EFFECT OF ACIDIFICATION AND PRELIMINARY Zn LOAD ON Zn SORPTION OF SOIL

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Abstract: The aim of the experiment was to determine how earlier Zn pollution or the acidification of the soil influenced Zn adsorption and desorption of adsorbed Zn. Previous Zn pollution levels were 0, 500 and 2500 mg·kg^{-1} Zn, while the shaking solutions used for adsorption analysis had concentrations of 0, 25, 50, 100, 250 and 500 mg·dm^{-3}. Desorption analysis was performed using the hot water percolation (HWP) method, resulting in ten 100 cm^3 fractions. The pH value was measured both for adsorption and desorption. Langmuir isotherms were fitted to the adsorption data and the maximum adsorbable Zn quantity and the value of the equilibrium constant were determined. As a modified Langmuir isotherm was applied, the quantity of Zn bound on the surface prior to adsorption analysis was also determined. Sorption properties of soil were changed by both reduction of soil pH and partial saturation of Zn binding sites. The change in pH (pH6-pH4) had the greatest influence on the soil buffer capacity and on the equilibrium constant of this process, while previous Zn pollution also reduced the adsorption capacity. Zn loads in excess of the sorption capacity of the soil resulted in a significant decrease in soil pH. A considerable part of the adsorbed zinc is bound to the soil in readily mobilisable form. More the pH of the soil differs from the original value the more pronounced this phenomenon becomes.

Keywords: Zn retention, pH, HWP (Hot water percolation)

1. INTRODUCTION

Zinc is a ubiquitous contaminant. The disposal of municipal waste, irrigation with industrial effluents, agricultural use of sewage sludge, and residues from metalliferous mining and smelting industry have contaminated large areas of cultivated land with Zn. Zinc is phytotoxic and may reduce crop yields. It may also represent a potential hazard to the food chain (Luo et al., 2000).

Various mechanisms are responsible for the adsorption and retention of heavy metals in polluted soils: specific adsorption, cation exchange, organic complexation and co-precipitation (Alloway, 1995). The affinity of different heavy metals for adsorption to different soil particles is a highly complex matter. They are adsorbed on the surface of colloidal particles in soils, principally humus, hydrous oxides of Fe, Mn and Al, alumino-silicate clays and some sparingly soluble salts such as calcium carbonate (Alloway, 2013). Although cation exchange, surface adsorption, chelating with organic materials and precipitation are important for the mobility of heavy metals, acid rainwater removes heavy metals which are weakly adsorbed on the soil (Gong & Donahoe, 1997; Stefanovits & Füleky 2000). Different soils show very diverse behaviour in terms of heavy metal sorption (Alumaa et al., 2002), because the concentration of each heavy metal is controlled by different parameters (soil pH, iron and aluminium oxide content, clay content, organic matter and cation exchange capacity) (Yuang & Lavkulich 1997; Hernandez et al., 2003; Takács & Füleky, 1996).

Metals are thus bound to a range of sites on humus, which contains a mixture of oxygen, nitrogen and sulphur donor atoms. The binding of heavy metals is probably dominated by the formation of two or even three bonds to a mixture of carboxyl and acidic hydroxyl groups. Spectroscopic techniques (Sarret et al., 2004) show that even relatively weakly bound metals such as zinc (Zn) are predominantly held as organic complexes in the soil. The removal of organic

matter (e.g. by peroxide treatment) causes a profound reduction in metal adsorption capacity (Palágyi et al., 2006). In the case of Cu, for example, up to 99% of Cu in the soil solution is commonly complexed to fulvic acid (Temminghoff et al., 1997). Both Mn and Fe hydrous oxides have a high adsorption affinity for heavy metals, which are bound as inner-sphere mono- and bidentate surface complexes. The sorption of positively charged metal cations is reduced by soil acidification due to the increased number of protons entering the system and the decrease in the negative charge of sorbent surfaces. In general, the dissociation of functional groups and the binding of metal ions seem to be influenced by pH (Benedetti et al., 1996). As the pH increased, more Cu than Zn was found to be adsorbed (Mesquita et al., 2002; Liao et al., 2007; Chaves et al., 2008). Generally, more highly acidified soil had lower sorption capacity for heavy metals (Brown et al., 1995; Temminghoff et al., 1997; Bang & Hesterberg, 2004).

It is generally recognised that metal ions added to soils in solution will rapidly attain an apparent equilibrium. However, most metals and metalloids exhibit further (slower) sorption over an extended period (months), in which metal ions are transferred from a 'labile' to a 'non-labile' state (Fischer et al., 2007; Tye et al., 2003; Wendling et al., 2009). This is generally referred to as 'the slow reaction', 'ageing' or 'fixation' (Wendling et al., 2009) and may be partly or wholly responsible for the phenomenon of 'desorption hysteresis' commonly observed for metal ions adsorbed from solution onto soil minerals such as calcite, zeolites and goethite (Barrow et al., 1989).

However, it is important to note that 'fixation' is not always a time-dependent process and may also be caused by very rapid reactions such as surface precipitation or possibly strong inner-sphere adsorption. Although quite extensive research has been conducted on the sorption and desorption phenomena (Markiewicz-Partkowska et al., 2005; Martinez & Motto, 2000; Zhao & Selim, 2010), no exact knowledge is available on the effects of heavy metal pollution and acidification on the heavy metal sorption of soil.

The present study was therefore conducted to investigate the effects of acidification and initial zinc load on zinc sorption in the soil.

2. MATERIALS AND METHODS

Samples taken from the upper 20 cm layer of a cultivated soil in Putnok were dried and prepared for analysis using standard laboratory methods. Before analysis the soil was passed through a 2 mm pore-size sieve.

Prior to the sorption experiments 50 g soil samples were placed in plastic sample holders and the pH was either maintained at the original ~6 value or adjusted to ~pH 4 or ~pH 5 by the addition of 1M HCl. A solution of $ZnSO_4$ was then added to represent Zn loads of 500 mg Zn/kg and 2500 mg Zn/kg. The moisture content of the samples was adjusted to 60% of field capacity by adding distilled water, after which the samples were incubated at 20±1°C for two weeks.

At the end of the incubation period the samples were dried, passed through a 2 mm sieve and used for the analysis of Zn sorption. Adsorption and desorption analyses were performed to investigate the sorption properties of the soil. The parameters of the untreated and treated soils are presented in Tables 1 and 2.

Adsorption experiment: Samples weighing 2 g were taken from the 2 mm particle size soil prepared for laboratory analysis and placed in centrifuge tubes to which 20 cm^3 Zn solution was added in a rising series of concentrations (0, 25, 50, 100, 250 and 500 mg·dm^{-3}). The Zn solution was prepared using $ZnSO_4·7H_2O$. After sealing the tubes, they were shaken in a circular shaker at 20±1°C for 17 hours, after which they were centrifuged at 5000 rpm for 3 min and then filtered (0.45 µm). The quantity of Zn remaining in the solution phase was determined from the equilibrium solution using a Perkin-Elmer 303 atomic absorption spectrophotometer.

Table 1. Parameters of the untreated soil analysed in the experiment

Soil type	K_A	Salt content %	pH (H₂O)	Humus %	CEC cmol·kg⁻¹	Exch. Ca cmol·kg⁻¹	Sand %	Silt %	Clay %	AL-P₂O₅ mg·kg⁻¹
Luvisol	38	0.03	6.03	2.0	27.33	12.5	11.6	57.1	31.3	75

Table 2. Codes of samples tested in the incubation experiment and the soil pH recorded at the end of the incubation period

Code	pH4/ 0Zn	pH4/ 500Zn	pH4/ 2500Zn	pH5/ 0Zn	pH5/ 500Zn	pH5/ 2500Zn	pH6/ 0Zn*	pH6/ 500Zn	pH6/ 2500Zn
pH₍H2O₎	4.20	4.10	3.96	4.83	4.67	4.38	6.03	5.40	4.94
Zn load mg·kg⁻¹	0	500	2500	0	500	2500	0	500	2500

*Untreated soil

The amount of Zn fixed on the soil was calculated as the difference between the Zn concentrations of the initial solution and the equilibrium solution. During adsorption analysis the pH of both the initial and the equilibrium solution was measured with a Radelkis OP-211/2 pH meter. All treatments and analyses were performed in three replications and the results were statistically analysed.

The Zn concentration of the equilibrium solution (mg·dm^{-3}) was plotted as a function of the bound Zn quantity (mg·kg^{-1}) and a Langmuir adsorption isotherm was fitted to the points.

$$q = \frac{A_L \cdot k_L \cdot c}{1 + k \cdot c} + m$$

q= amount of Zn adsorbed by the soil (mg kg^{-1})
A_L= maximum amount of Zn that can be adsorbed by the soil (mg kg^{-1})
k_L= Langmuir equilibrium constant of adsorption (dm^3 kg^{-1})
c= Zn concentration of the equilibrium solution (mg dm^{-3})
m = amount of Zn adsorbed before the Zn treatment (mg kg^{-1}).

The soil's Zn buffering capacity was obtained as the derivative calculated at the equilibrium concentrations (c=0, 0.1, 1, 10, 100) of the isotherm functions.

Desorption experiment (Hot Water Percolation – HWP method): During the desorption analysis, hot water (100±5°C) was percolated through 30 g soil samples according to the HWP method (Füleky & Czinkota, 1993) and 10 fractions (10x100 cm^3) were collected. The Zn concentration of the fractions was determined by atomic absorption spectrophotometry. As the time elapsing during the experiment was recorded, it was possible to fit a first-order kinetic curve to the experimental points.

$$y = Ae^{-kt}$$

y= amount of Zn desorbed (mg kg^{-1})
A= maximum amount of Zn that can be extracted (mg kg^{-1})
k = rate constant (s^{-1})
t = time (s)

3. RESULTS AND DISCUSSION

3.1. Adsorption

Adsorption analysis was performed on soil samples with both 500 and 2500 mg·kg^{-1} initial Zn pollution rates, but the isotherm curves only gave evaluable results for the 500 mg·kg^{-1} rate. Soil samples previously polluted with 2500 mg·kg^{-1} Zn were examined in detail using the HWP method, and in some cases the results of adsorption analysis were used to interpret the hot water desorption processes. The result of the adsorption experiments can be seen in Figure 1. The parameters of the Langmuir isotherms fitted to the data are shown in Table 3.

The isotherms of samples without Zn treatment came to equilibrium at similar saturation value, the only difference being in the initial steepness of the curves. The Langmuir adsorption isotherms plotted for soils with preliminary treatment with 500 mg·kg^{-1} Zn were quite distinct from each other regarding both the saturation value and the shape of the curve. The control soil (pH6 0Zn), with no initial pH adjustment and Zn treatment applied, had the greatest adsorption ability (Table 3).

The values obtained for the A_L parameter of the Langmuir adsorption isotherms (the maximum quantity of Zn that can be bound) demonstrated that there was no essential difference between the maximum adsorbable Zn quantities of soils given no preliminary Zn treatment (pH6/0Zn, pH5/0Zn, pH4/0Zn).
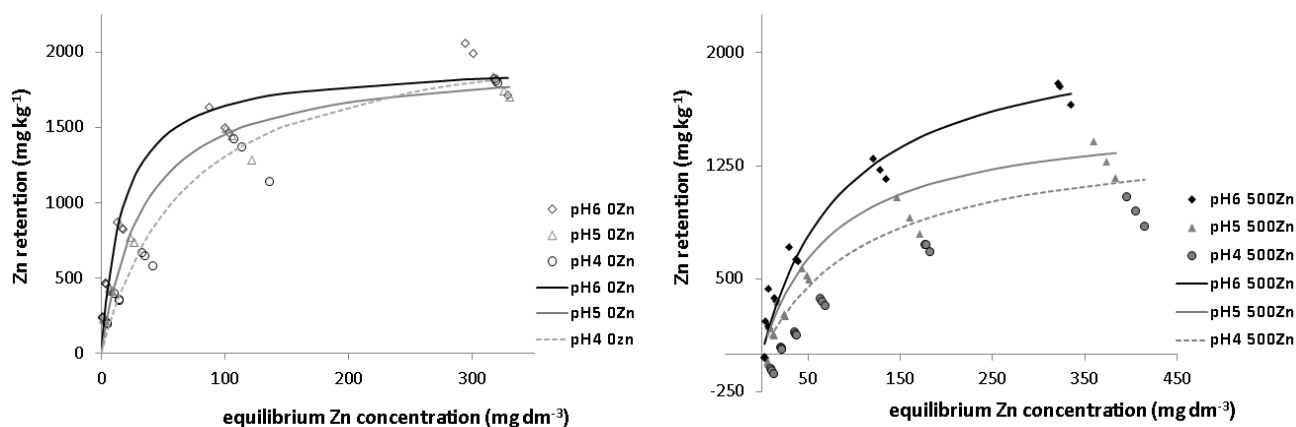

Figure 1. Effect of preliminary Zn treatment and pH on Zn adsorption (Langmuir adsorption isotherms)

Table 3. Parameters of the Langmuir isotherms applied to describe adsorption (with standard error of q_{max}, A_L and k_L ±95% confidence interval and goodness of fit R^2)

treatments	q_{max}		Langmuir isotherm				
			A_L		k_L	m	R^2
	$mg \cdot kg^{-1}$	SE	$mg \cdot kg^{-1}$	$mmol \cdot kg^{-1}$	$dm^3 \cdot kg^{-1}$	$mg \cdot kg^{-1}$	
pH4 0Zn	1806	103	2208±58	33.8	0.0145±0.001	0	0.9856
pH4 500Zn	947	95	1478±69	22.6	0.0087±0.002	-224	0.9944
pH5 0Zn	1758	70	1951±64	29.8	0.0292±0.002	0	0.9925
pH5 500Zn	1214	83	1600±100	24.5	0.0131±0.002	-166	0.9866
pH6 0Zn	1920	42	1924±80	29.4	0.0584±0.011	0	0.9771
pH6 500Zn	1764	50	2193±160	33.5	0.0111±0.003	0	0.9879

It could also be seen that, except for the soil sample with the original pH (~pH6), the saturation values of the isotherm curves for Zn-treated samples (pH5/500Zn, pH4/500Zn) were lower than the untreated soils with the same pH (Degryse et al., 2009). It was observed that if the quantity of Zn applied in the preliminary treatment (500 $mg \cdot kg^{-1}$Zn) was added to the adsorption maximum (A_L) of polluted soils with pH 4 and pH 5, the value obtained was close to the adsorption maximum of the untreated soil. By contrast, when the original pH of the soil was maintained (pH 6), it was able to bind almost as much Zn in addition to the preliminary load as was bound by the untreated soil. This suggests that during the two-week incubation period the 500 $mg \cdot kg^{-1}$ Zn diffused into the internal pores of the solid structure, leaving the surface Zn-binding sites free.

It can be seen from the equilibrium constants (k_L) of the Langmuir adsorption isotherms that the preliminary Zn treatment reduced the solid phase Zn affinity to a greater extent than a decrease in soil pH (pH6/0Zn). This tendency became more pronounced the more the pH diverged from that of the original soil. In other words, the *"k"* value of the pH5/0Zn samples was approximately the same after a change in soil pH (pH4/0Zn) as in the case of previous treatment with 500 $mg \cdot kg^{-1}$ Zn (pH5/500Zn).

The *m* parameter of the Langmuir isotherms provides a useful quantitative approach for calculating the readily mobilisable Zn quantity originally present on the soil. In samples given preliminary Zn treatment but no Zn in the shaking solution a proportion of the added Zn could be easily desorbed and appeared in the equilibrium solution during the adsorption experiment. Therefore, the isotherm did not start from the origin, but intersected the y axis at a certain value, providing a good approximation for estimating the quantity of easily mobilised Zn adsorbed on the original soil (Tolner & Füleky, 1995).

When the Zn species taking part in the adsorption process were investigated using MINTEQ software, it was found that Zn^{2+} ions were primarily involved in this process, as they were present at a ratio of almost 100% (96-98%) in the case of low equilibrium concentrations, while at higher equilibrium concentrations the ratio of Zn^{2+} ions was still over 80% (81.5–82.6%). Among the other Zn species, only the quantity and ratio of $ZnSO_4(aq)$ was considerable, being 1–2% at low concentrations and 16-17% in the case of higher concentrations (Table 4).

The adsorption isotherms could be clearly distinguished based on their shape. The steeper the curve, the higher the pH. Numerically this was proved most clearly by the buffering capacity, i.e. the derivative calculated for various points (c= equilibrium concentration $mg \cdot dm^{-3}$) on the isotherm curves (Table 5).

Table 4. Distribution of Zn species (%) in the shaking solution (0, 25 and 500 $mg \cdot dm^{-3}$ Zn) and the different treatments in the equilibrium solution concentrations of (%) (MINTEQ).

Initial concentration ($mg \cdot dm^{-3}$Zn)	Shaking solution		pH4 0Zn		pH4 500Zn		pH5 0Zn		pH5 500Zn		pH6 0Zn		pH6 500Zn	
	Zn^{2+} (%)	$ZnSO_4(aq)$ (%)	Zn^{2+} (%)	$ZnSO_4(aq)$ (%)	Zn^{2+} (%)	$ZnSO_4(aq)$ (%)	Zn^{2+} (%)	$ZnSO_4(aq)$ (%)	Zn^{2+} (%)	$ZnSO_4(aq)$ (%)	Zn^{2+} (%)	$ZnSO_4(aq)$ (%)	Zn^{2+} (%)	$ZnSO_4(aq)$ (%)
0	-	-	-	-	97	2,5	-	-	97	3	-	-	97	3
25	95	5	98	1,5	96	4	98	1.5	96	4	98	1.4	96	4
500	72	27	83	17	82	17	83	17	81	18	83	17	82	18

Table 5. Zn buffering capacity of the soils at different equilibrium solution concentrations

Treatment mg·kg⁻¹		Buffering capacity (dm³ ·kg⁻¹) at different c* values			
		0.1	1	10	100
pH 4	0 Zn	32	32	13	0.22
pH 5		57	55	15	0.20
pH 6		112	106	17	0.19
pH 4	500 Zn	13	13	6.8	0.15
pH 5		21	21	9.1	0.16
pH 6		24	24	12	0.22

*c= equilibrium concentration (mg·dm⁻³)

Both a drop in pH and the application of Zn treatment could be seen to reduce the Zn buffering capacity of the soil. This was particularly true of the derivative calculated for $c=1$, but could also be observed for the other buffering capacity values, providing further confirmation of the fact that preliminary Zn treatment caused a much greater reduction in soil buffering capacity than lower pH. The soil samples reached their saturation level by $c=100$, where the buffering capacity had a similar, very low value for all the samples.

3.2. Desorption

The kinetic curves of the hot water percolation experiment are shown in Figure 2, while the parameters of the first-order kinetic functions fitted to the data are presented in Table 6.

At both Zn levels (500 and 2500 mg·kg⁻¹ load) there was a slight increase in the quantity of Zn extractable from the soil with hot water as the pH dropped.

A similar picture of Zn adsorption on the soil was presented by the desorption analysis (Table 6). In the case of soils unpolluted with Zn there was only a slight difference in the level of Zn desorption from soils with different pH values (∼4 mg·kg⁻¹). In this case too, however, soils with lower pH lost their bound Zn more easily and rapidly than the higher pH soil (pH6) (Güngör & Bekbolet, 2010). This was demonstrated by the values of the rate constant.
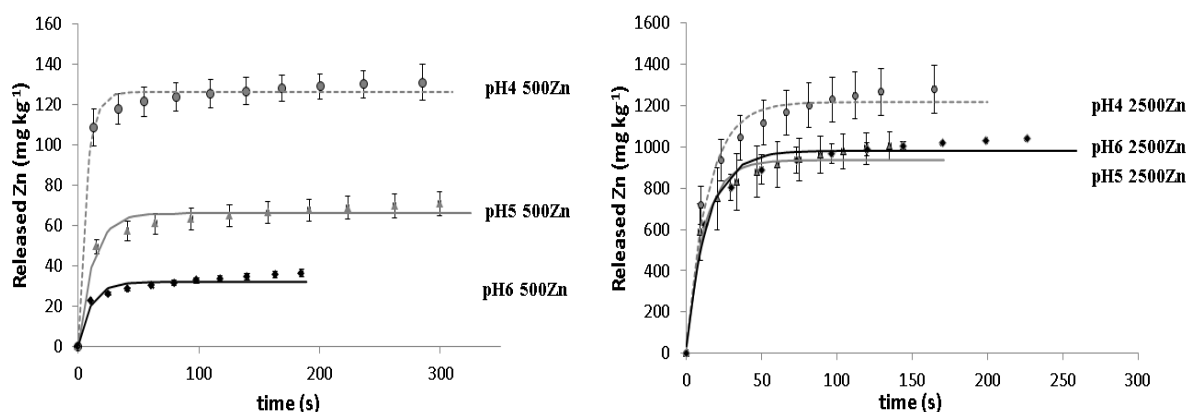

Figure 2. Effect of pH and preliminary Zn treatment on the desorption kinetics of Zn

Table 6. Parameters of the first-order kinetic equations used in the description of the HWP desorption (A and k ±95% confidence interval and goodness of fit R^2)

Code	pH4/ 0Zn	pH4/ 500Zn	pH4/ 2500Zn	pH5/ 0Zn	pH5/ 500Zn	pH5/ 2500Zn	pH6/ 0Zn*	pH6/ 500Zn	pH6/ 2500Zn
A (mg·kg⁻¹)	4.2±0.2	126±21	1216±53	4.1±0.1	64±15	949±33	4.2±0.1	33±8	989±28
k (s⁻¹)	0.067 ±0.002	0.148 ±0.011	0.072 ±0.001	0.025 ±0.03	0.121 ±0.03	0.086 ±0.02	0.003 ±0.001	0.085 ±0.003	0.069 ±0.001
R²	0.8764	0.9907	0.9759	0.8805	0.9720	0.9749	0.9947	0.9485	0.9789

*untreated soil

After previous Zn pollution the quantity of Zn desorbed increased significantly, being approx. 10 times as high at the 500 mg·kg⁻¹ pollution level and 100 times as high for 2500 mg·kg⁻¹. A considerable difference between soils with different pH values was again detected, with substantially greater quantities of Zn being desorbed from the pH4 soil than from the pH5 soil, and the smallest quantities from the pH6 soil. The effect of pH in the case of previous Zn pollution was also reflected in the desorption rate, as the bound Zn ions entered solution much more quickly on more acidic soils.

The data showed that the 2500 mg·kg⁻¹Zn treatment was so severe that the soil was unable to retain such a large quantity of Zn even at the original pH value. The kinetic curves describing percolation at the different pH values were close to each other. Here too the greatest quantity of mobilisable Zn was observed at pH4 (1216 mg·kg⁻¹), while the pH5 and pH6 treatments differed only as regards the time parameter. It took longer to extract 989 mg·kg⁻¹ from the control (pH6) soil than to extract a similar quantity (949 mg·kg⁻¹) from the pH 5 soil. This could be attributed to the fact that the more acidic reaction caused a slight deterioration in the colloidal structure of the soil, making it easier for the hot water to percolate through the soil.

It is clear from Figure 2 and Table 7 that while the soil was capable of retaining the 500 mg·kg⁻¹ Zn load, as this quantity was well below the adsorption capacity, a considerable proportion of the 2500 mg·kg⁻¹ Zn load could be extracted with hot water. Although some of the 500 mg·kg⁻¹ Zn load could also be extracted with hot water, the majority of this was removed in the first fraction at all three pH levels. A quarter of the initial load remained in the solid phase even at the lowest pH (pH4/500Zn). Less Zn could be extracted with hot water at the other pH values: a seventh of the 500 mg·kg⁻¹ Zn load at pH5 (pH5/500Zn) and less than a tenth at pH6 (pH6/500Zn).

In the case of the 2500 mg·kg⁻¹Zn load the quantity of Zn removed in the first fraction was approximately equal to the difference between the load and the adsorption maximum at the given pH (*A*). At this pollution level, it could also be observed that the Zn quantity extractable with all 10 hot water fractions was almost double that removed in the first fraction. The amount of zinc retained by the soil was found to be less than the maximum adsorption capacity (A_L), indicating that the quantity of zinc cations that could be mobilised by hot water was considerable.

Table 7. Zn quantities removed by hot water percolation (HWP), and a comparison of maximum adsorption capacity in the different treatments

Treatment		Adsorbed Zn/ treatment*		HWP I^st fraction		HWP Σ10 fractions		Zn remaining in the soil (calculated)	
		mg·kg⁻¹	mmol·kg⁻¹	mg·kg⁻¹	mmol·kg⁻¹	mg·kg⁻¹	mmol·kg⁻¹	mg·kg⁻¹	mmol·kg⁻¹
pH4	0Zn	1806±14	27.6	-	-	-	-	-	-
	500Zn	500*	7.6	111±8	1.7	133±5	2.0	367	5.6
	2500Zn	2500*	38.2	65±45	11.7	1318±97	20.2	1182	18.0
pH5	0Zn	1758±40	26.9	-	-	-	-	-	-
	500Zn	500*	7.6	49±3	0.7	68±3	1.0	432	6.6
	2500Zn	2500*	38.2	588±96	8.9	1006±49	15.4	1494	22.8
pH6	0Zn	1920±105	29.4	-	-	-	-	-	-
	500Zn	500*	7.6	23±1	0.4	36±1	0.6	464	7.1
	2500Zn	2500*	38.2	623±3	9.5	1040±7	15.9	1460	22.3

* preliminary load

Table 8. Quantity of zinc in solution phase after adsorption and hot water desorption at load levels of 500 and 2500 mg·kg⁻¹

Treatments		After adsorption		After HWP desorption	
		mg·dm⁻³	SE	mg·dm⁻³	SE
pH4	500 Zn	12.2	1.9	32.6	1.9
pH5		7.9	0.9	15.2	0.9
pH6		3.4	0.2	4.6	1.4
pH4	2500Zn	110.3	2.9	220.3	20.8
pH5		113.6	7.9	168.9	22.4
pH6		96.9	6.1	110.9	48.5

In all cases the Zn quantity extractable with hot water was greater than the quantity of zinc remaining in the equilibrium solution during adsorption (Table 8). This is understandable, as sorption processes are temperature-dependent. It can be stated, however, that at the original soil pH value of pH6 almost the same quantity of Zn entered the solution phase at $20\pm2°C$ (adsorption experiment, equilibrium solution) than at $100\pm2°C$ (HWP, 1st fraction) at both pollution levels (500, 2500 mg·kg⁻¹ Zn), proving that, without external interference, the soil is an extremely stable buffering agent. This ability of the soil is further diminished by preliminary Zn pollution than by a decrease in pH

3.3. Changes in pH during sorption processes

The pH of the shaking solutions used in the adsorption experiments and of the equilibrium solutions is shown in Figure 3 and that of the hot water percolation (HWP) fractions 1–10 in Figure 4.

The pH of the initial solution (shaking solution) fell steeply at first as a consequence of Zn hydrolysis, but when the hydrolysis process was suppressed and equilibrium was reached, the pH stabilised at a value of 5.5. By comparison, at low Zn

concentrations (25–250 mg·kg⁻¹Zn) the soils reduced the acidity of the solution phase as Zn hydrolysis declined, by binding the H⁺ ions that cause the drop in pH. In the higher Zn concentration range (250–500 mg·kg⁻¹Zn) the pH of the equilibrium solution was lower than that of the initial shaking solution, which could be attributed to the fact that a large quantity of Zn in the solution resulted in the desorption of an increasing number of H⁺ ions from the soil surface. Preliminary Zn treatment had little effect on the pH of the equilibrium solutions. Even the lowest equilibrium pH (pH 5.01), observed in the pH4 treatment, was found to be higher than the $pH_{(H2O)}$ value of the soil (pH 4.1). This could be attributed to the fact that the $Zn^{2+}/Zn(OH)_n$ system present in the solution phase buffered the pH of the suspension, thus suppressing Zn hydrolysis.

The pH changes observed in the case of hot water percolation also indicated that the negative effect of previous Zn treatment on the soil was more pronounced than that of changes induced in the soil pH in the pH 4–6 range. Even after percolating a large quantity of hot water through the soil it could be observed that a relatively low level of Zn pollution was able to cause soil acidification.
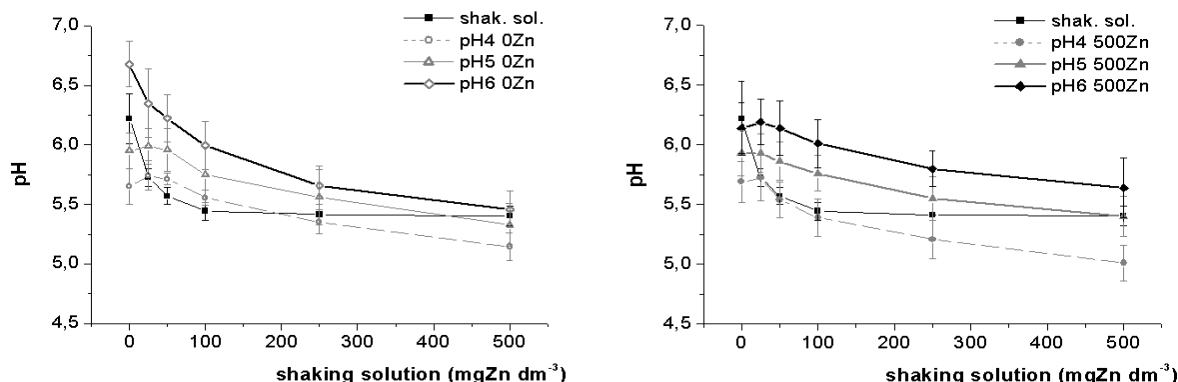

Figure 3. Changes in the pH of the initial (shaking) solution and the equilibrium solutions during the adsorption experiment (± standard errors). The extrapolation is for showing the tendency, however the intermediate values cannot be interpreted
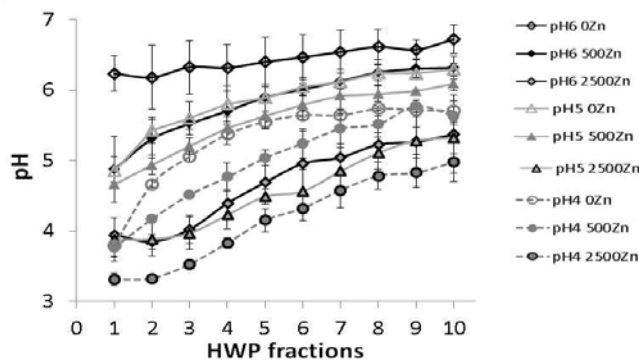

Figure 4. pH values in fractions 1-10 obtained after hot water percolation (HWP) in the desorption experiment (± standard errors). The extrapolation is for showing the tendency, however the intermediate values cannot be interpreted

This phenomenon was less obvious in the 500 mg·kg⁻¹Zn Zn treatment (pH difference of 0.5) than after the addition of 2500 mg·kg⁻¹Zn Zn, when the pH of the individual hot water extracts was 1–1.5 lower than that of parallel samples given no Zn treatment, even after percolation with 1000 cm³ hot water (Fig. 4).

4. CONCLUSIONS

The aim of the experiment was to determine how earlier Zn pollution or the acidification of the soil influenced the adsorption and desorption of Zn.

Langmuir adsorption isotherms give a good description of how Zn is bound on the soil. The Zn sorption properties of the soil were found to be influenced both by changes in pH (Silber et al., 2012; Girija et al., 2013) and by preliminary zinc treatment.

A change in pH (in the pH 4–6 range) did not influenced significantly the maximum quantity of Zn (approx. 2000 mg·kg⁻¹) that could be bound by the tested soil (from Putnok, Hungary), indicating that the soil was able to buffer this extent of acidification (Magdoff & Bartlett, 1984; Ngatunga et al., 2001). The artificial reduction of soil pH was only manifested in the soil buffering capacity, i.e. a smaller quantity of bound Zn was required in the lower concentration range to achieve the same Zn equilibrium concentration.

If the soil pH was not modified by the addition of acid, the soil was able to bind almost as much Zn, in addition to the previous load (500 mg·kg⁻¹Zn), as that bound by the control soil, indicating that Zn may diffuse into the internal pores of the soil particles during the incubation period, making the binding of further cations possible (Brümmer, 1986; Bruemmer et al., 1988; Alloway, 2013).

However, if acidification was combined with Zn pollution, the ability of the soil to bind further quantities of Zn was reduced by approximately the amount of Zn added. It appears that the negative effect of acidic pH (H⁺ ions) on the binding of Zn to adsorption surfaces was more pronounced on soils previously polluted with Zn.

A considerable quantity of Zn can be extracted from the soil by hot water percolation. This quantity may be as much as half the adsorption capacity.

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