

New Approach in Studying of Zinc Compounds in Soil

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Abstract: The simultaneously use the parameters of the sorption capacity of soils for metals and the composition of metals sorbed for the identification of metal compounds was offered. This approach allows the metal compounds to be classified in accordance with the binding strength to soil components. The results show a general tendency: the compounds of Zn formed during their sorption by the soil are less stable and, hence, more mobile than their natural compounds, which determines the ecological hazard of metal-contaminated soils.

Key words: Zn compounds • Chernozem • Contamination • Adsorption • Binding strength

INTRODUCTION

The effect of contaminated soils on the ecological status of an ecosystem directly depends on the composition of metal compounds [1, 2]. Mobile metal compounds in soil solid phases are in equilibrium with the liquid phases [3]. The equilibrium between metal compounds in a heterogeneous soil system is dynamic, which creates conditions for their transformation. The integrated study of metals sorption by soils and the formation of different compounds by the sorbed metals contributes to the understanding of metal compounds transformation mechanisms in the soils [4].

MATERIALS AND METHODS

Experiments were conducted with samples of ordinary chernozem, whose properties are follows: clay content of 286 g kg⁻¹ and a physical clay content of 471 g kg⁻¹, pH_(water) of 7.3, organic C content of 23 g kg⁻¹, CaCO₃ content of 1 g kg⁻¹, cation exchange capacity of 37.1 mmolc kg⁻¹ and exchangeable Ca, Mg and Na contents of 29.5, 5.5 and 0.1 mmolc kg⁻¹, respectively. Samples from the top layer (0-20 cm) were used in the experiment.

Experiments on metal sorption were carried out under static conditions [5]. Soil samples were triturated to <1 mm and treated with solutions of Zn acetates with the following concentrations (mmol/l): 0.05, 0.08, 0.1, 0.3, 0.5, 0.8 and 1.0 (at a soil: solution ratio of 1: 10).

The suspensions were shaken for 1 h and left to stand for 24 h. Then, the solutions were filtered and the concentrations of metals in the filtrates were determined by atomic absorption spectroscopy. The content of sorbed ions was calculated from the difference between the metal concentrations in the initial and equilibrium solutions. Experiments were performed in triplicate.

The capacity of soils to sorb metals is described by sorption isotherms. They show the amount of a metal sorbed by the soil (mg/kg, mmol/kg) as a function of its concentration in the solution (mg/l, mmol/l). The relationship between these parameters is described by different equations [6]. The empirical Langmuir equation is the most frequently used. It has the form:

$$X/m = S_{\max} kC/(1+kC),$$

where X/m is the amount of metal ions sorbed per unit mass of sorbent; C is the equilibrium concentration of metal in the contacting solution; S_{max} is the maximum adsorption of metal ions; and k is the equilibrium constant.

The methods of sequential and parallel fractionation of metal compounds are widely used separately, but they can form basis for their combined use [2]. It is advisable to use the Tessier scheme of sequential fractionation [7] in combination with the parallel extraction using individual reagents (Table 1).

Table 1: Sequential and parallel fractionation of metals

Metal compounds	Extractant	Soil: solution ratio	Extraction conditions
Sequential fractionation (Tessier <i>et al.</i> , 1979)			
Exchangeable	1 M MgCl ₂ , pH 7.0	1:8	Shaking at room temperature for 1 h
Bound to carbonates	1 M NaCH ₃ COO, pH 5.0 (with CH ₃ COOH)	1:8	Shaking at room temperature for 5 h
Bound to Fe, Al and Mn (hydr)oxides	0.04 M NH ₂ OH•HCl in 25% CH ₃ COOH	1:20	Heating at 96±3°C under periodical shaking for 8 h
Bound to organic matter	0.02 M HNO ₃ + 30% H ₂ O ₂ , pH 2.0 (with HNO ₃), then 3.2 M NH ₄ CH ₃ COO in 20% HNO ₃	1:20	Heating at 85±2°C under periodical shaking for 5 h
Residual fraction	HF+HClO ₄ , then conc. HNO ₃	1:25	Evaporation
Parallel extraction			
Exchangeable	NH ₄ Ac, pH 4.8	1:5	shaking for 1 min and settling for 18 h
Exchangeable + complex	1% EDTA in NH ₄ Ac, pH 4.8	1:5	shaking for 1 min and settling for 18 h
Exchangeable + specifically sorbed	1 N HCl	1:10	shaking for 1 h

RESULTS AND DISCUSSION

From the results of laboratory experiments Zn sorption isotherms were plotted (the concentration of metal in the equilibrium solution was used as the abscissa and the content of metal sorbed by the soil was used as the ordinate) (Fig. 1).

Four linear segments were found in each isotherm of Zn sorption by the soil. They corresponded to the following metal concentrations in the contacting solutions (mmol/l): 0.05, 0.5, 0.8 and 1.0. After the solutions were separated from the solid phases, 4 contaminated soil samples were obtained for Zn. In all samples, the contents of metals in 7 fractions were determined using the combined fractionation scheme: weakly bound compounds (exchangeable, complex, specifically sorbed by carbonates, specifically sorbed by Fe and Mn (hydr)oxides) and strongly bound to organic substances, Fe and Mn (hydr)oxides and silicates (Table 2).

Carbonates lost their predominance in the weak retention of metals under increasing metal load [8]. The tendencies revealed in the analysis of soils contaminated with metals under laboratory conditions confirmed the results obtained in the pot and field experiments.

The absolute content of all strongly and weakly bound metal compounds in the soil increased with increasing metal load [9]. Therefore, the content of metals retained by the soil in specific compounds as a function of metal concentrations in the contacting solution could be plotted for each of 7 separated metal fractions.

The curves plotted were satisfactorily described by the Langmuir equation for heterogeneous exchangers. Adsorption parameters were determined by the approximation of accumulation curves for each metal form (Table 3). The maximum adsorption value, S_{max} , corresponded to the largest amount of metal capable to bind to the surface due to the formation of the presumed

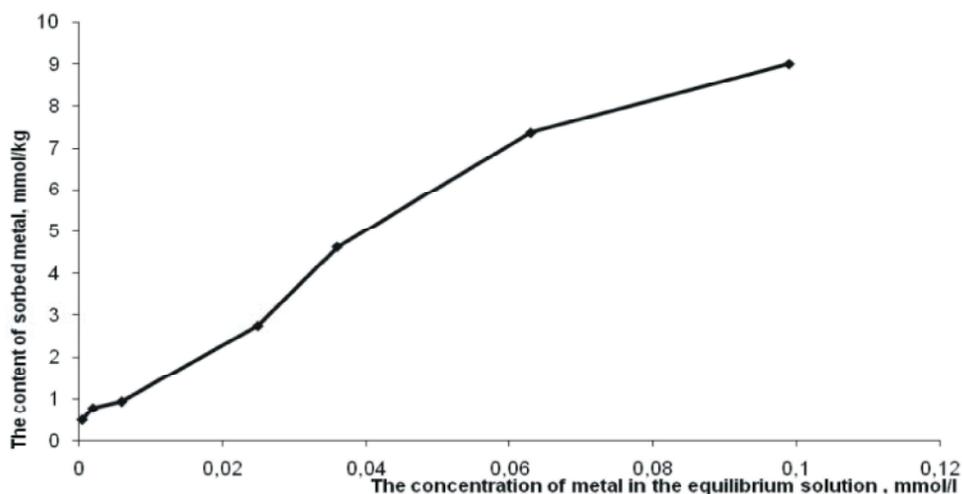


Fig. 1: Isotherms of Zn adsorption by ordinary chernozem

Table 2: The content of Zn adsorbed by chernozem and their distribution among of compounds, mM/kg

Dose of metal, mM/kg	Weakly bound compounds (WB)				Strongly bound compounds (SB)		
	Exchangeable	Complex	Specifically sorbed		With organic matter	With on Fe and Mn (hydr)oxides	With silicates
			On carbonates	On on Fe and Mn (hydr)oxides			
0,5	0,02	0,03	0,13	0,02	0,05	0,35	0,76
5	0,31	0,51	1,0	0,69	0,3	2,3	1,0
8	0,72	0,89	1,3	1,42	0,48	3,5	1,09
10	0,91	1,05	1,45	1,71	0,52	3,9	1,13

Table 3: Thermodynamic parameters of Zn compounds in the soil

Metal compounds	S_{max} mM/kg	k	R^2
Exchangeable	6,1±0,3/ 5,2±1,0	10,9±3,0/ 2,2±0,5	0,99/ 0,97
Complex	2,3±0,7	8,9±5,0	0,99
Specifically sorbed on carbonates	1,93±0,3	31,3±12,0	0,99
Specifically sorbed on on Fe and Mn (hydr)oxides	5,4±3,8	4,9±3,7	0,98
Strongly bound with on Fe and Mn (hydr)oxides	6,26±2,8	77,9±12,1	0,97
Strongly bound with organic matter	0,85±0,3	17,1±6,2	0,97
Silicates	1,1±0,04	4759±335,5	0,90

compound [10]. The affinity of metal for the adsorption center and the strength of the formed bond were estimated by the value of constant K.

The calculated parameters were characterized by a significant coefficient of determination (R^2). The potential capacity of soil for sorbing Zn ions in the exchangeable form was high. This form of metals was weakly retained by soil components and could rapidly transform into more strongly compounds [11-13]. Therefore, the actual content of exchangeable metal compounds in the soil was very low. This was also true for the metal compounds weakly retained by organic substances in the form of complexes. The lowest values of the maximum retaining capacity for Zn, were observed in silicate minerals; however, they fixed the metals most strongly.

According to the binding strength (K) to soil components, metal compounds formed the following series: bound to silicates >> bound to organic matter > bound to Fe–Mn (hydr)oxides > specifically sorbed on Fe–Mn (hydr)oxides > specifically sorbed on carbonates > complex > exchangeable. This series practically corresponds to the order of fraction separation in the proposed fractionation scheme.

CONCLUSIONS

The results show a general tendency: the compounds of heavy metals formed during their sorption by the soil are less stable and, hence, more mobile than their natural compounds, which determines the ecological hazard of metal-contaminated soils. The parameters of metal binding strength by different soil components are essential for ensuring the protection properties of an ecosystem.

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