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Effects of inorganic nitrogen application on the dynamics of the soil solution composition in the root zone of maize

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Received 11 July 1995. Accepted in revised form 5 December 1995

Key words: maize, nitrate, nitrogen fertilizer, root zone, soil solution, soil solution sampler with looped hollow fiber (LHF-sampler), *Zea mays* L.

Abstract

The effect of inorganic nitrogen (N) fertilizer on the ionic composition of the soil solution under maize (*Zea mays* L.) was studied. A pot experiment was carried out with two treatments combined factorially, with or without N application (Ca(NO₃)₂; +N and - N treatments, respectively), and with or without plants. Three looped hollow fiber samplers were installed in each pot to sample soil solutions nondestructively from the root zone, seven times during the 50-day growth period. Plants were harvested on the 50th day, and their nutrient contents determined.

Effects of N fertilizer on the soil solutions were observed by the first sampling, 2 days after sowing. The concentrations of Ca and NO₃⁻ and electrical conductivity (EC) increased significantly in the +N treatments as direct effects of fertilizer application. In addition, the concentrations of Mg, K, Na and H⁺ also increased and that of P decreased significantly as indirect effects caused by the re-establishment of chemical equilibria. This suggested the greater supply as well as the greater possibility of leaching loss not only of NO₃⁻ but also of Ca, Mg and K. In the treatments with plants, the concentrations of NO₃⁻, Ca, Mg and K decreased with time and pH increased significantly compared with the unplanted soil. The depletion of N in the soil solution roughly agreed with the amount of N taken up by the plant. The depletions of K from the soil solution amounted to less than 10% of the amount of the K taken up, suggesting intensive replenishment of K from exchange sites in the soil. Depletions of Ca and Mg were several times higher than the amounts taken up, indicating that the depletions resulted from the adsorption of the divalent cations by the soil rather than uptake by plants. Because NO₃⁻ is hardly absorbed by exchange sites in soil and was the dominant anion in solution, it was concluded that NO₃⁻ had a major role in controlling cation concentrations in the soil solution and, consequently, on their availability for uptake by plants as well as their possible leaching loss.

Introduction

Of all nutrients, nitrogen (N) usually has the largest effect on plant growth. Its availability also influences the uptake, not only of N itself, but also of other nutrients. This has been partly attributed to better plant growth by which N-fertilized plants have larger root systems for the capture of all nutrients. As well as

this direct effect on plants, increase of ionic concentrations in the soil solution following N application have been reported (Barraclough, 1989; Kishita and Obama, 1965; Okajima et al., 1974; White and Ross, 1936). Often, the change is a positive one, as demonstrated for N, P and K (Halevy et al., 1987) and for Ca, Zn and Cd (Lorenz et al., 1994). Because plants acquire most of their nutrients from the soil solution, an increase of ionic concentration in the soil solution should improve the availability of those ions to plants, other things

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being equal, even though they were not added in the fertilizer.

Little is known, however, about the soil solution composition of N-fertilized soils during plant growth. One reason for this is that there have been few suitable techniques to collect soil solutions nondestructively from the root zone. For studies that relied on destructive sampling (e.g. Barraclough, 1989; Gregory et al., 1979), it was not possible to study in detail the interrelations of ions in the soil solution. In addition most of the studies which relied on nondestructive sampling with a suction method concentrated mainly on cation uptake by the plant (Hansen, 1972; Nielsen and Hansen 1984) or on diagnosis of soil (Itoh, 1982) rather than on the composition of the soil solution itself.

Bouldin (1989) suggested that soil solution composition changes under the rule of electrical neutrality, and thus, ionic concentrations are interrelated rather than independent. Yanai et al. (1995) showed that cation and anion concentrations were related as the soil solution composition changed during plant growth, and the dynamics was mostly influenced by the change of NO_3^- concentration. N application was expected, therefore, to have complex effects on the dynamics of the soil solution composition during plant growth.

In this study the authors carried out a pot experiment in which maize was planted on soils with or without the application of N fertilizer, with special attention to the dynamics of the soil solution composition. The objectives of this study were as follows: (1) to investigate the effects of N application on the initial soil solution composition; (2) to investigate the effects of N application on the dynamics of the soil solution composition during plant growth; and (3) to quantify the relationship between the amount of elements taken up by plants and the apparent decrease of the elements in the soil solution, with special reference to N, K, Ca, Mg and P.

Materials and methods

Experimental design

The experiment had a factorial design with two treatments, each at two rates of N application with or without plants (*Zea mays* L., cv. Artus). Each planted treatment was replicated three times and each unplanted treatment duplicated. In all, ten pots were used.

Table 1. Selected general properties of the soil^a

Location	Dundee, Scotland, UK
Soil series	Carpow
Horizon	Ap
Textural class	Sandy loam
Loss on ignition	7.8 g 100 g ⁻¹
pH (in water)	6.31
CEC	23.2cmol(+) kg ⁻¹
Exchangeable cations	
Ca	14.9cmol(+) kg ⁻¹
Mg	2.99cmol(+) kg ⁻¹
Na	0.07cmol(+) kg ⁻¹
K	0.58cmol(+) kg ⁻¹
Total phosphorus ^b	434 mg P ₂ O ₅ 100 g ⁻¹

^aSource: Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, UK.

^bSodium hydroxide fusion method (Smith and Bain, 1982).

Soil and pot installation

Top soil, 0-50 mm depth, was collected in April 1993 from a field at the Scottish Crop Research Institute. The soil, classified as Eutric Cambisol (FAO-Unesco, 1974) and Eutrochrept (Soil Survey Staff, 1994), is a sandy loam derived from coarse sand and gravel. It was air-dried and sieved to remove gravel and debris >2mm. Some general properties of the soil are listed in Table 1.

13.2 kg of moist soil (volumetric water content 25%) was packed into each of ten plastic cylindrical pots, 40 cm high, 18.8 cm diameter, to a depth of 38 cm. The dry bulk density of the soil was 1.00 Mg m⁻³. The bottom of each pot was sealed with vinyl sheet to prevent leaching of the soil solution. Phosphorus and potassium (as KH_2PO_4 and K_2SO_4 solutions) were applied uniformly to the soil at rates equivalent to 15 g P₂O₅ m⁻² and 18.4 g K₂O m⁻². Nitrogen (as $\text{Ca}(\text{NO}_3)_2$ solution) was applied to the soil in 5 pots at a rate equivalent to 20 g N m⁻²: the '+N' treatment. The other 5 pots received no nitrogen fertilizer: the '-N' treatment. An inorganic N compound, $\text{Ca}(\text{NO}_3)_2$, was used to demonstrate the effects of NO_3^- as well as to simplify the experiment by avoiding nitrification process of fertilized nitrogen.

Looped hollow fiber (LHF) technique (Yanai et al., 1993) was applied to sample the soil solution nondestructively from the root zone. The LHF-sampler is composed of a thin, flexible, polyvinyl alcohol hollow fiber with an external diameter of 900 μm , a silicon

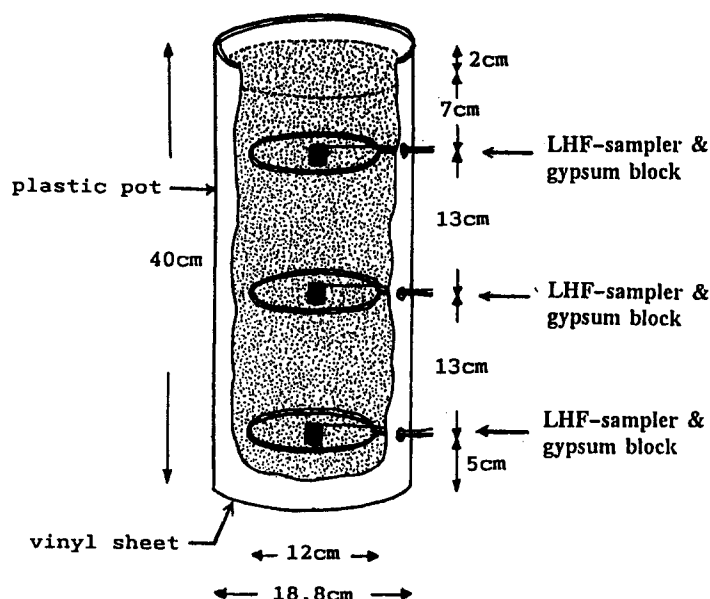


Figure 1. Schematic diagram of the pot.

tube and a disposable syringe, and can be used to collect soil solutions by suction method. Three samplers were installed in each pot, as shown in Figure 1. Samplers of 12 cm loop diameter were placed at depths of 7 cm, 20 cm and 33 cm: the top middle and bottom layers, respectively. A gypsum block was also placed at each depth to monitor the water potential at the sampling times by measuring the electrical resistance of the gypsum block. The soil surface was covered with black plastic beads to a depth of 1 cm to minimize water evaporation.

Plant and water management

For planted treatments, three caryopses of maize were sown initially in each pot at a depth of 1 cm. After five days, the seedlings were thinned to one per pot.

Pots were watered every two or three days to maintain the water content at 25%. Water additions were determined by repeated weighing of the pots. Deionized water was poured onto the surface of the pots. According to the moisture characteristic curve obtained by tension table and pressure plate methods, a water content of 25% was equivalent to a water potential of -7 kPa (pF1.8), which was regarded to be near the field capacity.

The experiment was carried out in a greenhouse at the Scottish Crop Research Institute for 50 days, from 27th of May to 15th of July, 1993.

Analyses of soil solution and plant material

Soil solutions were sampled seven times: 2, 9, 20, 30, 36, 42 and 50 days after sowing, 24 hours after watering on each occasion. The water potential of the soil was usually between -3.16 kPa (pF1.5) and -31.6 kPa (pF2.5). Ten to fifteen mL of soil solution was collected from each LHF-sampler, which was sufficient for the chemical analyses of this experiment.

For each solution, the following items were measured: sampling volume, electrical conductivity (EC), pH and the concentration of six elements (Ca, Mg, K, Na, S and P) and two ions (NH_4^+ and NO_3^-). EC and pH were measured electrochemically (Jenway Model 4070 EC meter, and Russell combined pH/reference cell). Ca, Mg, K, Na, S and P were analyzed by inductively coupled plasma emission spectroscopy (ICP Analyzer ARL 3580). NH_4^+ and NO_3^- were measured colorimetrically using a segmented-flow auto-analyzer (Skalar Analytics, Breda, The Netherlands).

Shoots of the plants were harvested on day 50. They were weighed, dried, reweighed, ground to powder in a ball mill, and analyzed for the seven elements as follows. Concentrations of total N were determined using a Tracermass stable isotope mass spectrometer (Europa Scientific, Crewe, UK) after the sample combustion in Europa Scientific Roboprep-CN. Concentrations of Ca, Mg, K, Na, P and S, were measured by ICP after digestion of the samples in HCl and HNO_3 solution.

Table 2. Correlations among the measurements of electrical conductivity(EC) of the soil solution at successive time points^a.

Time	1	2	3	4	5	6
2	0.99					
3	0.94	0.96				
4	0.71	0.75	0.83			
5	0.43	0.46	0.52	0.84		
6	0.37	0.40	0.46	0.80	0.99	
7	0.31	0.34	0.40	0.77	0.98	0.99

^a Time points of 1 to 7 correspond to 2, 9, 20, 30, 36, 42 and 50 days after sowing.

Statistical analysis

In this experiment repeated measurements of the soil solution composition were made on the same pots over a period of time. In such experiments, measurements on the same pots tend to be correlated, with the degree of correlation depending on the time between the measurements, and this must be taken into account in the analysis. Gabriel (1961, 1962) defined a set of repeated observations to have ante-dependence structure of order r if the observations at each time point, given the previous r observations, are independent of all further preceding observations. The statistical package Genstat 5 (Payne et al., 1987) has procedures to calculate the order of ante-dependence of a set of data and to test for overall treatment effects given the order of ante-dependence, using the method of Kenward (1987). Treatment effects at the individual time points may be examined by analysis of covariance, adjusting for the previous r observations. The analysis will be discussed in detail for EC and briefly for the other variables. In this analysis, H^+ concentrations were used instead of pH values.

The complete set of data for plants were subjected to an analysis of variance with Genstat 5.

Results

Soil solutions

Figure 2 shows the changes in EC over time for each treatment and position in the pot. The measurements at each time point are positively correlated, with strong correlations between successive measurements and a steady decrease in the correlation coefficients as the

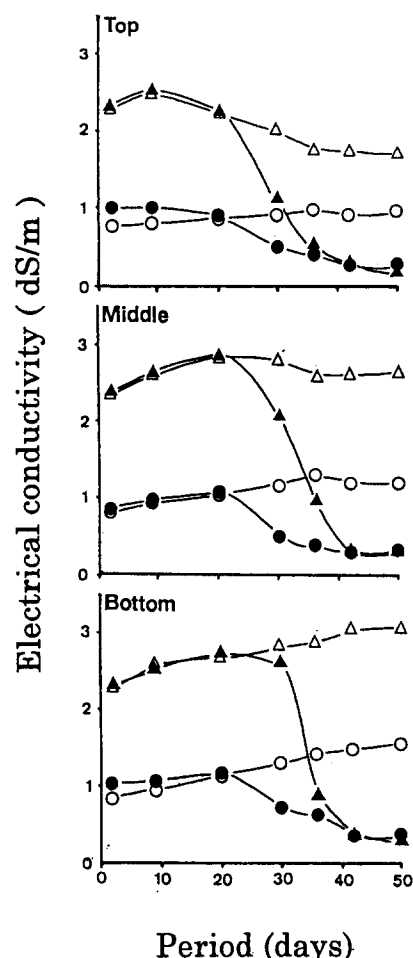


Figure 2. Dynamics of EC of the soil solution at the top, middle and bottom layers of the pots. ○: -Nitrogen without plant, ●: -Nitrogen with plant, △: +Nitrogen without plant, ▲: +Nitrogen with plant.

time between measurements increased (Table 2). The hypothesis of independence of the variables is rejected in favor of ante-dependence of order 1, with $p < 0.001$. The use of a higher order of ante-dependence structure does not improve the fit significantly. Therefore, analyses of variance at the successive time points will be highly dependent on each other, but analyses of covariance at each time point, with the preceding observation as a covariate, will be independent and will show how the effects of the treatment vary with time. The interactions between +N and -N, unplanted and planted pots and top, middle and bottom layers are complex and vary with time as shown in Figure 2.

At the first sampling time, the pots receiving N had a significantly higher EC than those not receiving N in both planted and unplanted treatments ($p < 0.001$). In the planted pots, this N effect continued until the third sampling time at day 20, but there was no significant

effect after that. Instead, by day 30, the EC was significantly lower in planted pots than in unplanted pots ($p < 0.05$). Spatial differences were also observed. By day 20 the EC in the top samples had decreased so that it was significantly lower than in the middle or bottom samples ($p < 0.01$), possibly due to stronger effects of roots which stretched from the top layer to deeper ones in soil. Also the difference in EC between +N and -N pots was smaller in the top samples than in the middle or bottom samples by day 30 ($p < 0.01$), due to greater amount of nutrient uptake in the +N pots. On day 36, however, the mean EC of the +N planted pots had decreased so much that it was no longer significantly different from the EC of the -N planted pots. In the unplanted pots, EC was significantly greater in the +N than the -N pots throughout the experiment ($p < 0.001$).

To present the general trends of the dynamics of the soil solution concentration of individual ions, we herein concentrate on the top layer, which would have been most intensively colonized by roots throughout the experiment and in which, therefore, nutrient depletions would have been most severe and prolonged. Again, the plant by nitrogen interaction is complex and varies with time.

Calcium and nitrate, as the dominant cation and anion, varied similarly to EC (Fig. 3), although NO_3^- concentration was less stable with time than EC. Not surprisingly, calcium nitrate application had a significant effect on the concentrations of both ions from the first sampling time ($p < 0.001$). For the treatments with plants, concentrations of calcium and nitrate decreased significantly after 30 days compared with the unplanted soils. After 36 days there was no significant effect of the N application on the concentrations of calcium and nitrate in the planted pots.

The application of calcium nitrate also had significant effects on the concentrations of other ions in the soil solution. Concentrations of Mg and K were increased following the application of calcium nitrate; pH and concentration of P were decreased (Fig. 3). In the planted soils, significant depletions in Mg and K were observed after 30 and 36 days, respectively ($p < 0.01$). The final concentrations of Mg and K were as low as 0.1 mM and 0.05 mM, respectively. In contrast, the concentration of P and pH increased in planted soils after 30 days ($p < 0.01$). Nevertheless, P was always dilute in the soil solution; ca. 0.01 mM. In the analysis, the sorption of P by the LHF-samplers was negligible, less than 0.001 mM (unpublished data).

The effects of N application and plants on the concentrations of other ions were variable. Concentrations

of Na in +N treatments were significantly greater than those in -N treatments ($p < 0.01$). Na concentrations of planted soils decreased significantly after 30 days compared with the unplanted soils. There was no significant effect of N application on the concentration of S, and on the concentration of NH_4^+ which was always as low as 0.03 mM.

Table 3 shows the correlations between the different components of the soil solution. NO_3^- is highly correlated ($r > 0.86$, $p < 0.001$) with EC and concentrations of Ca, M Na, K and H^+ . It has a negative correlation of -0.65 with P ($p < 0.001$). S and NH_4^+ are not significantly correlated with any other ions.

Plant growth and nutrient contents

Table 4 shows that the effect of N application on plant growth was significant in terms of any indices measured.

In Table 5, the total amount and concentrations of elements in the plants are indicated. The effects of calcium nitrate application on the total amount of Ca and N in plants were significant. On average, plants in +N treatment had twice as much Ca and 2.7 times as much N as those in -N treatment ($p < 0.01$). In addition, plants in +N treatment had significantly more of any element except Na than those in -N treatment. The increase was 206% in Mg ($p < 0.05$), 46% in K ($p < 0.01$), 44% in P ($p < 0.05$) and 65% in S ($p < 0.01$). Even Na showed the increase in 47%, although it was not significant statistically.

In contrast, N application increased the concentrations of only N and Ca significantly ($p < 0.05$). Concentrations of Ca, Mg and K were not statistically different between +N and -N treatments.

Discussion

Effects of N application on the initial soil solution composition.

Fertilization with calcium nitrate had a direct effect on the initial total concentrations of cations and anions in the soil solution as indicated by EC (White and Ross, 1936). Initial concentrations of Ca, NO_3^- , Mg, K, Na and H^+ were increased by the addition of calcium nitrate (Hansen, 1972; Kishita and Obama, 1965). Those of Ca and NO_3^- , increased directly; those of other ions presumably by exchange reactions that followed the addition of Ca and NO_3^- ions to the soil solu-

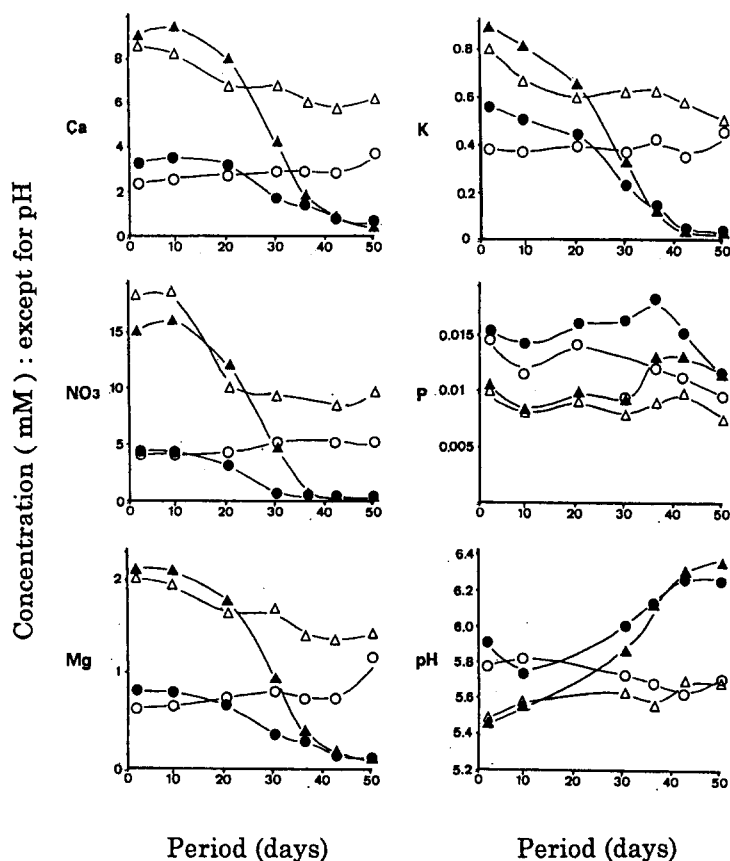


Figure 3. Dynamics of the concentration of Ca, NO₃, Mg, K and P as well as pH in the soil solution at the top layer. ○: -Nitrogen without plant, ●: -Nitrogen with plant, △: +Nitrogen without plant, ▲: +Nitrogen with plant.

Table 3. Correlation matrix of elements in the soil solutions^a

	EC	Ca	Mg	Na	K	P	S	NO ₃ ⁻	NH ₄ ⁺
Ca	0.99								
Mg	0.99	1.00							
Na	0.94	0.93	0.94						
K	0.91	0.90	0.90	0.96					
P	-0.74	-0.73	-0.73	-0.62	-0.54				
S	0.04	0.08	0.06	0.01	-0.06	-0.08			
NO ₃ ⁻	0.95	0.94	0.94	0.90	0.89	-0.65	-0.17		
NH ₄ ⁺	0.01	0.02	0.03	0.04	0.02	0.01	-0.07	0.02	
H ⁺	0.89	0.88	0.89	0.89	0.85	-0.66	0.00	0.86	0.03

^aThreshold value for the significance level of 0.01 is 0.19.

tion. The increase of cation concentration was consistent with the Gapon equation for cation exchange reaction (Nye and Tinker, 1977), and it was more dynamic for divalents than for monovalents: Ca, Mg, K and Na in +N treatment were 3.1, 2.9, 1.6 and 1.8 times more concentrated than those in -N treatment, respectively ($p < 0.01$). Additionally, cation composition of the soil solution was controlled in such a way that AR^K (Yanai

et al., 1995) and AR^{Na} values did not change significantly by N application, with the averages of 1.90 and 2.10, respectively, where

$$AR^K = -\log_{10}[(K)/\{(Ca) + (Mg)\}^{0.5}],$$

$$AR^{Na} = -\log_{10}[(Na)/\{(Ca) + (Mg)\}^{0.5}]$$

(M) : activity of the element M in the soil solution

Table 4. The effects of N application on plant growth^a

N applic. ^b	Height (cm)	Fresh weight (g)	Dry weight			Leaf area $\times 10^3 \text{ cm}^2$	Transpir. ^c $\times 10^3 \text{ cm}^3$
			Leaf (g)	Stem (g)	Root (g)		
-N	120	202	13.4	11.6	14.8	2.70	3.79
+N	143	351	22.1	21.4	22.0	4.41	5.73
	**	**	**	*	*	*	*

^a Values are the average of the three samples.^b Nitrogen application as calcium nitrate.^c Transpiration volume.Table 5. The effects of N application on the total amount and concentration of elements in the plant (shoot)^a

N applic. ^b	N	Ca	Mg	K	Na	P	S
				(mg)			
-N	184	52.6	22.9	608	1.61	59.5	17.4
+N	498	103.7	47.2	885	2.37	85.8	28.7
	**	**	*	**	ns	*	**
				($\text{kg kg}^{-1} \times 10^{-2}$)			
-N	0.74	0.211	0.091	2.43	0.006	0.237	0.070
+N	1.16	0.240	0.108	2.06	0.005	0.199	0.067
	*	*	ns	ns	ns	ns	ns

^a Values are the average of the three samples.^b Nitrogen application as calcium nitrate.

The increase of NO_3^- concentration of 15.2 mM agreed well with the calculated increase of 15 mM based on the assumption that all the NO_3^- applied dissolved in water at the water content of 25%. The increase in concentration of total cations (15.5 meq L^{-1}) was almost equal to calculated increase of NO_3^- concentration. This indicates that electrical neutrality was maintained in the soil solution (Bouldin, 1989; Sposito, 1981; Yanai et al., 1995), and thus, application of $\text{NO}_3\text{-N}$ inevitably increased the concentrations of cations as well. Because the soil solution concentration of an element is the intensity factor of the soil's supplying power of the element, an increase of soil solution concentration must account, at least partly, for the increased plant uptake not only of N but also of Ca, Mg and K.

Effects of N application on the composition of the soil solution in the root zone

In the treatments with plants, EC decreased significantly after 30 days as nutrient uptake by the plant became pronounced. At the same time, severe depletions of

NO_3^- , Ca, Mg, and K at later stages of growing period were found not only in -N treatments but also in +N treatments.

Because high positive correlations were observed between NO_3^- and concentrations of Ca, Mg, Na, K, H^+ as well as EC (Table 3) and because NO_3^- is the anion present in greatest quantity, it is concluded that NO_3^- concentration exerts the biggest influence on the composition of the soil solution. The total cation concentration counterbalances the total anion level (Bouldin, 1989; Okajima and Imai, 1975; Yanai et al., 1995). Severe depletions of not only N but also cations are, therefore, partly due to the severe depletion of NO_3^- (Yanai et al., 1995). This is expected to happen even in the field at later stages of plant growth.

Relationship between nutrient uptake by plants and depletion in the soil solution

To relate the plant uptake with the dynamics of the soil solution composition in both -N and +N treatments, the apparent decrease of elements in the soil solution was estimated by multiplying the difference between

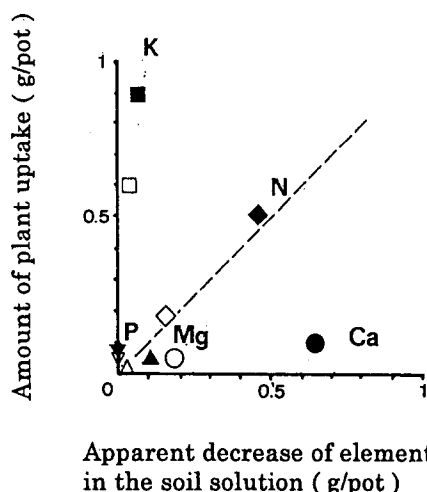


Figure 4. Relationship between the apparent decrease of elements in the soil solution and the amount of plant uptake. \blacklozenge , \diamond : N + and - $\text{Ca}(\text{NO}_3)_2$ application, respectively. \bullet , \circ : Ca + and - $\text{Ca}(\text{NO}_3)_2$ application, respectively. \blacktriangle , \triangle : Mg + and - $\text{Ca}(\text{NO}_3)_2$ application, respectively. \blacksquare , \square : K + and - $\text{Ca}(\text{NO}_3)_2$ application, respectively. \blacktriangledown , \triangledown : P + and - $\text{Ca}(\text{NO}_3)_2$ application, respectively.

the concentration in planted treatments at harvesting and the mean concentration in unplanted treatments throughout the experiment by the water volume at the water content of 25%. The calculation was carried out for each of the top, middle and bottom layers and their results were summed up to compare with the amount of plant uptake (Fig. 4).

The depletion of N from the soil solution corresponded to about 85% of the amount of N taken up in both -N and +N treatments. This suggests a close relation between the amount of nitrate in soil solution and plant uptake. Mineralization of N from the soil organic matter would presumably account for the remaining 15%.

This contrasts with the poor correspondence between the depletion of cations from the soil solution and their uptake. The depletion of K in the soil solution was only 6% and 7% of the amount of plant uptake in the -N and +N treatments, respectively. This indicates intensive replenishment of K from exchange sites of the solid phase into the soil solution. At the other extreme, depletions of divalent cations were far in excess of the amount taken up. The depletions of Ca were 343% and 623%, and those of Mg 144% and 206%, of the amount taken up in the -N and +N treatments, respectively. This suggests that the decrease of Ca and, to a lesser extent, of Mg were mainly due to the decrease of anion concentrations rather than plant uptake of the elements, and excess Ca and Mg which

were not absorbed by plants were adsorbed again on the exchange sites of the soil solid phase. The contribution of bulk soil solution on the plant uptake of P was negligible based on this calculation, suggesting the importance of the rhizosphere in the uptake of P.

The results further indicate that the apparent effectiveness of soil's supplying power of Ca and Mg decreased significantly with the increased concentrations of the elements. Intensive agriculture with a great amount of soluble salts application would, therefore, result in an apparent lower efficiency of nutrient supply, at least for divalent cations, compared with conventional agricultural systems, although N application increased plant growth and plant uptake of the elements significantly. These general tendencies discussed here would hold true, more or less, for other types of inorganic N fertilizers as well.

Acknowledgements

The authors are very grateful to Dr T Nakamura, Research and Development Center, Nagase Co, Ltd, for supplying the hollow fibers, the Macaulay Land Use Research Institute for the soil survey data and ICP analyses, and Alison Cooper, Neil Wilson and Winnie Stein for other analyses. The authors also acknowledge Tayside Regional Industrial Office, The Daiwa Anglo-Japanese Foundation and The British Council for granting research funds for these studies. SCRI is funded by the Scottish Office Agriculture Environment and Fisheries Department.

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Section editor: H Marschner