Effect of high nonexchangeable aluminium on nitrogen and phosphorus availability in a humus-rich acid forest soil*

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Abstract

The effect of high nonexchangeable aluminum on availability of nitrogen (N) and phosphorus (P) was studied in a Cryptopodzolic soil (Cademario) derived from mica schist in southern Switzerland. The research involved a greenhouse pot experiment comparing growth of barley on soil samples of three soil layers (10- to 25-, 40- to 60- and 70- to 90 cm) of the Cademario profile, representing a range of Al and organic matter properties, with the 10- to 40 cm layer of a profile of an acidic brown earth (Haplumbrept), derived from cherty limestone. The experiment, which included four nutrient treatments [check, N_0 (PKS), P_0 (NKS) and full (NPKS)], lime and no lime treatments and four replicates, was supplemented by soil chemical analysis. Results showed that liming alone produced greater yield responses in the Cademario soil than N or P added singly or together. On unlimed soils, barley yield for check, N_0 , and P_0 treatments showed a positive linear relation with exchangeable Ca of soils and a negative linear relation with organically-complexed Al. Failure of liming to influence P_{av} , especially when combined with P fertilization, suggests that P was quickly absorbed on highly active surfaces formed from initially exchangeable Al.

Introduction

Cryptopodzolic soils occurring on mica schist in the Ticino region of southern Switzerland are extremely rich in well-transformed organic matter, usually to a depth of more than 50 cm (Blaser, 1973). Generally, the entire profile of these soils is low in clay (i.e. <10%). Important properties for plant growth such as water holding capacity, pH, exchangeable cations and anions, soil aeration and nutrient availability are con-

ditioned largely by the organic fraction of the soil.

Similar soils occur elsewhere in Europe, chiefly in France (Coppenet, 1969; Dejou *et al.*, 1968; 1969; Warenbourg *et al.*, 1973). High aluminum status appears to play an important role in accumulation of organic matter and in nutritional characteristics of these soils. Those who have studied these soils (Blaser, 1973; Blaser and Klemmedson, 1987; Carballas *et al.*, 1978; 1979; 1980) hypothesize that Al-organic matter complexes are very stable and that biodegradation proceeds slowly; as a consequence, humus mineralization is inhibited.

Following the above reasoning, this study was conducted to test the hypothesis that N and P are not readily available in soils derived from mica

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schist parent rocks and that availability of these nutrients is related to Al chemistry of the soil. The research approach was a greenhouse pot experiment comparing growth of barley on limed and unlimed soils derived from mica schist and cherty limestone ("Kieselkalk") parent materials, supplemented with soil chemical analysis.

Materials and methods

Soils for the experiment were obtained from two soil profiles near Lugano, Switzerland. Near the village of Cademario samples were collected from the 10- to 25-, 40- to 60- and 70- to 90 cm layers (hereafter referred to as C1, C2 and C3 in the text). These samples represent the range of Al and organic matter properties typical for soils formed on mica schist in this region. From a profile of an acidic brown earth (Haplumbrept) near Sagno, formed from a cherty limestone and locally described as Kieselkalk (De Quervain and Frey, 1967), the 10- to 40 cm layer was collected to serve as a control. The chemistry of both soils is described elsewhere (Blaser and Klemmedson, 1987).

Soils were air-dried and passed through a 6-mm sieve to remove roots and coarse fragments prior to experimentation. The supply of available N and P was evaluated by a pot culture technique (Jenny *et al.*, 1950) using barley (*Hordeum vulgare* L. var. *Charlottetown*) as the test plant in a $4 \times 2 \times 4 \times 4$ factorial randomized block experiment with soils, lime treatment, and nutrient treatment as fixed effects. Plastic pots were filled with 300 g of soil (oven-dry basis) to which lime (or no lime) and various combinations of nutrients as solutions had been added individually to each pot. For pots designated to receive lime, an amount of reagent grade CaCO_3 sufficient to raise the soil pH to about 6.2 was mixed into the soil for each pot. Four nutrient treatments with four replicates each were used (Table 1). Soil that received the full treatment was assumed to supply test plants with sufficient nutrients for an optimum yield.

Five barley plants per pot were grown from seed and given tap water as required. Pots were arranged on a greenhouse table in randomized

Table 1. Nutrient treatments of the pot experiment

Treatment ^a	Nutrients added	Treatment recipe		
		Nutrient	Rate, (kg/ha)	Form
Check	—	N	300	NH_4NO_3
Full	NPKS	P	300	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$
N_0	PKS	K	100	K_2SO_4
P_0	NKS	S	40	K_2SO_4

^aAll treatments were applied with and without lime.

block fashion. Shoots were harvested after 42 days, oven-dried for 48 hours at 70°C, and weighed. Mean dry weight per pot was computed for each soil-lime-nutrient combination. After harvesting, soil samples were taken from replicates 1 and 4 for chemical analysis. Exchangeable and extractable elements were obtained following end-over-end shaking of the soil using a 1:10 soil/solution ratio. Extraction time was 1 hour. Extractants were as follows:

Exchangeable elements	— 1N KCl
Extractable elements	— 0.5 M ammonium acetate, 0.02 M EDTA, PH 4.65 (Lakanen and Ervio, 1971)
NO_3^- , SO_4^{2-} and NH_4^+	— distilled water
Available P	— NaHCO_3 (Olsen and Sommers, 1982)
Total P	— fusion with Na_2CO_3 (Olsen and Sommers, 1982)
Al (organic)	— calculated difference between extractable and exchangeable Al (Blaser and Klemmedson, 1987)
<i>Element determinations</i>	
Cations	— ICP spectroscopy (Bausch and Lomb ARL 3580)
NO_3^- , SO_4^{2-}	— single column IC

NH_4^+	– colorimetrically using the indophenol blue method (Keeney and Nelson, 1982)
Organic C and N	– dry combustion with a “Heräus C, H, N-Rapid” analyzer
PO_4^-	– molybdophosphoric blue method (Jackson, 1958)
P in barley shoots	– vanado-molybdophosphoric yellow color method following dry ashing (Jackson, 1958)

Results

Absolute and relative yields of barley

Although the barley variety used was selected for its tolerance to acid soils, it did not grow well under the experimental conditions. Dry weight yields of plants were low for the entire experiment (Table 2). Even so, yield differences among treatments were marked. For the check treatment, the pattern of yield with depth in

Cademario soils was not what one would expect for a normal soil (*i.e.* highest yield was obtained from the 70- to 90-cm soil layer). Yields for soils receiving the full treatment also were unusual. In theory, the full treatment should produce an optimum yield such that relative yields (ratio of X_0 yield to full treatment yield) for N_0 and P_0 treatments provide an accurate expression of the soil's ability to supply N and P (Jenny *et al.*, 1950). Obviously, the nutrients added in the full treatment did not always provide optimum conditions, especially in limed soils (Table 2). With these raw yields, relative yields calculated for N and P frequently exceeded 100%.

Because relative yields based on full treatment yields are difficult to interpret when this situation prevails, relative yields were calculated for all soils based on the unlimed checks (*i.e.* yield of the check treatment for each soil = 100%, Table 3). These data indicate that for unlimed soils the relative yield for the N_0 treatment was significantly higher than that of the P_0 treatment only in the reference soil from Sagno. For the C1 soil, both treatments influenced growth similarly, whereas for the C2 and C3 soils, the P_0 treatment had a much more pronounced effect on growth than the N_0 treatment.

Liming C1 and C2 soils without addition of N and P resulted in yields that were remarkably higher than yields for the full treatment of the unlimed soils. In the C3 soil, these treatments (*i.e.* lime alone and full treatment alone) had about the same effect. The stimulating effect of

Table 2. Dry weight yield (g/pot) of barley shoots for Cademario and Sagno soils with various nutrient treatments. The data are means $\pm$ SE; n = 4

Soil	Soil layer, (cm)	Nutrient treatment			
		Check	N ₀	P ₀	Full
Unlimed					
Cademario	10–25	0.12 ± 0.01	0.18 ± 0.02	0.18 ± 0.01	0.15 ± 0.02
	40–60	0.03 ± 0.01	0.04 ± 0.01	0.15 ± 0.02	0.20 ± 0.02
	70–90	0.16 ± 0.03	0.28 ± 0.05	0.34 ± 0.02	0.40 ± 0.04
Sagno	10–40	0.37 ± 0.04	0.75 ± 0.05	0.48 ± 0.03	0.72 ± 0.01
Limed					
Cademario	10–25	0.28 ± 0.04	0.38 ± 0.02	0.28 ± 0.02	0.50 ± 0.02
	40–60	0.45 ± 0.06	0.75 ± 0.05	0.40 ± 0.01	0.50 ± 0.04
	70–90	0.37 ± 0.02	0.60 ± 0.04	0.34 ± 0.05	0.51 ± 0.06
Sagno	10–40	0.53 ± 0.04	1.13 ± 0.06	0.56 ± 0.04	0.95 ± 0.06

Table 3. Relative yield (%) of the unlimed and limed soils based on the yield of unlimed check (*i.e.* = 100%)

Soil	Soil layer, (cm)	Nutrient treatment			
		Check	N ₀	P ₀	Full
Unlimed					
Cademario	10–25 (C1)	100	154	147	129
	40–60 (C2)	100	154	592	785
	70–90 (C3)	100	172	212	244
Sagno	10–40	100	203	130	197
Limed					
Cademario	10–25 (C1)	234	319	238	421
	40–60 (C2)	1742	2900	1542	1935
	70–90 (C3)	226	369	220	312
Sagno	10–40	143	307	153	259

lime was highest in the C2 soil where yield increased by 1742%. In the Sagno soil the response to lime was rather small.

In the limed soils, the relative yield for the N₀ treatment was higher in all soils than that for the P₀ treatment, and except for soil C1 was also higher than that for the full treatment. This cursory analysis of the barley yield data suggests the 40–60 cm layer of the Cademario soil is of critical interest and that lime and P are important to its fertility.

Analysis of yield response

For insight to the soil parameters which influenced growth response of barley, yield was related to soil chemical properties measured in the samples at the end of the experiment. Parti-

ent chemical properties of amended and unamended soil samples are shown in Table 4.

Unlimed soils

In view of the large yield increase noted above for barley growing on limed soils, one should expect a close relation between barley yield and exchangeable Ca content of the unlimed soils. This, in fact, was the case as shown in Figure 1. Raw barley yields for check, N₀ and P₀ treatments were linearly dependent on exchangeable Ca in the four soils. Compared with the check treatment the larger intercept of the P₀-curve indicates that addition of N resulted in a general yield increase of approximately 0.13 g/pot, but still growth depended primarily on exchangeable Ca. The most important result of the P₀ treatment, however, is not revealed well by com-

Table 4. Chemical properties of limed and unlimed, unfertilized soils at the end of the experiment

Soil	Lime Treatment	pH	C _{org} (g/kg)	N	Exchangeable cations (mg/kg)								
					Ca	Mg	Al	Al _{Lak} ^a	P _{tot}	P _{av}	NO ₃	NH ₄	SO ₄
Cademario													
10–25 cm	no lime	3.74	97	6.2	183	31	725	2766	706	4.2	380	28	47
	lime	5.35	–	–	3847	34	10	2226	709	2.8	300	61	128
40–60	no lime	4.22	69	4.2	73	12	434	2995	728	1.3	34	23	40
	lime	5.46	–	–	2454	14	15	2867	696	2.0	9	16	140
70–90	no lime	4.72	39	2.7	261	11	165	1654	563	2.0	16	7	82
	lime	5.59	–	–	1302	9	16	1653	542	2.2	6	6	156
Sagno													
10–40	no lime	4.27	24	1.7	540	21	200	801	238	7.4	20	10	66
	lime	5.41	–	–	1514	15	7	657	223	7.6	14	13	81

^aNH₄-Ac-EDTA extract.

Fig. 1. Dependence of barley yield on exchangeable Ca in the unlimed soils.

parison of raw yields. Relative yields for unlimed soils (Table 3) show that the strongest response to the P_0 treatment was from the C2 soil. The 6-fold response in yield to this treatment was not much lower than the 8-fold response of the full treatment (Tables 2 and 3), and when compared with the N_0 barley yield, indicates that in the absence of lime, N rather than P, was the most deficient nutrient for this soil layer.

The regression for barley yield as a function of exchangeable Ca for soils with the N_0 treatment (Fig. 1) had a steeper rate of yield increase than that for soils with the P_0 treatment. The slope of this curve is larger by a factor 2.2 compared with slopes for the check and P_0 treatments. Based on the curve for the check treatment, some increase in yield should be expected with the N_0 treatment because of the addition of Ca ($26 \mu\text{g}/\text{pot}$) in the nutrient treatment (i.e. P added as mono-calcium phosphate), but most of the yield response can be attributed to P added as part of the treatment. Despite the large yield response of 103% for the Sagno soil with the N_0 treatment (Table 3), this soil behaves like the Cademario soil with respect to exchangeable Ca, as manifested by the fit of the Sagno data to the regression line in Figure 1. Yield responses for the Cademario soils were still marked, ranging from 54 to 72% (Table 3).

To visualize the influence of aluminum on barley growth, yields were related to KCl-exchangeable Al, to NH_4Ac -EDTA-extractable

Al, and to an Al fraction which is expressed by the difference between extractable and exchangeable Al. Based on evidence of recent studies (Blaser and Klemmedson, 1987), we suggest the latter fraction represents mainly Al which is complexed by organic matter (Al_{org}). Interestingly, of these three Al fractions, Al_{org} showed the best correlation ($r^2 = 0.83$ to 0.91) with barley yield for the treatments portrayed in Figure 2. Correlations for the regressions between barley yield and KCl-exchangeable and NH_4Ac -EDTA extractable Al were rather poor.

As mentioned above, the full treatment produced unusual yield responses, suggesting that it was indeed not an optimum treatment. This was particularly true for limed soils. In unlimed Cademario soils, overall response of barley to the full treatment was similar to that of the P_0 treatment, whereas the full treatment yield response for the Sagno soil was closer to that of the N_0 treatment. In limed soils the full treatment yields for the C2, C3 and Sagno soils all showed negative interaction between N and P (Tables 2 and 3). This also was apparent for the unlimed C1 soil. This clearly suggests that of the two nutrients evaluated in this experiment, P was the key nutrient controlling nutrition of barley in these soils.

The relation between barley yield and Ca_{exch} as well as that between yield and Al_{org} described above suggests that barley yield was related to the $\text{Al}_{\text{org}}/\text{Ca}_{\text{exch}}$ ratio. Data for this relation was

Fig. 2. Yield of barley as a function of Al_{org} in the unlimed soils.

graphed (Fig. 3) for each treatment (unlimed soils) and fitted to the model $Y = 1/(a + bX)$ where Y is barley yield and X is the Al_{org}/Ca_{exch} ratio. When expressed in the linear form ($1/Y = a + bX$), the intercepts for regressions of various treatments did not differ significantly from zero. Moreover, fitting the model without the intercept improved the statistical fit for all treatments. Inspection of the curves and regression statistics (Fig. 3) reveals good fits (visually and statistically) of the data for the check and N_0 treatments. The fits for P_0 and full treatments (curve for full treatment not shown here) were less satisfactory and regression coefficients for these curves differed significantly from those for the check and N_0 treatments. Addition of N in the P_0 and full treatments increased yield sufficiently for the C1 soil (high Al_{org}/Ca_{exch} values) relative to that of the other soils that a poor fit of curves to the data resulted. Significantly, curves in Figure 3 show that as the Al_{org}/Ca_{exch} ratio drops below a value of about five, yield increases rapidly. The explanation for this relationship presumably lies in an understanding of the nutrition of barley in these soils. Relating barley yield to other soil parameters (Table 4) provides no explanation.

Limed soils

In the presence of lime, the raw yield response of barley to the P_0 treatment was nonsignificant for all soils (Table 2). By contrast, the N_0 treatment stimulated barley growth and produced marked yield increases for all soils. Thus, once soils were limed, addition of P produced good yield responses ranging from 36% for the C1 soil to 113% for the Sagno soil.

Table 5 shows available P (P_{av}) status of unlimed soils for the four treatments. There was good agreement in P_{av} between check- and P_0 -treatments among all soils; P_{av} was especially low in C2 and C3 soils for these treatments, averaging only about 1.3 and 2.0 mg/kg in absolute terms and only 0.2 and 0.4% of total P, respectively. Available P was about three-fold higher (absolute and relative terms) in C1 than in C2 or C3 soils, even though P_{tot} was similar (Table 5). In the Sagno soil, P_{av} for the check- and P_0 -treatments was up to four times greater and (P_{av} as a percentage of P_{tot}) was 8 to 15 times greater)

Barley yield (g/pot)

Barley yield (g/pot)

Barley yield (g/pot)

Fig. 3. Yield of barley shoots grown in unlimed soils as a function of Al_{org}/Ca_{exch} ratios for a check, b N_0 and c P_0 treatments. Regression coefficients were significant at $p < 0.001$ for the check and N_0 treatments and at $p < 0.005$ for the P_0 treatment.

Table 5. Availability of phosphorus in unlimed soils as a function of nutrient treatment at the end of the experiment

Soil	Treatment	P _{av}		Increase in P _{av} with added P _{tot}	
		mg/kg	% of P _{tot}	mg/kg	% of added P
Cademario					
10–25 cm	check	4.2	0.6	–	–
	N ₀	11.4	1.6	7.2	5.4
	P ₀	4.0	0.6	–	–
	full	11.0	1.4	6.8	5.1
40–60	check	1.3	0.2	–	–
	N ₀	5.0	0.6	3.7	2.8
	P ₀	1.7	0.2	–	–
	full	5.0	0.6	3.7	2.8
70–90	check	2.0	0.4	–	–
	N ₀	5.5	0.8	3.5	2.6
	P ₀	2.2	0.4	–	–
	full	5.6	0.8	3.6	2.7
Sagno					
10–40	check	7.4	3.1	–	–
	N ₀	73.4	19.2	66.0	49.3
	P ₀	6.8	2.9	–	–
	full	72.3	18.6	64.9	48.5

than that for Cademario soils. Close agreement also occurred in P_{av} between the N₀- and full treatments. The addition of P in these treatments resulted in a 3- to 4-fold increase in P_{av} in the Cademario soils and a 10-fold increase in P_{av} in the Sagno soil. However, of the P added as part of the nutrient treatment, only 3 to 5% was recovered or remained as soil P_{av} at the end of the experiment in Cademario soils, while 49% was recovered in the Sagno soil. This suggests that much of the P added to the Cademario soils was fixed during the 42 d experimental period. Presumably, Al_{org} which was 2- to 4-fold higher in Cademario than in Sagno soils, played a role in this process (Boudot *et al.*, 1986). Liming together with P fertilization (N₀ and full treatments) had very little effect on P_{av} (results not shown here).

Discussion

The association between barley yield and Ca_{exch} and Al_{org} shown in Figures 1 and 2 was consistent among all nutrient treatments. It was especially strong for the N₀ treatment. The addition of P with this treatment produced the greatest

yield increase in soils with the highest amounts of exchangeable Ca and the lowest amounts of complexed Al (*i.e.* Al_{org}). This result is inconsistent with other research on Al-rich, highly organic soils (Borie and Zunino, 1983; Boudot *et al.*, 1986). The strong negative relation between barley yield and Al_{org} is not inconsistent with research that has shown detoxification of Al and improved plant growth with addition of humic acids or organic matter (see review of Tan and Binger, 1986). Most of that research involved nutrient solutions or soils low in organic matter, hence is not directly comparable with our study.

Results of these experiments show that liming alone produced greater yield responses in the Cademario soils than N or P added singly or together. With addition of lime to these soils, pH and exchangeable Ca were increased and exchangeable Al was markedly decreased, as others (*e.g.* Sims and Ellis, 1983) have observed. Simultaneously, the fraction designated Al_{org} increased for all soils. This new Al_{org}, amounting to an increase of 9 to 17%, evidently represents Al that was in exchangeable form before liming. The large increase in barley yield with liming, especially for the C2 soil (Table 3), apparently is associated with removal of Al_{exch} (Table 4) and

hence reduction in activity of aluminium in solution. Plotting barley yield against Al_{org}/Ca_{exch} for limed as well as unlimed soils shows that the model employed for unlimed soils (Fig. 3) is valid also for limed soils (Fig. 4).

Failure of liming to influence P_{av} more substantially, especially when combined with P fertilization, strongly suggests that phosphate was quickly absorbed on new highly active phosphate absorbing surfaces formed from initially exchangeable Al (Haynes, 1982; Reeve and Summer, 1970; Sims and Ellis, 1983) or by formation of organic matter-P complexes through Al-

bridges (Borie and Zunino, 1983). Increase in barley yield may then be interpreted as a primary response to reduced Al toxicity. A common characteristic of Al toxicity, which occurs in the presence of monomeric Al (Blamey *et al.*, 1983), is inhibition of P uptake and translocation by plants (Foy and Fleming, 1978; Jones and Fox, 1978). Thus, the yield response noted with liming may have reflected increased uptake of the limited amounts of P_{av} as Al toxicity was reduced (Haynes, 1982). As Haynes (1982) noted, in acid soils it is often difficult, if not impossible, to separate the effects of Al toxicity and P deficiency. Moreover, our evidence for Al toxicity (swollen, stubby and gnarled roots, absence of root hairs) obtained in auxiliary pot experiments with corn seedlings, although manifesting some of the characteristic symptoms in appearance of roots (Foy and Fleming, 1978) was inconclusive (Klemmedson and Blaser, unpublished data).

Organic matter complexed by Al in the Cademario soil represents a pool of trapped nutrients. Companion studies (Brunner and Blaser, 1989) have shown that Al probably plays a central role in mineralization of organic matter of the Cademario soils. Although N metabolism was not inhibited, as shown for similar soils (Boudot and Chone, 1985), Al seems to influence degradation of water-soluble organic compounds in the Cademario soil, affecting both growth rate and biomass (Brunner and Blaser 1989). This would, of course, impede release of nutrients for uptake by plants (Boudot *et al.*, 1986). If the organic matter of the Cademario soils does represent the major pool of P, as well as of N and probably S, liming can be expected to stimulate mineralization of these compounds (Awan, 1964; Halstead *et al.*, 1963) by creating a more favorable environment for microbial activity (Anderson, 1980). Although improved P mineralization by virtue of liming may have contributed to increased barley yields, we have no direct evidence of this. Increase in SO_4 with liming (Table 4) is perhaps the best evidence of improved mineralization of organic matter and C/N as well as C/P ratios were in a range that net mineralization rather than immobilization could be expected (Enwezor, 1976; Jansson and Persson, 1982).

Fig. 4. Yield of barley shoots grown in limed and unlimed soils as a function of Al_{org}/Ca_{exch} ratios for a check and b N_0 treatments. Regression coefficients were significant at $p < 0.001$.

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