



Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Ions association in soil solution as the cause of lead mobility and availability after application of phosphogypsum to chernozem

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ARTICLE INFO

Article history:

Received 4 July 2016

Revised 19 August 2016

Accepted 29 August 2016

Available online xxx

Keywords:

Heavy metals

Soil solution

Equilibrium

Ion association

Phosphogypsum

Utilization

ABSTRACT

The thermodynamics has been studied of Pb forms in soil solution for the case of calcareous ordinary chernozem of the Southern Russia, northern zone of the Krasnodar krai for conditions of phosphogypsum utilization into the soil layer of 20–40 cm at doses of 0, 10, 20, and 40 t ha⁻¹. The application of phosphogypsum increased the contents of total Pb by 4.2; the content of water-soluble forms – by 17.7. As a result of ion association in soil solution are presented electrically neutral ion pairs CaCO₃⁰; CaSO₄⁰, MgCO₃⁰, MgSO₄⁰, and charged ion pairs CaHCO₃⁺, MgHCO₃⁺, NaCO₃⁻, NaSO₄⁻, CaOH⁺, MgOH⁺. The contents of soluble Pb²⁺ forms in water extracts were calculated by mathematical chemical-thermodynamic model of ion pairs association in soil solution using algorithm and computer program ION-2. The coefficient of heavy metal ion association *k*_{as} in soil solution is proposed for calculation of the heavy metal equilibrium concentration in soil solution.

The model shows that calculated association coefficient of Pb²⁺ is up to 25.0, Pb²⁺ is presented mostly in the form of PbOH⁺ and Pb(OH)₂⁰. The quantity of PbCO₃⁰ + Pb(CO₃)₂⁻ and PbHCO₃⁺ is lower than content of hydroxide-complexes by 10–15 times. At the phosphogypsum dose of 40 t ha⁻¹, the association coefficient of Pb²⁺ ion decreases by 2.0 times comparing to initial soil, and its activity increases by 60.0%. The molar fraction of hydroxo complexes decrease for 4.0, carbonate for 5.0, and sulfate associates – increase for 4.5%. The dangerous increase of activity of Pb²⁺ ion in soil solution after phosphogypsum apply up to 90.0% of its concentration is revealed.

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1. Introduction

The increasing content of heavy metals (HMs) of anthropogenic origin in biosphere is a cause to search the proper limitation, and methods to recycle the wastes containing HMs as soil amendment properly: reduce their uncontrolled transfer, passivate these chemical elements into soil, limit an excessive influence on carbon stock, trophic chains, use the HMs correctly as the microelements for plant nutrition (Adriano, 2001; Kalinitchenko, 2016; Minkina et al., 2012a, 2014; Sparks, 2003; Xiong et al., 2014). It is one of the ways to improve the living systems algorithms (Tsvetkov, 2016), which will help to ease and overcome the conflict of biosphere and technology (Glazko and Galzko, 2015), provide the soil health (Semenov and Sokolov, 2016).

Pb is a soil pollutant of the first hazard class, especially in dissolved form. The total content of Pb in Russian soils is not too high, not >20 mg kg⁻¹ soil DW. All over the world the content of Pb in soil is approximately the same, and much variable. Limiting concentration of Pb according to different regulations depends on soil and landscape use, the value is from 10 to 2000 mg kg⁻¹ and higher (Land contamination, 2015; McGrath and Loveland, 1992; Okolelova et al., 2013). The heavy metals are dangerous for landscape as a result of water mass-transfer on the earth's surface, through the soil, and vadose zone (Sposito, 2013; Motuzova et al., 2014; Pichura and Breus, 2015; Lisetskii et al., 2015). There are new data on the HMs selective chemical extraction from soil and lithosphere (Favas et al., 2011a, 2011b) – a cause for developing the ways of HMs passivation. The origin and possibilities to form the biological, geochemical and other barriers for HM are of great importance.

Good practice to reduce soil HM transfer to plants is liming (Land contamination, 2015; McGrath and Loveland, 1992), remineralization

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(Tskhovrebov, 2012), composts (Belyuchenko and Antonenko, 2015). The Pb input into plant depends on soil carbonates content and pH value. It is linked to the Pb^{2+} free ions thermodynamic activity, the degree of Pb^{2+} ion bound into associates with other ions. As it was shown for the soil solution of alkaline calcareous solonchic soil, the molar fraction of active concentration (activity) of Pb^{2+} ion does not exceed 0.13%, in the water extract activity of Pb^{2+} is only 0.24% (Endovitsky et al., 2009a, 2014).

Phosphogypsum is a byproduct of water acid phosphorus fertilizer technology, its amount is 150–280 t year⁻¹. Phosphogypsum contains >60 chemical elements including Pb (Goswami and Nand, 2015; Pérez-López et al., 2016), and is one of the leading pollutants of biosphere. The common practice for phosphogypsum utilization is the open stack. It causes different adverse, direct and delayed, pollution effects, is hazardous in terms of further ingress of pollutants into the landscape soils and waters. The phosphogypsum stacks are the source of pollutants aeolian transfer, unfavorably affect vast adjacent areas, abruptly deteriorate the area's image, habitation and recreation.

In the Russian Federation, the phosphogypsum is produced from apatite, from Kovdor deposit. Its quality in respect of environment is much higher than of phosphogypsum from ores from the Morocco, Florida, as well as many others (Lapin and Lyagushkin, 2014; Soil Liquid Phase Composition, 2001). The radioactivity and HMs content of Kovdor apatite is smallest over the world deposits, it is safe for the soil (Gázquez et al., 2014). The utilization of phosphogypsum is possible in chernozem – the soil which has no morphological and physicochemical signs for chemical reclamation. Potential accumulation of HMs in soil after application of phosphogypsum was noted by some authors, but no significant changes were observed compared to natural contents of HMs (Mays and Mortvedt, 1984; Nayak et al., 2011; Minkin et al., 1992; Endovitsky et al., 2009a; Sheudzhen et al., 2015). The degree of HMs passivation into the soil is conjugated to ions activity according ion association in soil solution (Endovitsky et al., 2014).

The aim of this research was to characterize quantitatively the thermodynamics of Pb^{2+} in soil solutions of Chernozems Calcic on example of water extract before and after the application of phosphogypsum produced at the Belorechensk chemical plant (Fig. 1) to reveal the possibility and rate of environmentally safe recycling of phosphogypsum in chernozem.

2. Materials and methods

2.1. Experimental area

The studied area is situated in the southwest of the Russian Federation, Krasnodar krai, called Kuban. The object of research Kanevskaya belongs to the steppe zone (Fig. 1). It is Chernozems Calcic (non-saline slightly frozen chernozem calcareous ordinary) of the southern European facies of the northern geographical zone of the Krasnodar krai.

The climate of Krasnodar krai is continental, semiarid, with an annual precipitation of 450–550 mm. The parent rocks are Carbonate and Carbonate-sulfate loess-like loam and clay. The chernozem common is thick, not solonized, humus 4.2%, the particles with size <10 μ m 49.3%, clay (the particles with size <1.0 μ m) 31.3%, CaCO₃ 0.14% (up to 3–6% at the depth of 1.3–1.6 m), pH = 7.6, exchangeable cations: Ca²⁺ – 342 mmol kg⁻¹, Mg²⁺ – 27 mmol kg⁻¹, Na⁺ – 6 mmol kg⁻¹.

2.2. Soil analyses

Soil were sampled from the 20 to 40 cm soil layer. The soil layer was appointed in a view of the highest need for reclamation of illuvial soil horizon. At the same time, this approach helps to avoid a possibility of aeolian distribution of waste after its utilization in upper soil layer, and excess of anthropogenic HM in this soil layer.

In procedure of soil samples preparation, the soil was crushed and sifted with openings 2 mm. After sifting the soil was mechanically mixed with water in ratio 1:5 for 5 min for water extraction of soluble salts. The water extraction was made on paper filter. The extracted volume of 20–60 mL was analyzed by standard methods (Carter and Gregorich, 2007; Minkina et al., 2012b; Visconti and de Paz, 2012; Shtiza and Swennen, 2011; Amakor et al., 2013).

The pH and concentration of main ions in water extracts from soils was determined by commonly used analytic methods. Dry residual of the soil was determined by thermostat 105 °C method. pH was measured in thermostat (20 ± 0.2 °C) by pH-meter with a glass electrode. The carbonate and bicarbonate anions were titrated directly by 0.01 M hydrochloric acid detecting titration, endpoint on color change of indicators – phenolphthalein and methyl orange. The chloride ion was analyzed by argentometric method with potassium chromate. The total

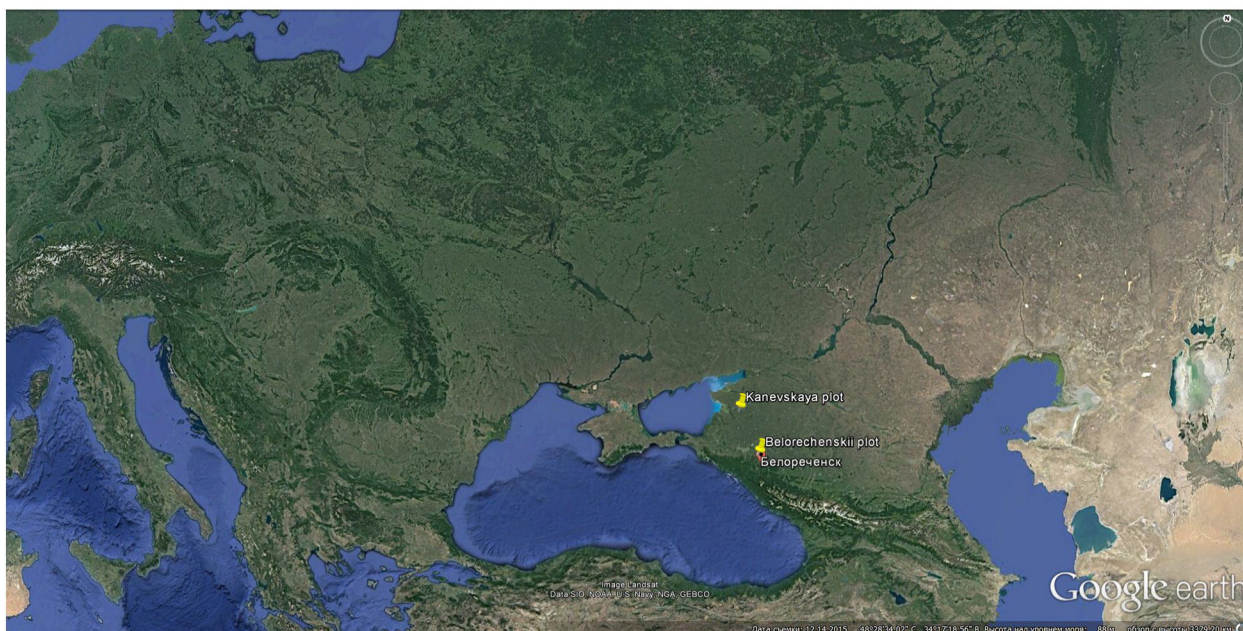


Fig. 1. The sampling area.

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