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Release of trace metals to the soil solution from a phosphate rock containing soil at different acid loads

ABSTRACT. In agricultural practice basic phosphate rocks (PRs) may be efficient P sources if applied on acidic soils. However, due to their potentially toxic elements content environmental hazards may arise. In a laboratory bulk experiment the appearance and accumulation of such elements (As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr and Zn) in the soil solution of an acidic sandy soil was studied after various PR and acid treatments. The degree of pH elevating effect of PR treatments was also tested. In the liquid phase of the PR-enriched soil, metal concentrations were generally lower than in the control sample because their release to the soil solution was influenced less by the amount of the pollutants carried into the soil with PR doses than by the pH increasing and/or solubility altering effect of PR. Acid loads, as expected, considerably increased the concentrations of cation forming elements in the soil solution, but their concentrations – due to the immobilizing effect of PR – decreased in the acid treated soil, as well. Extreme strong acid treatment was necessary to compensate for this effect and, while Ba, Co, Cu and Mn concentrations practically did not change with the increasing PR doses, Cd, Sr and Zn concentrations were eleveated. In contrast, the immobilizing effect of PR in case of Pb dominated even under the extreme acid treatment, its concentration decreased with increasing PR doses. Concentration of the anion forming elements (As, Mo) in the acidic soil solution was negligible even at the highest P dose.

KEY WORDS: soil solution, trace metals, phosphate rock, acid load

In agricultural practice slowly dissolving (reactive) basic phosphate rocks (PRs) may be efficient P sources if applied on soils with moderate or high soil acidity [Gatiboni et al. 2003]. PRs, as low release fertilizers, are added directly

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to the soil and – compared to the annually applied, highly expensive water soluble P fertilizers (superphosphates) – they maintain P supply in the soil for longer period. Owing to their free lime content and to the proton consuming dissolution of the P mineral component (apatite), PRs are also able to neutralize acids and provide liming value for the soil [Bolan et al. 2003].

PRs, similarly to conventional P fertilizers, contain not only P, Ca and other major elements required for plant nutrition but also potentially toxic elements [Kpomblekou, Tabatabai 1994; Van Kauwenbergh 1997; Kabata-Pendias, Pendias 2001]. An indication of the environmentally hazardous accumulation of these components might be their appearance and elevated concentration in the soil solution. It is necessary to gain information about the effects of PRs on soil solution composition, because with extension of soil acidification in many regions, the role of directly applicable basic (non-acidulated) PRs as P sources is getting more significance.

The objective of this research was to measure potentially toxic element concentrations in the liquid phase of an acidic sandy soil after various PR and acid treatments. The degree of pH elevating effect of PR treatments was also tested.

METHODS

An acidic sandy soil (from Nyírlugos, Hungary) was used in this study, samples were taken from the ploughed (0-20 cm) layer. Main chemical and physical parameters of the soil were the following: pH_{H2O} 5.0; pH_{KCl} 3.8; organic matter content: 0.6 %; cation exchange capacity: 3.0 $cmol_c$ kg^{-1} soil; clay + silt and clay contents (< 0.02 mm and <0.002 mm, respectively): 5.0 % and 2.2%, respectively.

Trace metal and macro element content in the soil and in a Senegal sedimentary PR (which was previously ground to pass a 500 µm sieve) was determined after 65% HNO_3 + 30% H_2O_2 microwave wet digestion in a Teflon bomb, by ICP-AES method (Tab. 1). Total P content of the PR sample (13.5%), which was also measured in this extract, and its 10% HCl soluble carbonate content determined in Scheibler calcimeter and expressed as $CaCO_3$ (4.3 %) were in the ranges reported by Kpomblekou and Tabatabai [1994] for twelve PR samples of different origins. Its pH_{H2O} (at 1 : 2.5 = PR : water ratio) was 8.5, which, with the exception of one PR sample, was higher than those given by Kpomblekou and Tabatabai [1994].

The PR sample was mixed to the air dried soil in doses of 0 mg, 655 mg and 1310 mg P kg^{-1} soil (0 mg, 1500 mg and 3000 mg P_2O_5 kg^{-1} soil), marked as D0, D1 and D2 PR treatments. In case of D1 dose, for example, the metal amount carried into the soil with PR was 416, 592, 160 and 2580 μg kg^{-1} soil for Cd, Cr, Ni and Zn, respectively.

Table 1. Concentrations of potentially toxic elements in the studied soil and PR sample determined by 65% HNO_3 + 30% H_2O_2 digestion and the corresponding threshold levels (TL) in soils and fertilizers

	Element												
	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sr	Zn
	mg kg^{-1}												
Soil	1.2	32	0.04	3.4	13	2.8	<dl[a]	212	<dl[a]	7.9	6.2	11	16
TL[b]	10	150	0.5	15	30	30	0.15		3	25	25		100
PR	<dl[a]	77	86	2.5	122	46	<dl[a]	125	2.5	33	4.5	745	532
TL[c]	10		6[d]		100		1			50	100		

[a] detection limit (As 0.5, Hg 0.5, Mo 0.08 mg kg^{-1})

[b] KöM-EüM-FVM-KHVM: threshold levels: background concentrations of contaminants in soils in Hungary

[c] FVM: max. permitted contents of toxic elements in P-fertilizers in Hungary

[d] allowed Cd content in case of the applied PR sample, which contained 13.5% P

Joint KöM-EüM-FVM-KHVM ministerial decree (10/2000. (VI. 2.)): threshold values for the protection of the quality of subsurface water and soil

FVM ministerial decree (50/2003. V. 9.): authorization, storage, distribution and utilization of fertilizers and other soil amendments

The PR enriched soil was wetted to field capacity (-10 kPa water potential) with deionised water (Ac0) and HNO_3 solutions of various concentrations (0.05, 0.075, 0.1 and 1.5 mol l^{-1}: Ac1, Ac2, Ac3 and Ac4 treatments, respectively). After one week incubation and homogenization of the wet soil, the plant available soil solution was extracted with a centrifugation method [details see in Csillag et al. 1999] by applying a rotor speed corresponding to -1500 kPa (the conventional wilting point of plants). As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr, Zn concentrations in the centrifuged solutions were determined by ICP spectrometry.

To control reproducibility, treatments were made in duplicates (data in the tables are their averages), and at the D1-Ac3 treatment five parallel samples were prepared to determine the combined error of sample preparation, extraction method and chemical analysis of the soil solution. Coefficient of variation values were low for Cd and Ni (less than 5%), 7–20% for Ba, Co, Cu, Mn, Sr, Zn and high (about 30%) for Cr and Pb. Data of the duplicate measurements at the various treatments showed good agreement in most cases, so the reproducibility of the analyses was considered as acceptable.

RESULTS

Potentially toxic elements content in the untreated, original soil was lower than the background concentrations given in the corresponding Hungarian standard (Tab. 1). In the PR sample, however, Cr and especially Cd concentrations considerably exceeded the strict Hungarian limit values for P fertilizers. In a data set of 207 sedimentary PR samples Van Kauwenbergh [1997] reported 21 mg Cd kg^{-1} PR as average, but much higher Cd containing samples were also included (such as those originated from Senegal and having, as an average, 87 mg Cd kg^{-1} PR, very similar to that of our sample (Tab. 1). According to Kabata-Pendias and Pendias [2001] Cd content of PRs might exceed 100 mg kg^{-1} fertilizer.

Table 2. Effect of increasing acid loads on element concentrations in the liquid phase of the soil moistened to field capacity

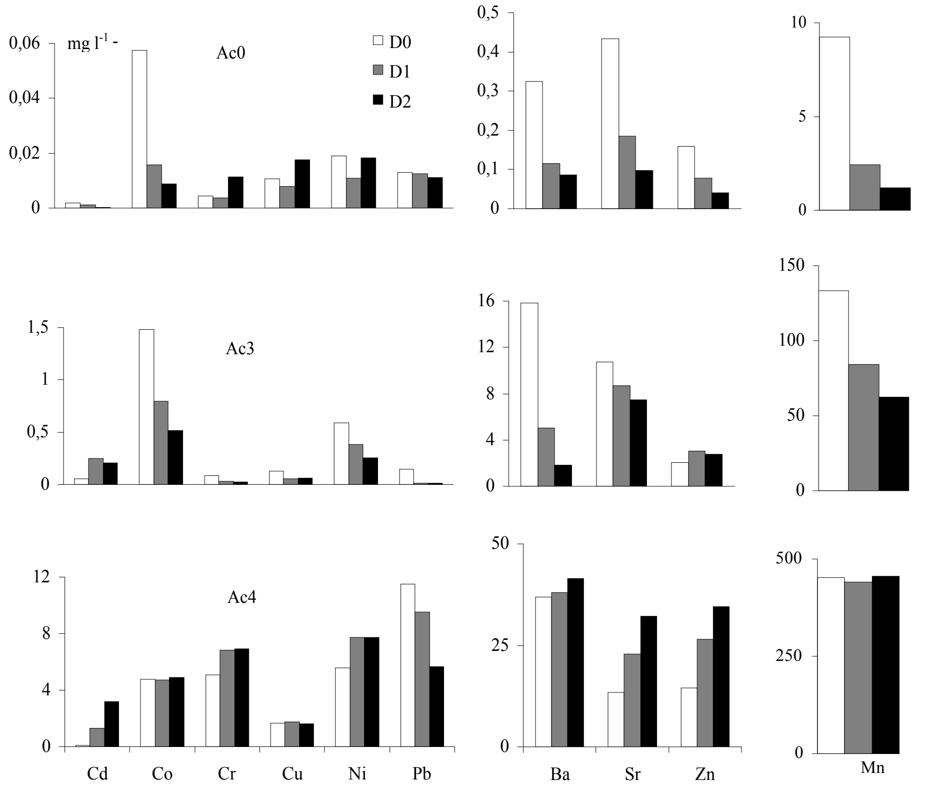
Extractant HNO_3 mol l^{-1}	pH	Element											
		As	Ba	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sr	Zn
		µg l^{-1}											
0	4.5	<dl[a]	320	1.8	57	4.4	11	9240	<dl[a]	19	13	430	160
0.1	2.6	<dl[a]	15850	56	1480	87	120	133500	<dl[a]	590	150	10750	2070
1.5	0.2	<dl[a]	36900	110	4750	5070	1670	453000	<dl[a]	5590	11500	13350	14500
TL[b]		10	700	5	20	50	200		20	20	10		200

[a] detection limit (As 8, Mo 1.5 µg l^{-1})

[b] KöM-EüM-FVM-KHVM, threshold levels (TL): max. permitted (tolerable) concentrations of contaminants in subsurface waters in Hungary

Concentrations of potentially toxic elements in the liquid phase of the untreated soil were, with the exception of Co, lower than or near the maximum permitted (tolerable) concentrations in subsurface waters (Tab. 2).

Due to acidic treatment, with an increasing H^+ concentration of the solution, which results in, among others, the decrease of surface charge of soil particles [Filep 1999], concentrations of cation forming elements in the soil solution increased in a great extent (Tab. 2). It was in good agreement with observations of several authors [Csillag et al. 1999; Kabata-Pendias, Pendias 2001; Bolan et al. 2003; Smal, Ligeza 2003]. At high acid loads metal concentrations were several orders of magnitude higher than those in the control samples. Cd concentration, for example, increased about 30 times as compared to the unacidified sample, while a two unit drop in pH of the soil solution occured. The extreme strong acid treatment (application of 1.5 mol HNO_3 l^{-1} solution) mobilized the stable ele-



[a] D0, D1, D2 and Ac0, Ac3, Ac4: see Table 3

Figure 1. Element concentrations (mg l^{-1}) in the liquid phase of the PR (D0, D1, D2)[a] and acid (Ac0, Ac3, Ac4)[a] treated soil

ments, Cr and Pb in the greatest extent. Concentration of anion forming elements (As, Mo) in the acidic soil solution was below the detection limit.

In the liquid phase of the PR-enriched soil, metal concentrations were lower (at D1 dose) than in the control sample (D0 dose), and elevation of PR dose (to D2) further decreased the concentration of many elements (Ba, Cd, Co, Mn, Pb, Sr, Zn) in the soil solution (Fig. 1, Ac0 treatment). This means that trace metal concentrations in the soil solution, following one week incubation of the wet soil, were often less influenced by the amount of pollutants carried into the soil with PR doses than by the pH increasing and/or solubility altering effect of this material. Data from the literature about chemical immobilization of metals in contaminated soils by applying PR [Basta, McGowen 2004], supports this tendency.

Table 3. Change of soil solution pH at different PR doses and acid loads

PR dose	Ac0	Ac1	Ac2	Ac3	Ac4
D0	4.5*	nm	nm	2.6	0.2
D1	5.2	4.1	3.5	3.2	0.5
D2	6.4	4.6*	4.0	3.7	0.9

D0, D1 and D2 PR doses equal to 0 mg, 655 mg and 1310 mg P kg^{-1} soil, when 0 g, 4.85 g and 9.70 g PR, respectively, were added to one kg soil; Ac0, Ac1, Ac2, Ac3 and Ac4: acid loads, i. e. concentrations of HNO_3 solutions (0, 0.05, 0.075, 0.1 and 1.5 mol l^{-1}, respectively) applied to moisten the soil to field capacity;

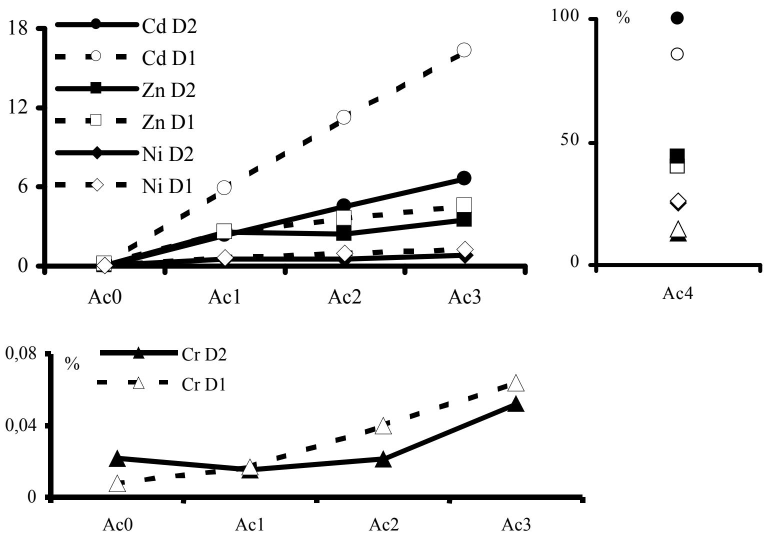
nm. in case of 0.05 and 0.075 mol HNO_3 l^{-1} acid loads (Ac1 and Ac2, respectively) only PR-treated soils (at D1 and D2) were analysed;

*shows the acid load, which compensates for the pH-elevating effect of the basic PR sample between D0 to D2 dose

The concentration of the anion forming Mo exceeded the detection limit (1.5 µg l^{-1}) at the higher PR dose: it reached 1.9 µg l^{-1} at D2. Its appearance in the liquid phase of the PR-enriched soil may be the consequence of the increase of solution pH and its small dissolution from PR added to the soil. It is known that in acidic soils availability of Mo as micronutrient is increased by liming, elevating the pH of the soil [Kabata-Pendias, Pendias 2001].

Application of high dose of PR elevated the pH in the soil solution of the acidic soil by about two units: from 4.5 at the D0 dose to 5.2 at the D1 and 6.4 at the D2 doses, shifting its reaction to nearly neutral (D2-Ac0 treatment in Tab. 3). The acid load ensured by the 0.05 mol HNO_3 l^{-1} treatment (D2-Ac1 treatment in Tab. 3, marked with asterisk) was necessary to compensate for this pH elevating effect of the high dose PR treatment.

Compared to the deionized water treatment, application of acid load on the PR-enriched soil considerably increased the release of cation forming metals to the soil solution (Fig. 1). As expected, concentration of Mo was below the detection limit in the acidified samples. The immobilizing effect of PR, however, generally decreased metal concentrations in the soil solution of the acid treated soil. Extreme strong acid treatment (Fig. 1) was necessary to compensate for this effect. Ba, Co, Cu and Mn concentrations practically did not change with the increasing PR doses. On the other hand, increase of Cd, Sr and Zn concentrations means that the higher amount of contaminants carried into the soil with the elevation of PR doses prevailed the pH increasing and/or solubility decreasing effect of the basic PR. In contrast, in agreement with literature data [Basta, McGowen 2004], the immobilizing effect of PR in case of Pb dominated even under the extreme acid treatment and its concentration decreased with increasing PR dose.



[a] for pH at D1, D2 and Ac0–Ac4 see Tab. 3;
% = 100 c_s / (c_{soil} + c_{PR}), where c_s and c_{soil}: metal concentrations in the soil solution and in the soil, respectively, (µg kg^{-1} soil), c_{PR}: metal amount carried into the soil with PR (µg kg^{-1} PR)

Figure 2. Relative amounts of metals (%) entering the soil solution at increasing PR doses (D1, D2)[a] and acid loads (Ac0–Ac4)[a]

To characterize the release of the metals to the soil solution due to the various PR and acid treatments, their concentration in the soil solution (c_s) was expressed as percentage of their total amount in the soil and in the PR sample (Fig. 2). c_s was related to mass unit of the air dried soil: µg kg^{-1} = (µg l^{-1} × gravimetric water content of the soil) 100^{-1}.

The mobilized (relative) amounts of the metals showed similar tendencies as the absolute concentrations. Release of Cd (expressed as percentage of the total amount) was of the highest degree with increasing acid loads (Fig. 2). In case of the extreme high acid load (the 1.5 mol HNO_3 l^{-1} treatment, Ac4) the immobilizing effect of PR was observed only at Pb (52%, 42% and 24% at D0, D1 and D2, respectively, not shown in Figure 2), while from Cd, Zn (Fig. 2) and Sr, with the increase of metal contamination (D0<D1<D2 doses) higher amounts entered the soil solution than at the smaller dose.

CONCLUSIONS

1. Although PRs, similarly to conventional P fertilizers contain potentially toxic elements and their application as P source on acidic soils may involve the hazard of carrying them into the soil, the present experiment did not make it likely that they would present a direct environmental threat.

2. At a one-time, high dose PR application, release of trace metals to the soil solution became even lower as compared to the control treatment due to the simultaneous immobilizing effect of PR. Only extreme strong acid treatment was able to mobilize considerably the metals present in the soil + PR system.

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