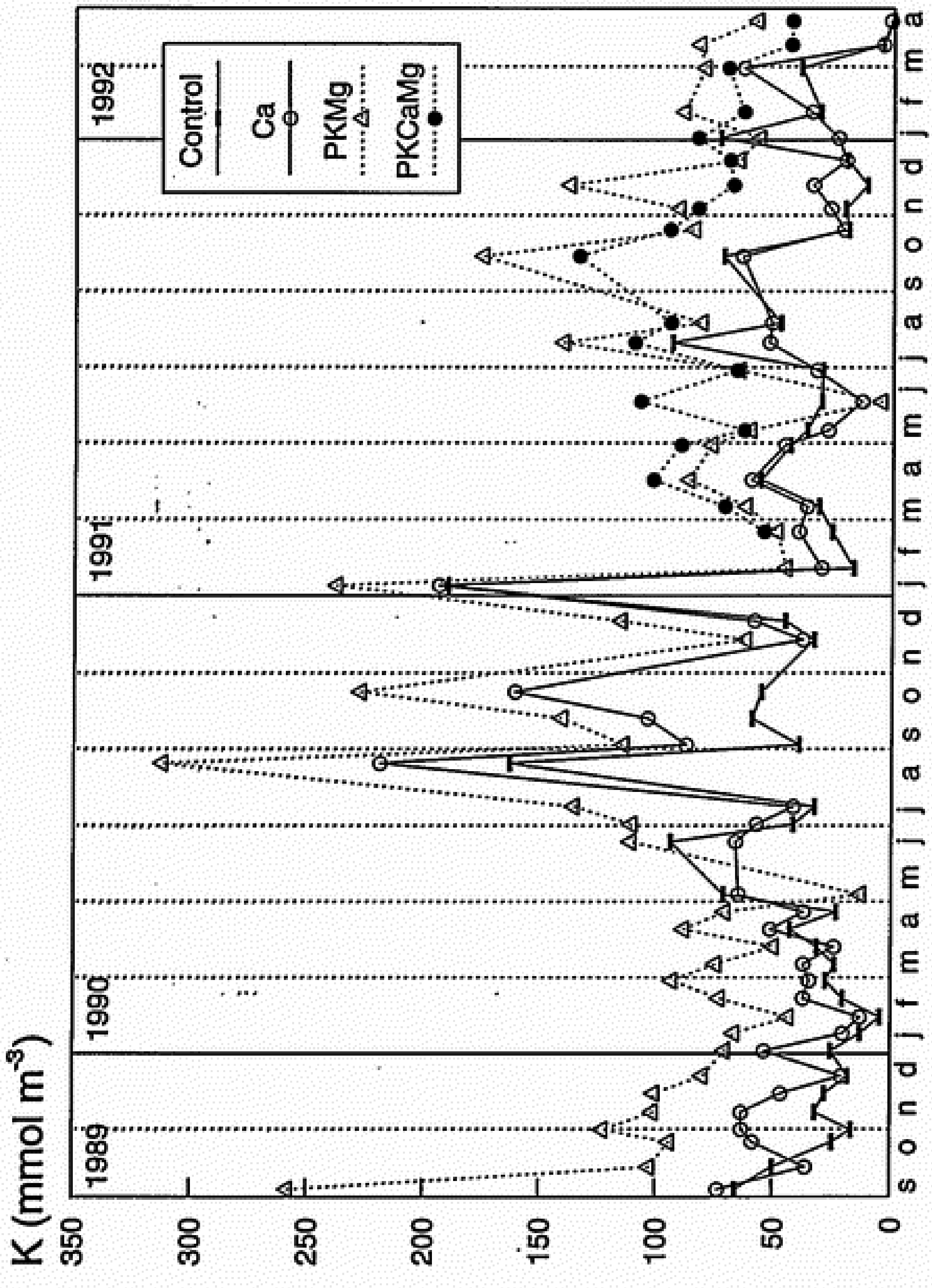

Fig. 4. *top.* K in the soil solution at 30 cm: concentrations.

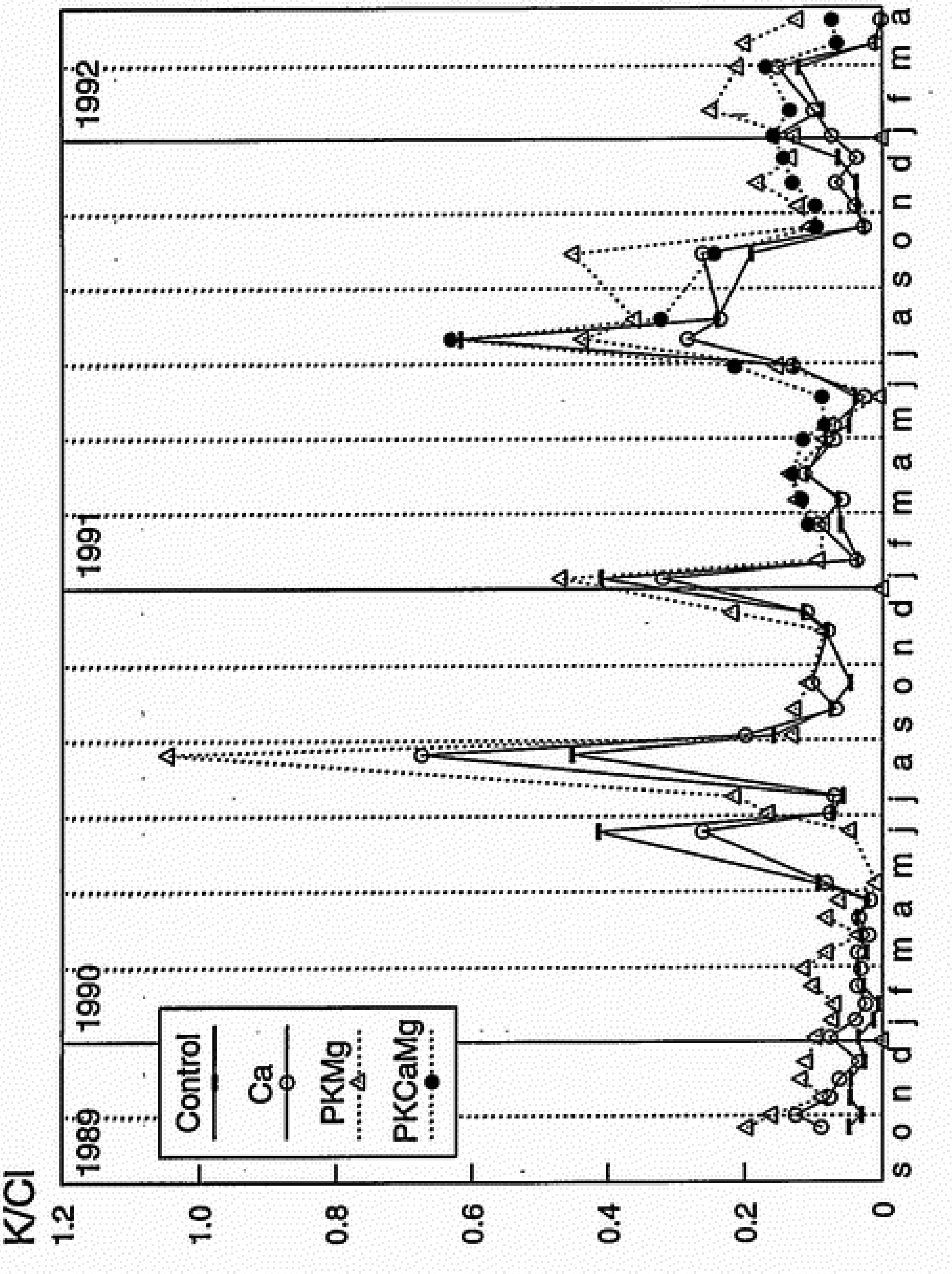

Fig. 4. *bottom*. K in the soil solution at 30 cm: estimated indices of amounts.

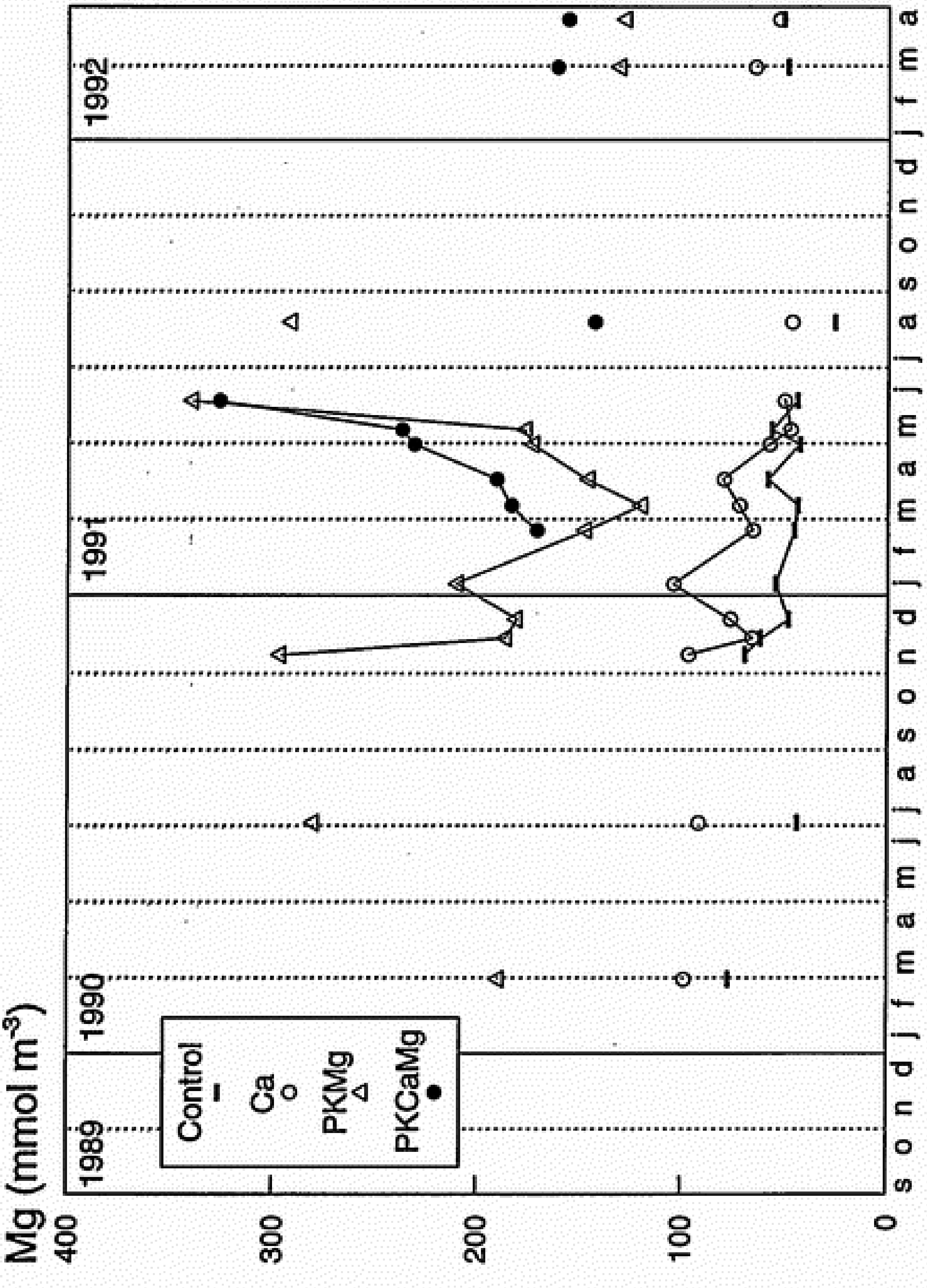

Fig. 5. *top*. Mg in the soil solution at 30 cm: concentrations.

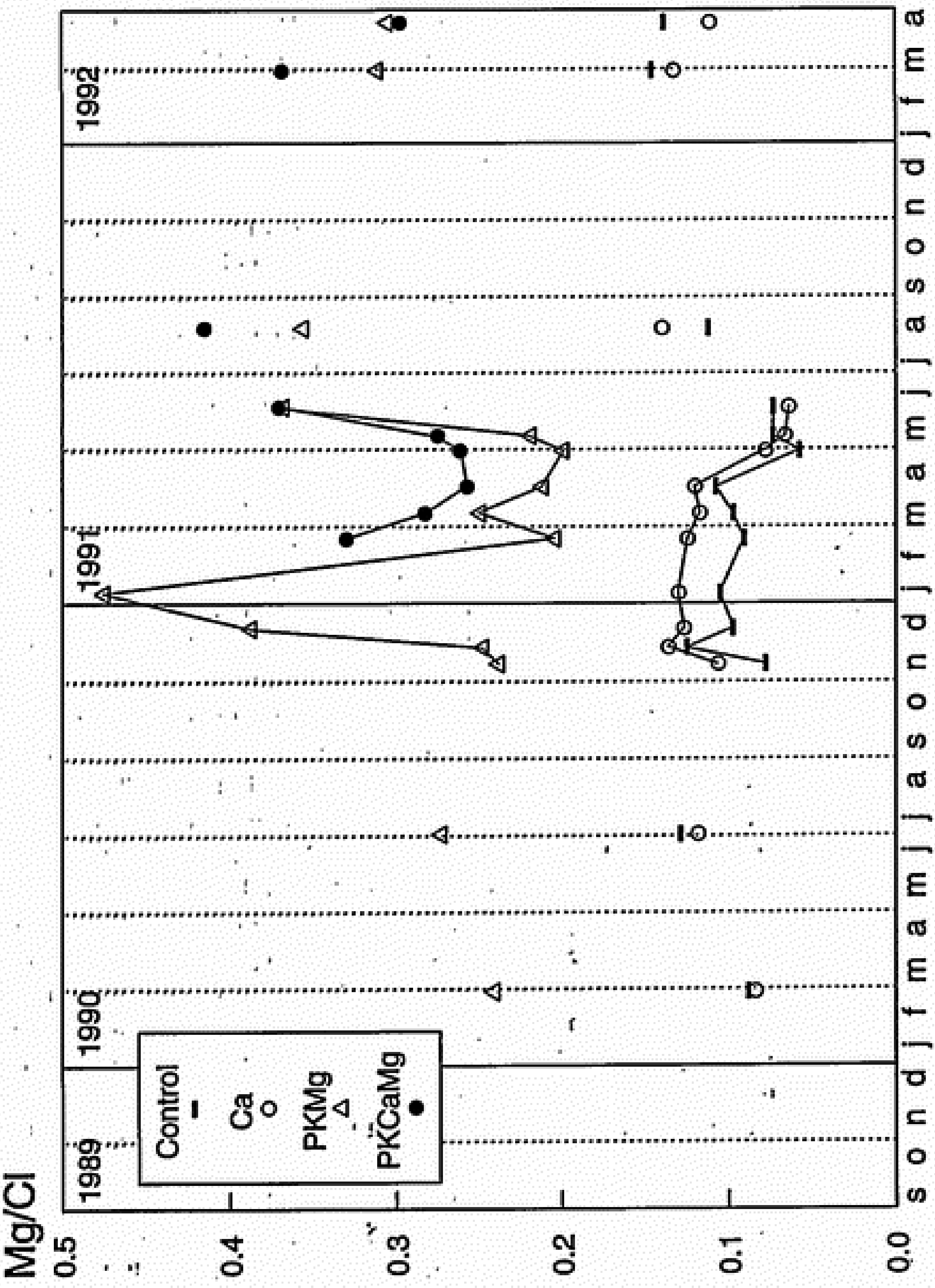

Fig. 5. *bottom*. Mg in the soil solution at 30 cm: estimated indices of amounts.

However, the model was calibrated for a different location. The actual Al peak in Harderwijk may have covered a longer period, which will probably have made it less extreme. In such a case, the eventual effect may be more harmful than that of a short and intense peak. However, the observed Al concentrations (Table 3) are lower than those known to impair Scots pine seedling roots, which are generally mentioned to be > 1 m*M*, (Arovaara and Ilvesniemi, 1990; Keltjens and Van Loenen, 1989; Eldhuset et al., 1987). Al tolerance may even be higher when ectomycorrhizae are present (Göransson and Eldhuset, 1990), which is the case in the present experiment (Kuyper, 1990). On the other hand, at the unlimed plots the Ca:Al ratios may be critical (Table 3). Ca:Al ratios < 0.2 are suspected to cause root damage in spruce (Ulrich, 1983).

Soil solution composition at 100-150 cm depth

In April 1989, Denier van der Gon (1990) analyzed the soil solutions at a 100-150 cm depth in the Control and PKMg treatments and in plots that had been treated with 6000 kg lime ha^{-1} and P, K and Mg according to Table 2. For comparison with the present data, his results were reprocessed. Median instead of mean concentrations per plot were calculated after which significance of treatment effects was assessed using the REGWF test. Therefore, the data given here (Table 4) differ slightly from those published earlier (Denier van der Gon, 1990).

NO_3 and NH_4. The present observations (Table 5) show increased NO_3 leaching after liming, as was expected (see above). On an average, liming doubled the NO_3 concentrations (Table 5). With an assumed soil moisture content of 10% (w/w), in the 100-150 cm layer of the limed plots compared to the unlimed plots an additional amount of ca. 4.5 kg NO_3-N ha^{-1} was present below the root zone. Taking the present concentrations as annual averages, a precipitation excess of 200 mm y^{-1} would effect a NO_3 leaching of ca. 9 and 21 kg N ha^{-1} y^{-1} in the unlimed and limed plots, respectively. These amounts are lower than those found to leach to a 22-cm depth in an in-situ incubation experiment carried out at the same site (Arnold et al., 1993). This, and the fact that the NO_3 concentrations at 30 cm are higher than at 100-150 cm suggest that the trees absorb NO_3 from soil segments deeper than ca. 30 cm. Denitrification probably played not more than a minor role in this well-aerated sandy soil (Grofman & Tiedje, 1989). The annual N deposition in the region where the experiment was conducted amounts to approx. 30 kg NH_4-N and 10 kg NO_3-N ha^{-1} (Beier & Rasmussen, 1993). Thus, total N deposition is higher than the estimated quantities of N annually lost due to NO_3 leaching. NH_4 leaching could not be estimated, but was probably negligible. In a pine forest in Germany with throughfall depositions of NH_4 and NO_3 almost identical to those mentioned above, Van Grinsven et al. (1991) found NO_3 fluxes at a 1 m depth amounting to ca. 17 kg N ha^{-1} y^{-1}, whereas NH_4 did not leach to that depth.

In 1989 no effect of liming on NO_3 was found (Table 4), which was due to the high NO_3 concentrations in the unlimed plots in 1989, relative to those in 1991 (Table 5). This may be a result of a higher mineralization and/or nitrification, a low-

Table 4. Median concentrations of elements in the soil solution at a 100-150 cm depth in several experimental plots with Scots pine in April 1989 (from: Denier van der Gon, 1990).

Treatment	mmol m^{-3}							
	NH_4	NO_3	K	Ca	Mg	Al	Cl	SO_4
Control	85 a[z]	518 a	53 a	141 a	102 a	151 a	642 a	317 a
PKMg	119 a	422 a	106 a	192 a	466 b	206 a	708 a	832 b
PKMg + 6000 kg lime ha^{-1}	27 a	599 a	52 a	646 b	375 b	134 a	623 a	1027 b

[z] Averages followed by a common letter are not significantly different (REGWF test at $P = 0.05$).

Table 5. Median concentrations of elements in the soil solution at a 100-150 cm depth in several experimental plots with Scots pine in April/May 1991.

Treatment	mmol m^{-3}						
	NH4	NO3	K	Ca	Mg	Al	Cl
Control	61	250	85	238	110	47	1006
PKMg	84	405	181	312	320	57	1107
Ca	97	826	101	484	173	48	895
PKCaMg	76	669	142	607	306	51	1025
P values per treatment (dashes: $P > 0.10$):							
Ca	–	0.008	–	0.0001	–	–	–
PKMg	–	–	0.001	0.003	0.0002	–	–
Ca×PKMg	0.06	–	0.05	–	–	–	–

er N uptake, or both, in 1988 than in 1990. Because the relatively moist summer conditions in 1988 were favourable for Scots pine growth (Arnold & van Diest, 1993b), it is likely that tree N uptake was stimulated, rather than reduced. But mineralization and nitrification were probably more stimulated than tree uptake, because microbial processes can more readily respond to changing external conditions. Further, the NO_3 concentrations at 30 cm showed a pronounced difference between the limed and unlimed plots at the end of 1990 (Figure 2), which may be a reason that in spring 1991 a liming effect was observed in the subsoil. Marschner et al. (1989) found rather steady NO_3 concentrations of ca. 140 mmol m^{-3} at a 2 m depth in the control plot of a Scots pine liming experiment. A sharp increase to ca. 800 mmol m^{-3} was observed 6 months after liming and a gradual decrease to ca. 280 mmol m^{-3} in the subsequent 2 y.

There were no significant effects of PKMg on the NO_3 concentrations (Table 5) because at the time of sampling these effects just started to appear in the topsoil (see above).

It is unusual to find higher NH_4 soil solution concentrations in the subsoil than in the topsoil (Table 5, Figure 3). But the measured NH_4 concentrations were probably too high, because the filters that were used during the centrifugation contained NH_4.

However, as this contamination was probably systematic, comparison of treatments is still valid, which shows no significant main effects and a weak Ca×PKMg interaction (Table 5). The centrifugation procedure of the 1989 samples was similar to that of the present research, and may also have caused a systematic NH_4 contamination. The data suggest that liming lowered the NH_4 concentration in 1989 (Table 4), but the effect was not significant (overall F test: $P = 0.06$). Lowering of NH_4 in the soil solution by liming was not expected, because in this Scots pine stand liming increased N mineralization, but not the proportion of mineralized N that was nitrified (Arnold et al., 1993).

K and Mg. K and Mg were significantly increased in the PKMg-amended plots. With the assumptions mentioned above, the estimated additional annual leaching of K and Mg caused by fertilization would amount to 5 and 8 kg ha^{-1}, respectively. In 1989 these values were 4 and 18 kg ha^{-1}, respectively (recalculated from Denier van der Gon, 1990). The obvious conclusion that Mg is more susceptible to leaching than K is contradicted by previous results (Arnold & van Diest, 1993a), which suggested a direct and complete loss of added K from the forest floor, while Mg was retained to some extent. With the present data the apparently lower K leaching is hard to explain. It can be speculated that large quantities of K leached deeper than 1.5 m within 1 year (after the final 1988 application). Marschner et al. (1989) found the maximum increase in K concentration in the soil solution at a 2 m depth only 2 months after K application on a sandy soil. Another explanation may be the larger crop demand for K than for Mg.

Al and Ca. The Al concentrations (Table 5) are low when compared to those in Table 4. In the present research a 3-fold dilution was used during the measurements, which may have caused an error. Unfortunately, this can not be verified any more from the original results. However, it is clear that Al was not influenced by any treatment, as was found earlier (Table 4). Marschner et al. (1989) found persistently increased Al concentrations in the soil solution at a 2 m depth in 2 years directly after additions of K_2SO_4 and lime, whereas those at 50 cm were only slightly raised for ca. 1 year. The Table 4 data were obtained 3 years after the second and last lime application (3000 kg lime ha^{-1}) in the 6000 kg lime treatment and 1 year after the 3rd and last K and Mg applications, in which time a possibly induced Al flush (Van Grinsven et al., 1989) may have passed beyond the 100-150 cm layer. The unaffected Al concentrations at 100-150 cm suggest that the observed increases at 30 cm in the PKMg plots (see above) are occasional. The seemingly lower Al concentration at the limed plots in Table 4 is not confirmed by later observations (Table 5).

Ca was significantly increased by liming in 1989 and 1991 (Tables 4 and 5). In 1991 the Ca concentration was also increased by PKMg (Table 5). This may be due to exchange processes, which created a Ca front that had not yet reached the 1 m depth in 1989 (Table 4). In 1991, this effect was not found at 30 cm (Table 3), indicating that a new equilibrium had established.

Relationships between cation and anion concentrations

To examine whether liming may have increased cation mobilization by an increased nitrification, multiple regression analysis of individual cation concentrations on anion concentrations was carried out with log-transformed data. Correlations between cation- and NO_3 concentrations suggest the occurrence of this mobilization process (Mulder & Van Breemen, 1987; Van Breemen & Jordens, 1983).

In most cases positive correlations between cation- and Cl concentrations were found (Tables 6 and 7). These can be attributed to evaporation/dilution effects.

For Mg and especially for K at 30 cm poor correlations with anions were found and liming did not improve correlations with NO_3 (Table 6). Generally, Al and Ca at 30 cm correlated better with Cl and/or NO_3 than did K and Mg. Liming caused Al to become correlated with NO_3 (Table 6), indicating that in 1991 NO_3 played a role in Al mobilization in the topsoil of the limed plots. However, the latter was not paralleled in the deeper soil solution, where Al was correlated with NO_3 irrespective of treatment, or where liming even cancelled this correlation (Table 7). Of the other cations in the soil solution at 100-150 cm only Ca in 1991 was correlated with NO_3 as a consequence of liming (Table 7). It can thus be concluded that there is no direct evidence of liming to increase leaching of nutrient cations through the formation of nitric acid.

Table 6. Results of (multiple) regression of cation on anion concentrations in soil moisture at 30 cm sampled at two dates. Models with overall P values < 0.05 and T values < 0.05 for each anion; + : positive correlation; (+) : regression model with slightly smaller R^2 value.

Cation	Period[a]	Treatment	Anions		R^2
			Cl	NO_3	
K	1	–Lime	+		0.09
		+Lime	+		0.13
	2	–Lime		+	0.07
		+Lime	+		0.03
	3	–Lime		+	0.02
		+Lime		+	0.06
Mg	1	–Lime		+	0.18
		+Lime	+	(+)	0.37
	2	–Lime	+	+	0.35
		+Lime	+		0.10
	3	–Lime	+	+	0.64
		+Lime	+	+	0.34
Al	May-Aug 1991	–Lime	+		0.56
		+Lime	+	+	0.51
Ca	May-Aug 1991	–Lime	+	+	0.40
		+Lime		+	0.28

[a] 1 = Sept. 1989 - April 1990; 2 = April 1990 - April 1991; 3 = April 1991 - April 1992.

Table 7. Results of (multiple) regression of cation on anion concentrations in soil moisture at 100-150 cm sampled at two dates. Models with overall P values < 0.0002 and T values < 0.05 for each anion; + : positive correlation; (+) : (multiple) regression model with slightly smaller R^2 value.

Date	Cation	Treatment	Anions			R^2
			Cl	NO_3	SO_4	
April 1989	K	Control	(+)		+	0.67
		Limed[a]	+			0.56
	Ca	Control	+		(+)	0.43
		Limed	+		+	0.84
	Mg	Control	+	+ (+)	(+)	0.87
		Limed	+		+	0.90
	Al	Control	(+)	(+) +	+	0.92
		Limed	+	+ (+)	(+)	0.88
	Na	Control	(+)		+	0.62
		Limed	(+)		+	0.57
April	K	–Lime	+	+	nd[b]	0.64
		+Lime[c]	+		nd	0.71
	Ca	–Lime	+		nd	0.50
		+Lime	+	+ (+)	nd	0.53
	Mg	–Lime	+		nd	0.43
		+Lime	+		nd	0.40
	Al	–Lime	+	+	nd	0.55
		+Lime	+		nd	0.67
	Na	–Lime	+		nd	0.92
		+Lime	+		nd	0.91

[a] 6000 kg lime ha^{-1}. [b] Not determined. [c] 3000 kg lime ha^{-1}.

Conclusions

When Scots pine was treated with P, K, Mg and lime, the concentrations of each of the involved cations was increased in the soil solutions in the root zone. Consequently, the main objective of these applications, an increased nutrient availability and subsequent uptake by the trees, was realized, as was also shown by foliar analysis (Arnold & van Diest, 1993b). Several treatments increased the soil solution concentrations of K, Ca, Mg, NO_3 and SO_4 below the most densely rooted soil zone, indicating that these ions were subjected to leaching. Part of the increased leaching was due to the use of highly soluble K- and Mg sulphates. In the period 1988-1990, ca. 5% and 8-18% of the applied K and Mg, respectively, annually leached to below a 1 m depth. Moreover, K leaching directly following application may have been considerable. Nevertheless, K was successfully incorporated in the biomass and strongly increased the trees' volume growth (Arnold & van Diest, 1993b). This indicates that the applied amount of K greatly exceeded the uptake potential of the trees, and that little K was necessary for a considerable growth response.

When growth responses occur in a narrow range of nutrient availability, the use of slow-release fertilizers may be appropriate, because they reduce leaching. However, they are not necessarily always the proper choice. In principle, fertilizers should release nutrients at a rate not higher than the expected maximum uptake rate during the growing season. A lower release rate may be beneficial, maintaining a continuous nutrient demand that keeps the nutrient pool in the soil solution at a low level until the end of the growing season and, thus, reduces subsequent nutrient leaching. In most cases, this will be accomplished by using slow-release fertilizers, but for fast-growing tree species or in stands before canopy closure easily soluble fertilizers may be necessary to meet the stand's nutrient requirements.

In the year following a heavy storm, NO_3 concentrations reached maxima in the root zone of the plots that had received lime only (Fig. 2). This suggests that liming may corroborate NO_3 leaching invoked by physical disturbance.

The often quoted hazard of liming to increase NO_3 leaching appeared to possibly apply to fertilization as well. The former will occur in the short term, while the latter may be a long-term effect. Increased soil solution NO_3 concentrations as a result of PKMg additions were measured from mid 1991 on at a 30 cm, but not below a 1 m depth. In spite of an increased nitrification, the estimated annual N leaching was lower than the annual N deposition for each treatment, indicating that N is retained in the ecosystem and that a situation of 'N saturation' is not (yet) reached.

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