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Effect of attendant anions on zinc adsorption and transformation in chernozem

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ABSTRACT

The effect of anions on the adsorption and mechanism of interaction of zinc cations with a solid soil phase was established. Acetic acid anions had the greatest influence on bond strength between metal and soil particle surfaces, while the effect of nitric acid anions was the lowest. The difference in amount of mobile forms of zinc extracted by the soil depends on the dose and form of the zinc. The influence of the attendant anions on the content of mobile metal forms in the soil decreases in the order: $PO_4^{2-} \approx Cl^- > NO_3^- > SO_4^{2-} > CH_3COO^- > O^-$.

1. Introduction

Heavy metals (HMs) are common pollutants and may pose a threat to the environment. Their mobility, ability to migrate, availability to plants and animals and their toxic effect depends on their formation in soils. These formations are related to the chemical compound composition or form in which they are deposited in the soil as a result of human activity (Guisti, 2011; Minkina et al., 2008, 2009a, 2012).

Two main groups exist which differ in solubility: soluble complexes form from the salts of mineral acids while less soluble complexes that are difficult to dissolve are represented mainly by oxides. Soluble HM complexes react immediately with soil components once deposited in the soil. By contrast, insoluble complexes must dissolve before they can react chemically and this may take six months to several decades (Zaplina, 1994).

The amount of HM adsorbed using different salts is dependent on soil properties (Cerqueira et al., 2011; Dube et al., 2001; Mouni et al., 2009; Wang and Harrell, 2005). The anion of the added salt affects zinc adsorption in the following order: $Cl^- > NO_3^- > H_2PO_4^-$ and $H_2PO_4^- > Cl^- > NO_3^-$ for calcareous soils and acid soils, respectively.

Chang Chien et al. (2008) have shown that high concentrations of chloride, sulfate and particularly dissolved organic carbon (as fulvic acid anions) affect the transformation of Cd^{2+} in soil and soil solutions. There is an increase in cadmium absorption by soil at low fulvic acid anion concentrations as well as the possibility of specific adsorption by ligand exchange with chloride and the precipitation of $CdSO_4$.

As shown by Zhang and Sparks (1996), Na-montmorillonite absorbs Cu^{2+} equally from 0.25 M chloride, perchlorate, sulfate and nitrate solutions in the pH range from 4.31 to 4.54.

Zinc is one of the most common widespread environmental pollutants and has been found to exist in the Rostov region (southern Russia). The transformation of zinc in soil still requires investigation. Most zinc is absorbed by highly dispersed clay minerals while a number of studies have shown that there is a correlation between zinc and iron and manganese oxide contents in soils (Manceau et al., 2000; Minkina et al., 2008, 2009b; Pinskii et al., 2010). Using synchrotron X-ray technology, we have proven experimentally the existence of insoluble metal phosphates (Manceau et al., 2002). The interaction of zinc with organic material is unclear. Often the content of organo-zinc compounds is not high in the humus of automorphic soils. However, zinc acetate $Zn(CH_3COO)_2$ and Zn-arginine may form in peat soil (Martinez et al., 2006).

The transformation mechanism of zinc in soil is unclear and requires investigation. The aim of this research is to establish the effect of different anions on zinc absorption and to investigate the transformation pathway of zinc in soil.

2. Materials and methods

2.1. Soil

The samples of clay loamy ordinary chernozem on loess-like loam (Haplic Chernozem, FAO) were prepared by hand digging collecting at depth of 0–20 cm in the Rostov region (southern Russia). Soil was homogenized, air dried, and passed through a 1 mm sieve.

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Soil properties were analyzed using Russian standard methods (Agrochemical methods of soil study, 1975). Soil organic carbon was measured using 0.4 N potassium bichromate (the Tyurin method modified by Simakov). Soil particle size distribution (silt and clay content) was determined by the pipette method after the pyrophosphate treatment. Cation exchange capacity (CEC) of the soil was determined using 1 M ammonium chloride (the Bobko–Askinazi method). The exchangeable potassium was determined by the Machigin (molybdenum blue) method. Adsorbed Na was analyzed by flame atomic adsorption spectrophotometry (FAAS). Soil pH was measured with a pH electrode using a 1:5 suspension of a soil to water ratio. Exchangeable calcium and magnesium were measured by titration at pH 12.5–13 and 10 respectively. Carbonates were measured by the Kudrin method using 0.005 NH_2SO_4 and then an excess of the acid was titrated with alkali.

The obtained results of soil sample are: a clay content of 286 g kg^{-1} and a physical clay content of 471 g kg^{-1}, pH of 7.3, organic C content of 23 g kg^{-1}, $CaCO_3$ content of 1 g kg^{-1}, CEC of 37.1 mM kg^{-1} and exchangeable Ca, Mg and Na contents of 29.5, 5.5 and 0.1 mM kg^{-1}, respectively.

The total concentration of heavy metals was analyzed by X-ray fluorescence spectrometer Spectroscan MAKS-GV (Spectron, Russia).

2.2. Adsorption experiment

The metal absorption was investigated using solutions of Zn^{2+} nitrate, Zn^{2+}acetate, Zn^{2+}chloride and Zn^{2+}sulfate. Solutions of zinc phosphates and zinc oxides were not used because of their low solubility. Zinc salts (1:10 soil to solution ratio) were added to the sieved soil (<1 mm). The initial concentrations of the Zn salt solutions taken for the studies were 0.05, 0.08, 0.1, 0.3, 0.5, 0.8, 1.0 mM L^{-1}. The selected concentration of solutions was chosen because it would be approximately equal to the existing level of heavy metal contamination of soil in Rostov region (southern Russia). Suspensions were shaken for 1 h, left to settle for a further 24 h and then filtered through paper (pore size 2–3 μm). The heavy metal concentration in the filtrate was determined by atomic absorption spectrophotometry (Scientific Buck 200 A). The quantity of adsorbed metal was calculated from the difference between its initial concentration and an equilibrium concentration. Sorption isotherms were constructed for each metal by plotting the sorbed metal content of the soil (mM per gram of dry soil) against the concentration of the metal in solution at equilibrium (mM L^{-1}).

Heavy metal adsorption is described by the Langmuir equation which is based on a model approximate approach:

$$C_{ads} = C_\infty K_l C/(1 + K_l C), \tag{1}$$

where C_{ads} is the content of adsorbed cations; C_∞ is the maximum adsorption of HMs, (mM 100 g^{-1} soil), K_l is the Langmuir affinity constant and C is the HM concentration in the equilibrium solution (mM L^{-1}).

This equation describes limited adsorption. When the adsorbent takes up low concentrations of HM cations, the adsorption is proportional to the HM concentration in the equilibrium solution (Henry region). For this range of concentrations, the isotherm is described by a straight line ($C_{ads} = C_\infty K_f C$), known as the “Henry isotherm”. The isotherm plateaus gradually (region of maximum filling of the surface) when adsorption is complete.

The Freundlich equation is purely empirical:

$$q = K_f C^{1/n}, \tag{2}$$

where *q* is the amount of substance adsorbed onto the solid phase divided by the mass of the adsorbent; C is the equilibrium concentration of the substance in the solution; K_f is the Freundlich adsorption coefficient which characterizes the interaction energy of the absorbed cations and the solid phase ((mM kg^{-1}) / (mM L^{-1})1/*n*) and 1/n is the empirical exponent. If n = 1, the Freundlich equation reverts to the Henry equation and the dimension of the constant is L kg^{-1}.

The Freundlich equation better describes adsorption on slightly crystallized or amorphous adsorbents with a non discrete distribution of sites which differ in their activity of surface adsorption (Sparks, 2003).

2.3. Pot experiment

Investigation of Zn transformation process was conducted in the pot experiment. The soil was contaminated with salts of Zn^{2+} oxide, Zn^{2+} acetate, Zn^{2+} sulfate, Zn^{2+} chloride, Zn^{2+} nitrate and Zn^{2+} phosphate with different doses (300, 2000 ppm) introduced separately. Artificially polluted soil (1 kg) was placed in plastic containers. To ensure drainage, a thick layer (1 cm) of haydite was placed on the bottom of the container. Soil was maintained at 60% water holding capacity during the experiment by regular application of distilled water to the pots. The experiment was performed in triplicate. The experiment was carried out during May–July 2010. A subsample was removed each second year and used for analysis. Results of analysis of polluted soil were compared with the control sample (unpolluted soil).

2.4. Extraction

Parallel extractions of soil samples following the protocol of Minkina et al. (2008) were conducted. The main purpose of parallel extraction was to investigate the mobile forms of Zn through several different steps: (1) in soil solution and in exchangeable form (extraction for 18 h, using a 1: 10 suspension of a soil to 1 N NH_4OAc, pH 4.8, ratio), (2) in organically bound forms and represented complex compounds of metals together with their exchangeable forms (extraction for 18 h, using a 1:10 suspension of a soil to 1 N NH_4OAc with 1% Ethylene diamine tetra-acetic acid (EDTA, disodium salt), pH 4.8, ratio). The concentrations of the metals in the complex compounds were calculated by the difference between the concentrations in extracts 2 and 1. (3) Bound to amorphous compounds and carbonates (adjusting by shaking for 1 h, using a 1:10 suspension of a soil to 1 M HCl ratio). The amount of specifically absorbed metal compounds was calculated by the difference between the metal concentrations in HCl and NH_4OAc extracts. The extract from each step were filtered through paper (pore size 2–3 μm) and analyzed by atomic absorption spectrophotometry (Scientific Buck 200 A).

2.5. Statistical analyses

The statistical significance of the differences between the amounts of Zn mobile form in various variants was examined using Student's t-tests and least significant difference (LSD) tests. All statistical calculations were performed using Microsoft Excel 2010. The approximation of the experimental isotherms by the Langmuir equation was performed using the SigmaPlot 2001 statistics package at a confidence probability of 0.95.

3. Results and discussions

The adsorption isotherms of metal cations from solutions of hydrochloric, nitric, acetic and sulfuric acid salts are shown in Fig. 1. The isotherms differ in shape from almost linear to convex. The form of the isotherms is determined by the nature of interaction of the adsorbate with the adsorbent. For instance, a convex isotherm shape indicates a more vigorous interaction between adsorbate and adsorbent. One equation is insufficient for describing the isotherms and it is necessary to use a combination of the Henry, Langmuir and Freundlich equations.

The adsorption isotherms for zinc chloride solutions are best described by the Henry equation. The absorption of zinc by soil from a solution of sulfate salts is best described by the Freundlich equation. The