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Some negative chemical properties of acid soils

MIODRAG JAKOVLJEVIĆ, MIRJANA KRESOVIĆ, SRDJAN BLAGOJEVIĆ*# and SVETLANA ANTIĆ-MLADENOVIĆ

Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Belgrade, Serbia and Montenegro (e-mail: sblagoje@EUnet.yu)

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Abstract: Some important chemical properties of various samples of two types of acid soil from Western Serbia (pseudogley and brown forest) are presented in this paper. Mobile Al was found in elevated and toxic quantities (10–30 mg/100 g) in the more acid samples of pseudogley soil. All samples of brown forest soil were very acid and the quantities of mobile Al were in the range from 12.8 to 90.0 mg/100 g. In a selected number of pseudogley soils, the influence of pH and other soil properties on the mineralization and nitrification processes was investigated. Strong inhibition of nitrification at low soil pH was found to be related to high quantities of mobile Al. At pH values less than 4.0 (in 1 M KCl), processes of chemical nitrification and denitrification of applied nitrites were registered in the pseudogley soils.

Keywords: mobile Al, mineralization, chemical nitrification denitrification.

INTRODUCTION

Acid soils occupy a considerable area of Serbia and investigations of their properties are nowadays of great interest. The increase of the area under acid soils is, among other things, due to the fact that pure chemical compounds are used as NPK fertilizers, as well as to pollution with acid gases from the atmosphere.[1] Hence, problems of using acid soils for plant production are becoming more pronounced and the necessity for improving their chemical (and other) properties is more evident.

The basic problems concerning chemical properties of more acid soils are, besides acidity itself, the presence of toxic compounds and elements, such as soluble forms of Al, Fe and Mn, nitrites and various toxic organic acids.

In acid soils with pH below 5.5 (in water), the content of mobile Al is rather high. Simultaneously, there is an increase in the uptake of this element by plants which cause damage to roots and a decrease in the uptake of other nutrient elements. This is easily noticed in the case of phosphorus, when plant leaves have a visible red colour.[2–4]

* Author for correspondence.

\# Serbian Chemical Society active member.

The toxicity of Al in acid soils is very often connected with increased levels of soluble Fe and Mn, which can be toxic to plants when present in large amouns.[5]

In soils having higher acidity, nitrogen transformation processes occur in a specific manner in comparison with other soils. Retardation of the nitrification process is particularly emphasised and this can lead to increase in the amounts of toxic nitrites.[6] On the other hand, chemical denitrification of produced nitrites occurs, when one part of the nitrogen is lost in the form of gases.[7,8]

Besides, the occurence of toxic elements in more acid soils, the solubility of microelements is increased and this leads to their movement into deeper soil layers and increased uptake by plants. As a consequence of this effect, deficiency of some microelements, especially of boron and zinc, occurs in such soils.

In this paper, the appearance of toxic amounts of aluminium in pseudogley and brown forest soils, as well as its relationship with some basic chemical properties of these soils, was investigated with the aim of evaluating the influence of acidity and mobile Al on the processes of mineralization and nitrification. These processes are the source of available N in a soil. The significance of such an investigation lies in the fact that both processes are reduced in conditions of high soil acidity. Special attention was paid to the processes of chemical nitrification and denitrification in the samples with higher acidity.

EXPERIMENTAL

A considerable number of samples of the two acid soils from Western Serbia (25 samples of pseudogley – Šabac, Loznica, Valjevo and 17 samples of brown forest soil – Loznica) was investigated in this work. Fifty samples of pseudogley were collected, whereby 25 of them were been selected for further investigation, in order to cover a wide range of pH (3.65 to 5.75). Sampling was carried out from a depth 0 to 20 cm.

The following chemical properties were determined: pH, mobile Al, humus, nitrogen (total and available forms), sum of basic cations and hydrolytic acidity.

The pH value was determined by pH meter Iskra using a glass (indicator) and a calomel (reference) electrode in suspensions: soil: water = 1:2.5 and soil: 1 M KCl = 1:2.5.

For the determination of the mobile Al, the soil was shaken with 1 M KCl (1 h, room temperature) and filtered (Whatman No. 40). A suitable aliquot was titrated with 0.01 M NaOH using phenolphthalein as the indicator for the determination of the total exchangeable acidity (H^+, Al^{3+}). In a second aliquot, the acidity from H^+-ions was determined by the same titration, after precipitation of the Al^{3+} -ions with 3.5 % NaF, by the equation:

$$AlCl_3 + 6NaF \rightarrow \underset{\downarrow}{Na_3Al_6} + 3NaCl$$

The quantity of mobile Al was calculated as the difference between the first and second titration. The NaOH solution was standardized by pure Na_2CO_3.

The humus content was determined volumetrically after redox reaction with excess 0.07 M $K_2Cr_2O_7$. The $K_2Cr_2O_7$ remaining after the oxidation of the organic C was determined by another redox reaction with 0.1 M $(NH_4)_2Fe(SO_4)_2$ using phenilanthranilic acid as the indicator. The $K_2Cr_2O_7$ was standardized volumetrically with $KMnO_4$, the molarity of which had been determined using pure oxalic acid as the standard substance.

The determination the total N involves two steps: (1) degistion of the sample to convert organic N to NH_4^+ – N and (2) determination of the NH_4^+ – N in the digest. Digestion was performed by heating (380 °C) the soil samples with $H_2 SO_4$ p.a. NH_4^+–N in the digest is determined by collection of NH_3 liberated by distillation of digest alkali and analysis of the distillate for NH_4^+ – N by titremetric procedure with 0.05 M H_2SO_4, standardized by NaOH.

Determination of available N (NH_4^+, NO_3^-) was performed by steam distillation method[10] of 2 M KCl soil exctract. This distillation method uses MgO as the alkali reagent and Devarda alloy as the reductant of NO_3^- – N to NH_4^+. Analysis of the distillate for NH_4^+ – N was performed by a titrimetric procedure with 0.0025 M H_2SO_4.

The sum of the exchangable basic cations was determined after the soil samples had been mixed with an excess of 1 M NH_4OAc. The remaining NH_4^+ – N was determined by the distillation procedure described for the determination of the available N, and the sum of exchangeable basic cations was calculated.

For the determination of the hydrolytic acidity, soil samples were treated with 1 M NaOAc (pH 8.2) for 1 h, at room temperature. The formed HOAc was neutralized by a titrimetric procedure with 0.1 M NaOH.

The methods used for the determination of these properties are described in detail in the laboratory manual of soil and water chemistry.[9]

With aim of investigating the process of mineralization and nitrification of soil a nitrogen incubation experiment was performed with 17 samples of pseudogley soil whereby 10 g of each soil and 3 ml of water were placed in glass jars, which were closed with plastic foil and thermostated at 30 °C for 4 weeks. The content of available forms of nitrogen was determined before and after incubation by extracton with 2 M KCl employing the distilation method according to Bremner.[10]

With the aim of determining the influence of acidity on the chemical nitrification and denitrification processes, an experiment with 3 samples of pseudogley was carried out according to the previously described procedure but with the following differences. Nitrite nitrogen (100 ppm) was added together with water in the form of a $NaNO_2$ solution and the incubation lasted for 0, 1, 3, 5 and 7 days. The temperature was kept at +1°C in order to prevent the occurrence of biological processes, especially nitrification and denitrification, in the incubated samples. Before and after incubation, the mixture was extracted with 2 M KCl solution and the available forms of nitrogen (NH_4^+, NO_3^- and NO_2) were determined by means of the distillation method.

RESULTS AND DISCUSSION

Chemical characteristics of the examined pseudogley and brown forest soils are presented in Tables I and II, respectively.

The results of the investigation of the content of mobile Al in the samples of pseudogley and brown forest soil, as well as the relationship between the content of this element and some basic chemical properties of the corresponding soils, are presented in the first part of this paper. The results are, due to their abundance, expressed in the form of minimum and maximum values (Table III) of the investigated chemical properties and the degree of their relationship with mobile aluminium is expressed in the form of correlation coefficients.

The content of mobile Al in the investigated samples of pseudogley soils lies within a very wide range, from 0.0 to 38.7 mg/100 g of soil. Toxic quantities of mobile Al (>10 mg/100 g) occur at pH values of 5.0 (in water) and 4.0 (in 1 M KCl). Hence, it is necessary to determine by chemical analysiss the mobile Al in soils having similar acidity. By undertaking adequate agrotechnical measures (liming), these toxic quantities should be brought to levels which do not cause damage to plants.

On the basis, of the obtained values for the correlation coefficients (Table III) a strong dependence of the determined quantities of mobile Al on the degree of pseudogley acidity, as well as on the composition of the soil exchangers can be seen.

TABLE I. Chemical properties of the examined pseudogley soils

Sample No.	Mobile Al/(mg/100 g)	pH		H	S	T	V/%
		1 M KCl	H_2O	(meq/100 g)			
1	25.4	3.65	4.80	7.79	11.08	18.87	58.7
2	18.2	3.70	4.80	6.92	6.72	13.64	49.3
3	18.9	3.70	4.70	8.66	5.92	14.58	40.6
4	14.0	3.70	4.90	6.06	13.08	19.14	72.1
5	18.7	3.75	4.60	8.20	9.52	17.74	53.7
6	13.3	3.75	5.20	5.19	13.84	19.03	72.7
7	16.4	3.80	4.70	7.36	11.48	18.84	60.9
8	19.8	3.80	4.60	8.66	7.92	16.58	47.8
9	23.4	3.80	4.25	11.6	8.32	20.1	41.2
10	11.9	3.80	4.40	9.09	11.08	20.17	54.9
11	12.4	3.80	4.40	6.92	6.32	13.24	47.7
12	20.7	3.85	4.40	10.82	7.12	17.94	39.7
13	38.7	3.85	4.85	6.06	7.12	13.18	54.0
14	9.0	3.90	5.00	6.49	13.08	19.57	66.8
15	8.1	3.90	5.20	4.33	10.68	15.01	71.2
16	13.7	3.90	4.70	6.92	7.52	14.44	52.1
17	0.7	4.15	6.50	2.59	16.24	18.83	86.2
18	1.8	4.20	5.20	4.3	–	–	–
19	2.25	4.25	5.25	3.46	13.84	17.3	80.0
20	1.08	4.40	5.40	4.33	18.2	22.53	80.8
21	0.50	4.55	5.60	3.46	17.4	20.86	83.4
22	1.35	4.80	5.80	3.00	19.8	22.8	86.7
23	1.35	4.90	6.00	3.46	19.4	22.86	84.9
24	1.35	5.30	6.40	2.60	26.9	29.5	91.2
25	•	5.75	6.90	1.70	21.76	23.49	92.6

•Below the detection limit of 0.1 mg/100 g; H – hydrolytic acidity; S – sum of the basic cations; T – cation exchange capacity (S + H); V – degree of base saturation of the soil (S.100/T)

TABLE II. Chemical properties of the examined brown forest soils

Sample No.	Mobile Al/(mg/100 g)	pH		H	S	T	V/%
		1 M KCl	H_2O	(meq/100 g)			
1	75.6	3.25	3.70	–	–	–	–
2	68.8	3.30	3.80	31.61	0	31.61	0
3	28.7	3.35	4.00	13.20	9.52	22.72	41.9
4	19.0	3.55	4.15	–	–	–	–
5	90.0	3.55	4.40	16.45	7.12	19.60	30.2
6	32.6	3.60	4.40	12.12	7.48	18.87	38.2
7	82.6	3.70	4.40	15.58	5.56	21.14	26.3
8	12.8	3.70	4.05	12.99	4.76	17.75	26.8
9	46.8	3.70	4.35	11.25	5.48	16.73	32.8
10	18.6	3.75	4.60	8.66	7.92	16.58	47.8
11	23.8	3.75	4.60	69.92	4.76	11.68	40.8
12	45.2	3.85	4.25	12.12	5.12	17.24	29.7
13	39.8	3.90	4.40	9.62	5.88	15.40	38.2
14	41.8	3.95	4.30	15.58	1.60	17.18	9.3
15	29.7	4.00	4.40	8.66	3.92	12.58	31.2
16	14.6	4.00	4.50	4.33	5.12	9.45	54.2
17	18.0	4.00	4.40	19.05	2.36	21.41	11.0

TABLE III. Correlation coefficients between the amounts of mobile Al and the chemical properties of the soil

Number of samples	Mobile Al/(mg/100 g)	pH		H	S	T	V/%
		Water	1 M KCl	(meq/100 g)			
Pseudogley soils							
25	• to 38.7	4.25 to 6.90	3.65 to 5.75	1.70 to 11.66	5.92 to 26.9	13.18 to 29.5	39.7 to 92.6
Correlation coefficients Al-soil properties	–	-0.71^{**}	-0.68^{**}	0.85^{**}	-0.77^{**}	-0.60^{**}	-0.80^{**}
Brown forest soil							
17	12.8 to 90.0	3.70 to 4.60	3.25 to 4.00	4.33 to 31.61	1.60 to 9.52	9.45 to 31.61	9.30 to 54.20
Correlation coefficients Al-soil properties	–	NS	NS	0.52^{*}	NS	NS	NS

*Statistically significant at the 0.05 probability level; **statistically significant at the 0.01 probability level; NS not statisticaly significant; • below the detection limit 0.1 mg/100 g

All the samples of the brown forest soil had high acidity with pH values below 4.6 (in water) and 4.0 (in 1 M KCl). It is understandable why toxic values for the content of mobile Al (usually above 20 mg/100 g) were found in all samples. Under these conditions the relatiionship between the content of mobile Al and the other chemical properties were not very expressed.

Toxic amounts of mobile Al were found in half of the investigated samples of the pseudogley soil and in all samples of the brown forest soil. From this fact it can be seen how important this problem is, especially for arable areas under pseudogley soils, where liming has to be performed. The toxic effect of Al on plants is connected with disturbances in their metabolism and with a reduced uptake of many nutrient elements. Since ligher quantities of Al occur only in soils having higher acidity, its toxicity is very often connected with a deficiency of some nutrient elements, such as Mg, B, Zn and others, in the soil. For this reason, when liming such soils, care must be taken not to inactivate the already small amounts of B and Zn or to a cause magnesium deficiency by increasing the ratio of Ca to Mg. In connection with this fact, partial neutralization of soil acidity (1/4 of the value required for total neutralization) is very often performed and where it is necessary, dolomite is applied instead of lime. Since the investigated pseudogley soils generally contained less than 2 % of humus, it is useful to apply farmyard manure and other organic fertilizers in combination with liming and other ameliorative measures.

The results of the investigation of the influence of acidity and other chemical properties of pseudogley soils on the nitrogen mineralization process are presented in Table IV. As pseudogley is an arable soil, the investigation of mineralization and nitrification is significant regarding the availability of soil N. The second investigated soil type (brown forest soil) is not arable soil. In addition, the pH of the samples was very low, so that nitrification had ceased while mineralization was very reduced. For these reasons, mineralization and nitrification were not evaluated in the samples of brown forest soil. Pseudogley soil samples were incubated under optimal moisture and temperature conditions for a period of 4 weeks. The obtained results on the mineralized soil nitrogen can be best explained through correlation coefficients.

In the investigated soil samples, ammonification did not depend on any of the chemical properties of the pseudogley soils. This was to be expected, since the microorganisms responsible for ammonification (bacteria, fungi, actinomycetes) have a high tolerance to soil pH[11]. In the samples having a higher acidity, mineralization ceased with the formation of ammonium – N, and as the acidity decreased, according to the obtained correlation coefficients (Table IV), nitrification occurs. Under conditions of high soil acidity, the amount of nitrates produced by biological nitrification decreased and the process of nitrification mostly ceased after the formation of nitrites.

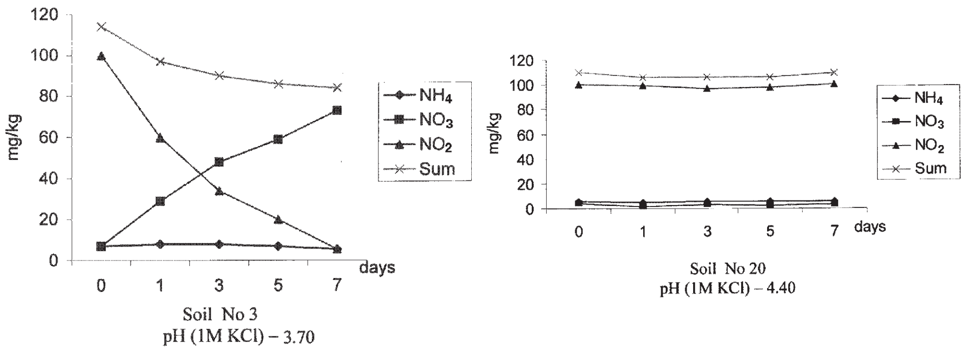
A negative influence of mobile Al on the nitrification process was also found which is in very close relationship with the degree of soil acidity.[12] Although it can

TABLE IV. Influence of basic chemical properties of pseudogley soils on mineralization and nitrification processes

Number of samples	pH		Humus (%)	Nitrogen (%)	C/N	Available N/ppm			Mobile Al (mg/100 g)	Mineralized N/ppm		
	Water	1 M KCl				NH_4^-	NO_3^-,+NO_2^-	Sum		NH_4^+	NO_3^-+NO_2^-	Sum
17	4.25 to 6.90	3.65 to 5.75	0.43 to 3.52	0.05 to 0.21	4.8 to 10.3	0.3 to 53.5	1.4 to 79.1	6.6 to 89.9	• to 25.4	• to 66.1	• to 57.0	0.7 to 66.1
Correlation coefficients												
NH_4	NS	NS	NS	NS	NS	NS	NS	NS	NS	–	–	–
NO_3+NO_2	0.62*	0.79*	NS	NS	NS	NS	NS	NS	–0.52*			
Sum	NS	NS	NS	NS	NS	NS	NS	NS	NS	–	–	–

*statistically significant at the 0.05 probability level; **statistically significant at the 0.01 probability level; NS not statisticaly significant; • Below the detection limit of 0.1 mgAl/100 g and 0.1 ppm N be considered that higher quantities of Al express, by themselves, toxic effect on the microorganisms which perform nitrification, this phenomenon could be conected with the accumulation of toxic quantities of nitrites. This is due to the inhibition of the second phase of nitrification by means of mobile Al. In addition, under conditions of reduced nitrification in a soil, the amounts of ammonium – N are higher, especially when ammonium fertilizers had been applied, the uptake of which by plants leads to a more expressed toxicity effect of mobile Al. This is due to the greater uptake of cations in relation to anions, so that a greater release of H^+-ions from plant occurs, leading to a decrease of the pH in the rhizosphere.

The results on the processes of chemical nitrification and denitrification in more acid samples of pseudogley soil are presented in Fig. 1.



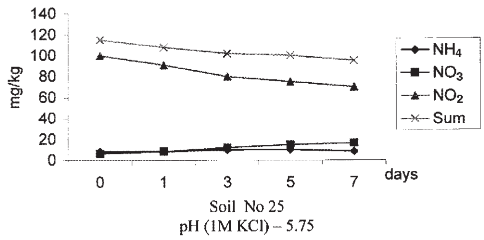


Fig. 1. Processes of nitrification and denitrification in representative pseudogley soils.

The results presented in Fig. 1 show that at pH values below 4.0 in 1 M KCl chemical nitrification of the applied nitrites certainly occurred rapidly in the investigated samples of pseudogley. At pH values above 5.0 (in 1 M KCl), the applied nitrites practically underwent no change. Additionaly, an apparent deficit in the balance of the available forms of nitrogen was found in most acid samples after only one day of incubation. As nitrites and nitrates do not bond to soil particles, and as biological processes are practically halted at the low incubation temperature, this loss could only be explained by chemical denitrification of the applied nitrites to gaseous products (N_2O, N_2, NO).[13]

Losses of nitrites, whether added or produced in the soil, in the conditions of inhibited biological activity, might occur by the following chemical reactions: 1. Decomposition of nitrous acid (3 $HNO_2 \rightarrow 2NO + HNO_3 + H_2O$); 2. Reaction of nitrites with organic soil constituents (phenolic compounds), with formation of N_2O, N_2 and NO; 3. chemical decomposition of hydroxylamine ($2MnO_2 + 2NH_2OH \rightarrow 2MnO + N_2O + 3H_2O$); reaction of nitrite with hidroxyl amine ($NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O$).[12]

These phenomena could explain why nitrites are not usually found in soils having higher acidity, which is, bearing in mind their toxicity, desirable. Toxic quantities of nitrites could be expected in pseudogley soils having somewhat lower acidity (above 4.0 in 1 M KCl). However, due to the process of chemical denitrification, considerable losses of nitrogen in the form of gases are possible in pseudogley soils having higher acidity.

CONCLUSIONS

On the basis of the obtained results, it is possible to draw the following concslusions:

1.Toxic amounts of mobile Al were found in a large number of samples of pseudogley and brown forest soil. The amounts were in close relationship with the acidity of these soils, increasing with increasing acidity.

2. Higher acidity and higher content of mobile aluminium in the samples of pseudogley soils exerted a negative influence on the nitrification process.

3. Processes of chemical nitrification and denitrification of added nitrites were registered in the most acid samples of pseudogley soils.

ИЗВОД

НЕКА НЕГАТИВНА СВОЈСТВА КИСЕЛИХ ЗЕМЉИШТА

МИОДРАГ ЈАКОВЉЕВИЋ, МИРЈАНА КРЕСОВИЋ, СРЂАН БЛАГОЈЕВИЋ и СВЕТЛАНА АНТИЋ-МЛАДЕНОВИЋ

Пољопривредни факултет Универзитета у Београду, Немањина 6, 11081 Београд-Земун

Истраживања су обављена на два типа земљишта Западне Србије (псеудоглеј и смеђе шумско земљиште). Оба испитивана земљишта карактерише ниска pH вредност. Код свих узорака смеђег шумског земљишта утврђене су токсичне количине мобилног Al за биљке и за микроорганизме, а код псеудоглејног земљишта токсичне количине Al су утврђене само за неке узорке. На процес нитрификације, који је праћен у одабраним узорцима псеудоглеја, директно су деловали ниска pH вредност (киселост) и висок садржај мобилног алуминијума. Додавањем $NaNO_2$ утврђено је одвијање процеса хемијске нитрификације и денитрфикације у псеудоглејном земљишту при pH мањем од 4,0 у 1 M KCl.

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