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EFFECT OF ACIDIFICATION ON BASE CATION EXCHANGE CAPACITY OF TWO GREY-BROWN PODZOLIC SOILS UNDER DIFFERENT FERTILIZATION MANAGAMENT FOR 36 YEARS

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Abstract. The effect of acidification by adding 0-320 mmol HCl/kg soil on base cation exchange capacity of two grey-brown podzolic soils with three different manner of fertilization for 36 years was studied. Without acid the BCEC ranged from 5.17 to 7.96 cmol(+)/kg soil, pH from 6.60 to 7.20. Adding of 0-320 mmol HCl/kg soil reduced the BCEC to 1.03-3.32 cmol(+)/kg soil and lowered the pH to 2.50-2.77. The acid-neutralizing capacity of both soils was changeable according to fertilization. Response of soils to low doses of added HCl was in the following order: control>NPK+lime (or FYM+lime+clay)>NPK. At higher doses of acid the reverse order of treatments was found. The decrease of BCEC was by 3.09-6.28 cmol(+)/kg soil, corresponding to 47-79 % of the initial value. The quantity of acid needed to reduce the soil pH to 5.0 (ANC 5.0) ranged from 55.4 to 137.1 mmol HCl/kg soil. The acid neutralizing capacity of both soils for almost all treatments had a maximum between 1-10 mmol HCl/kg soil and was broken up by adding 80 mmol HCl/kg soil.

Keywords: soil acidification, cation exchange capacity, 36 years fertilization

INTRODUCTION

Higher plants and soil microorganisms are very sensitive to rapid changes in soil pH. Both may be affected either directly by increased concentration of H^+ ions or indirectly due to imposed nutrient deficiency or elements toxicity [1]. Soil acidity is common in all regions where precipitation is high enough to leach appreciable amounts of exchangeable bases from surface layers of soils.

Soils are acidified through a number of processes. These include: atmospheric inputs of H^+ and SO_2; soil nitrogen transformations; net assimilation of cations by biomass; additions of fertilizers; deprotonation of CO_2 or organic acids; weathering of soil minerals [1,2,5,7,8].

The purpose of this study was to investigate the extent of the acidification-induced reduction in the base cation exchange capacity of two grey-brown podzolic soils without any fertilization, fertilized by NPK or NPK+Ca and, and FYM+lime+clay for 36 years.

MATERIAL AND METHODS

Soil samples used in this work were collected from the surface of two long-term fertilization experiments established at the Agricultural Experimental Station at Baborówko (Institute of Soil Science and Plant Cultivation) and at Brody (University of Agriculture Poznań) on a light loamy sand in the year 1957. The treatments were as follows:

BRODY (Br)	BABORÓWKO (Ba)
1. Control	Control
2. NPK	2. NPK
3. NPK + lime	3. FYM+lime+clay

Representative soil samples were taken in the summer of 1992 from the surface horizon (0-20 cm). In the analyses reported in Table 1,

Table 1. Characteristics of soil samples

Soils	pH in 1 mol KCl dm^{-3}	Org. C g/kg	Base*1 saturation	Free oxides (mg/kg)		
				AL	Fe	Mn
BRODY (Br)						
1. Control	5.7	6.30	77.5	86.9	436.5	180.5
2. NPK	5.7	6.50	85.0	212.9	436.5	148.4
3. NPK + lime	7.1	7.50	86.3	342.0	577.0	162.0
BABORÓWKO (Ba)						
4. Control	7.5	6.49	92.0	355.0	816.0	217.0
5. NPK	5.4	4.80	83.7	219.0	732.9	287.0
6. FYM+lime+clay	7.4	7.66	91.3	219.0	684.5	150.0

*1 at '0' HCl treatment.

organic C was determined by the Tiurin procedure; pH was measured in a 1 mol KCl dm^{-3} solution (1:2.5); amorphous aluminium, iron and manganese were determined using ammonium oxalate at pH 3.0. Iron and manganese were measured by atomic absorption spectrophotometry, while aluminium colorimetrically with aluminon.

The soils were treated with solutions of different HCl concentrations at a constant ionic strength of 0.04 adjusted with NaCl as follows (mmol dm^{-3}):

HCl	0	0.1	1.0	8.0	16.0	32.0
NaCl	40	39.9	39.9	32.0	24.0	8.0

Soil, 5 g, was weight into a centrifuge tube, and 50 ml of solution was added. The suspension was shaken for one hour and allowed to stand overnight. Thereafter the suspension was reshaken by hand, and the pH of the supernatant was measured by a pH-meter [4].

The H^+ consumption was calculated by subtracting the final H^+ concentration (mmol H^+/kg soil) from the sum of added H^+ concentration and H^+concentration in the zero treatment (mmol H^+/kg soil). Cation exchange capacity of HCl treated soils was determined by the Mehlich method (pH 8.2) [3]. Hydrolytic acidity of these soils was measured using sodium acetate. The experiment was carried out with two replicates.

RESULTS AND DISCUSSION

As a result of a long-term differentiated nutrient input into soils, the investigated plots had undergone great changes in pH levels, total content of organic C and base saturation (Table 1).

Addition of HCl to each of investigated soils caused a marked lowering of their pH, base cation exchange capacity (BCEC) and buffering capacity.

The acid treatments of 10 mmol HCl/kg soil decreased the pH in suspension in ascending order: NPK(Ba)=FYM+lime+clay<control (Ba)<NPK+lime<NPK(B)r<control(Br). For five of six soils their buffering capacity was nearly broken up by acid treatments of 80 mmol HCl/kg soil. For the FYM(+lime+clay) sample 160 mmol of HCl was needed to break up its acid neutralizing capacity (Tables 2 and 3).

Decreasing values of soil pH were strongly related to the increasing hydrolytic acidity of HCl treated soils (Fig. 1). Lower values of slopes of regression equations indicate higher buffering capacity of Brody soils (data not presented, but available by the authors).

As a result of soil acidification a marked decrease in a BCEC was found (Fig. 1). At the treatment without acid the BCEC was strongly dependent on soil organic content and may be expressed by the following regression equation:

$$BCEC = -0.654 + 1.077 \text{ Org. C}; \quad r = 0.94 \text{ for } P < 0.01.$$

The acid treatment of 1 mmol HCl/kg soil did not cause any essentially decrease of the BCEC, but even for five of six soils a marked rise from 4.1 to 24 % was noted (Table 3).

Table 2. pH of suspension and hydrolytic acidity of soils with different HCl treatments (added HCl, mmol HCl/kg soil)

Soils*	0		1		10		80		160		320	
	pH	Hh	pH	Hh	pH	Hh	pH	Hh	pH	Hh	pH	Hh
1	6.90	1.86	6.62	2.17	5.25	2.54	3.55	5.29	3.05	5.99	2.77	7.02
2	6.57	1.19	6.10	1.83	5.85	2.26	3.75	5.37	3.03	6.44	2.60	8.01
3	7.03	1.10	6.90	1.18	6.50	1.36	4.30	3.77	3.38	6.28	2.70	8.50
4	6.90	1.13	6.80	1.33	6.75	1.85	4.70	2.91	3.10	3.48	2.50	4.18
5	6.60	0.58	6.50	0.66	5.50	1.07	3.20	3.03	2.80	3.80	2.50	4.42
6	7.20	0.76	7.10	0.88	7.10	1.12	6.00	2.12	3.60	3.72	2.65	4.45

*All descriptions are the same as in Table 1.

Table 3. Decrease in pH, H^+ consumption and decrease in base cation exchange capacity with different HCl treatments (added HCl, mmol/kg soil)

Soils*	1	10	80	160	320
1.a. decrease in pH	0.28	1.65	3.35	3.85	4.13
b. H^+ consumption (% of addition)	100.0	88.8	53.7	37.5	24.1
c. decrease in BCEC (% of initial value)	-4.1	4.9	36.7	38.0	48.2
2.a. decrease in pH	0.47	0.73	2.82	3.54	3.97
b. H^+ consumption (% of addition)	100.0	100.0	41.0	36.7	25.7
c. decrease in BCEC (% of initial value)	1.7	10.1	41.1	50.0	55.4
3.a. decrease in pH	0.13	0.53	2.73	3.65	4.33
b. H^+ consumption (% of addition)	100.0	100.0	41.1	36.7	25.7
c. decrease in BCEC (% of initial value)	-11.4	0.0	30.5	32.9	54.6
4.a. decrease in pH	0.1	0.15	2.20	3.80	4.40
b. H^+ consumption (% of addition)	97.1	67.9	53.3	22.9	13.6
c. decrease in BCEC (% of initial value)	-24.1	10.9	47.1	34.6	63.1
5.a. decrease in pH	0.1	1.10	3.40	3.80	4.10
b. H^+ consumption (% of addition)	100.0	87.0	68.0	20.3	12.6
c. decrease in BCEC (% of initial value)	-13.8	3.0	48.0	60.3	80.1
6.a. decrease in pH	0.10	0.10	1.20	3.60	4.55
b. H^+ consumption (% of addition)	100.0	63.6	94.2	22.2	13.6
c. decrease in BCEC (% of initial value)	-14.2	-24.3	26.1	57.3	78.9

* All descriptions are the same as in Table 1.

The same reaction has been found for the 10 mmol HCl/kg soil HCl treatment in the manured sample from Baborówko, while in the other samples the BCEC decreased by 3-11 %. This phenomenon could be explained by the facts that during mineralization of organic N, anion uptake, reduction reactions including denitrification and decomplexion of metal ions negative charge of a soil could increase [2,6].

The acid treatments of 80 mmol HCl/kg

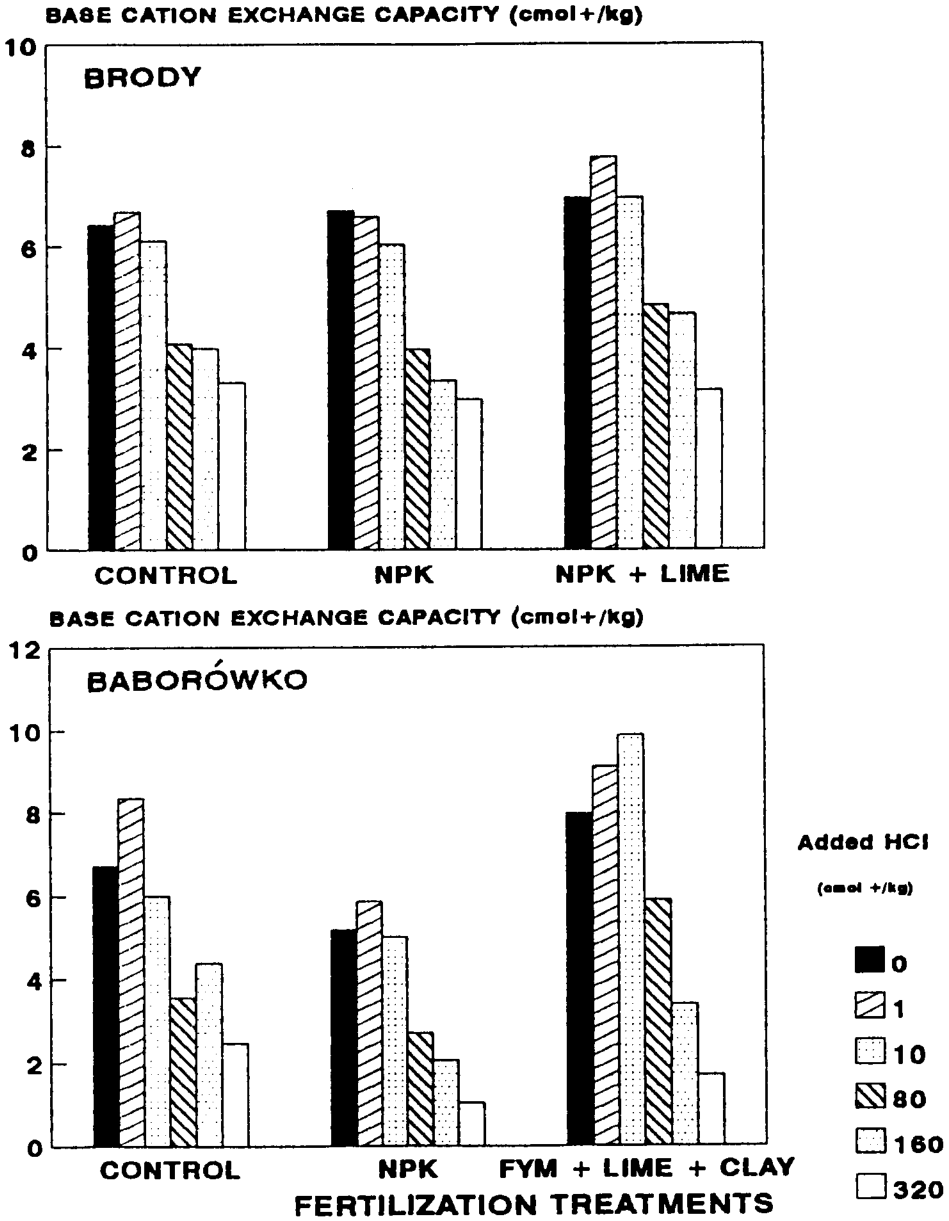

Fig. 1. Base cation exchange capacity (cmol(+)/kg soil) of soils treated with different HCl doses at Brody and Baborówko.

soil was the break point of BCEC for almost all soils in their response to acidification. The only manured soil had its break point at the 160 mmol HCl/kg acid treatment. As compared with the acid treatment of 10 mmol HCl/kg soil reduction in BCEC of Brody soils was by 2.28-2.67 cmol(+)/kg soil, corresponding to 33-50 % of the initial value, whereas in Baborówko soils was by 1.59-6.42 cmol(+)/kg soil (35-60 %).

The greater decrease in BCEC of Baborówko soils is due to their lower buffering capacity at higher acid treatments (Fig. 1). The relationships between BCEC and hydrolytic acidity may be described using the following equations:

BRODY

1.Control	$BCEC=3.95-0.21\ Hh$	$r=-0.95$	$P<0.01$
2.NPK	$BCEC=7.43-0.60\ Hh$	$r=-0.99$	$P<0.001$
3.NPK+ lime	$BCEC=7.74-0.54\ Hh$	$r=-0.96$	$P<0.01$

BABORÓWKO

4.Control	$BCEC=9.25-1.61\ Hh$	$r=-0.92$	$P<0.01$
5.NPK	$BCEC=6.24-1.15\ Hh$	$r=-0.99$	$P<0.001$
6.FYM+ lime+ clay	$BCEC=10.66-2.00\ Hh$	$r=-0.96$	$P<0.01$

The consumption of H^+ ions was the highest at the acid treatment of 1 mmol HCl/kg soil. All added HCl was neutralized, except the control Ba, where reached 97 % (Table 3). At the acid treatment of 10 mmol HCl/kg soil investigated soils neutralized H^+ ions in ascending order: FYM(+lime+clay)(64 %)< control(Ba)(68 %)<NPK(Ba)(87 %)<control(Br) (89 %) <NPK(Br)=NPK+lime(100 %). In the limed soils and control Ba at the acid treatment of 80 mmol H^+/kg soil proton consumption was lowered down 50 %. In the other soils 160 mmol of acid/kg soil was needed to rich this limit.

The amount of strong acid required to reduce the pH of a system to a reference pH value is termed acid-neutralizing capacity (ANC) [2]. The correspondence value of 5.0 as suggested by Breemen [2] for agriculture soils was adopted to the present material. The corresponding reduction in BCEC was also estimated (Table 4).

Table 4. Acid-neutralizing capacity (ANC 5.0) and corresponding decrease in BCEC of HCl treated soils

Soil	ANC 5.0 (cmol(+)/kg)	Decrease in BCEC cmol(+)/kg soil	Decrease in BCEC % of initial value
1	6.9	1.05	16.3
2	67.2	1.44	21.4
3	104.6	1.40	20.0
4	103.8	1.60	23.8
5	55.4	0.95	18.3
6	137.1	2.63	33.0

Considering all ANC 5.0 values together we can divide investigated soils into three groups according to the amount of HCl needed:

10 NPK(Ba), NPK(Br), control(Br)	from 55 to 69 mmol HCl/kg soil
20 control(Ba),NPK+lime	about 104 mmol HCl/kg soil
30 FYM+lime+clay	137 mmol HCl/kg soil.

The values of ANC 5.0 are highly related to the initial pH ($r=0.93$ for $P<0.01$), organic C content ($r=0.83$, for $P<0.05$) and the initial BCEC ($r=0.88$, for $P<0.05$). The other soil parameters were not so clearly related to ANC 5.0. The changes in BCEC as a result of addition of acid to the reference value of 5.0 were relatively high. The BCEC decrease at ANC 5.0 as a function of its initial value is shown on the simple regression equation:

$$BCEC\ ANC = -2.368 + 0.583\ BCEC0$$
$$r=0.88; \quad P<0.05.$$

The decrease in BCEC was probably related to the protonation of cation exchange sites of organic soil constituents. An intimation of this is given by the fact that in the NPKBa soil low in organic C its acidification to pH 5.0 caused only a small decrease in BCEC. Reverse situation took place for the FYM soil.

As is shown by our results all investigated soils had their inflection points near pH 5.5. This pH value is in the range, in which organic matter contributes to CEC of soil [4,6,8]. Limed soils had prolonged their acid-neutralizing capacity due to probably formatted stable Ca-humus complexes, which are important sink of H^+ [8].

According to Schwertmann *et al.* [8], the acid neutralizing capacity of soil at lower pH is derived from aluminium and iron oxides. The aluminium buffer is included between 3.0 and 4.8 and iron buffer below 3.0. At the range of 4.5-4.8 the reduction in BCEC might be due to inactivation of cation exchange sites by hydrous oxides or oxide polymer coating the positive charge of which increases with decreasing pH and increasing proton consumption. However, these buffers were rather weak in both soils. Proton consumption decreased linearly with the amounted added acid.

CONCLUSIONS

1. Acidification of two grey-brown podzolic soils caused increase of their hydrolytic acidy and simultaneously decrease in the base cation exchange capacity.

2. The acid-neutralizing ability of unmanured soils had the maximum between 1 and 10 and the munured one between 10 and 80 mmol HCl/kg soil.

3. The acid neutralizing capacity of experimental soils was related to the initial BCEC, which was strongly dependent on organic C content.

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WPŁYW ZAKWASZENIA NA POJEMNOŚĆ WYMIENNĄ KATIONÓW ZASADOWYCH W DWÓCH GLEBACH PŁOWYCH PRZY RÓŻNYM NAWOŻENIU PRZEZ 36 LAT

Badano wpływ zakwaszenia na pojemność wymienną kationów zasadowych w dwóch glebach płowych o różnym sposobie nawożenia. Gleby zakwaszano przy użyciu 0-320 mmol HCl/kg gleby. Wartości S w warunkach naturalnych kształtowały się od 5.17 do 7.96 cmol(+)/kg gleby a pH od 6.60 do 7.20. Dodanie 0-320 mmol HCl/kg spowodowało redukcję S do 1.03-3.32 cmol(+)/kg gleby przy jednoczesnym obniżeniu pH do 2.50-2.77. Zdolność gleby do neutralizacji kwasu zmieniała się w zależności od nawożenia. Przy niskich dawkach dodanego HCl reakcja gleby na zakwaszenie zmniejszała się w następującym kierunku: kontrola>NPK+Ca (obornik+Ca+glina)> NPK. Przy niższych dawkach kwasu stwierdzono odwrotną kolejność badanych obiektów nawozowych. Spadek S wyniósł od 3.09 do 6.28 cmol(+)/kg co odpowiadało 47-79 % początkowej jego wartości. Ilość potrzebnego do zredukowania pH gleby do 5.0 (ANC 5.0) kształtowała się w zakresie 55.4-137.1 mmol HCl/kg gleby. Obie gleby dla prawie wszystkich wariantów nawozowych miały maksymalną zdolność neutralizacji kwasu w zakresie 1-10 mmol HCl/kg, która została przełamana po dodaniu 80 mmol HCl/kg gleby.

Słowa kluczowe: zakwaszenie gleb, pojemność wymienna kationów, nawożenie przez 36 lat.