



Cadmium status in chernozem of the Krasnodar Krai (Russia) after the application of phosphogypsum

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Abstract. The thermodynamic state of Cd in Haplic Chernozem with phosphogypsum for soil reclamation in doses of 10, 20, and 40 t ha⁻¹ was evaluated. The role of chemical equilibrium in soil solutions as a cause of Cd status in soil was shown. Based on a carbonate–calcium equilibrium algorithm, a computer program was developed to calculate the real equilibrium ions forms in the soil solution. The association of ions was calculated by an iteration procedure according to the analytical ion concentration considering ion material balance, linear interpolation of equilibrium constants, the method of ionic pairs, laws of initial concentration preservation, and concentration constants of ion pair dissociation. To characterize the binding of Cd²⁺ ions in the soil solution the coefficient of heavy metal ions association k_{as} is proposed. The application of phosphogypsum increases the content of the Cd²⁺ free form in soil by 57.1%. There is no hazard if phosphogypsum from Kovdor phosphate ore is applied for soil reclamation because the Cd²⁺ content in the ore and phosphogypsum is low, and the small additional quantity of Cd²⁺ is spread throughout the soil continuum during soil processing at concentrations lower than the clark value.

Key words: soil reclamation, cadmium, soil solution, equilibrium, ion association, phosphogypsum.

1. INTRODUCTION

Phosphogypsum, a by-product of phosphorus fertilizer production, is important for soil reclamation and remediation, especially for Solonetz (Minkin et al., 1992; Michalovicz et al., 2014; Crusciol et al., 2016; Hideo and Crusciol, 2016). However, phosphogypsum, as well as phosphorus fertilizers, contains adverse and dangerous substances, in particular, heavy metals (HMs) (Enamorado et al., 2014; Nisti et al., 2015). Natural and anthropogenic HMs, including Cd, a pollutant of the first hazard class, have a toxic effect on soil and are hazardous to the environment (Adriano, 2001; Sparks, 2003; Minkina et al., 2012b, 2014; Motuzova et al., 2014; René et al., 2014; Xiong et al.,

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2014; Glazko and Galzko, 2015; Sokolov et al., 2015), and their biogeochemical cycle is uncertain (Kalinitchenko, 2016a, 2016b; Endovitsky et al., 2017). The water-diluted form of Cd is the most dangerous, and dilution increases its availability to plants (Degryse et al., 2006).

The content of total and dissolved Cd^{2+} forms in soil depends on the geographical location, ionic composition of soil solution, and soil genesis. The content of total Cd in Russia generally does not exceed 1 mg kg^{-1} soil dry weight (DW) in agricultural soils or in urban conditions; its concentration in contaminated areas is up to 3 mg kg^{-1} DW (Endovitskii et al., 2009b; Endovitsky et al., 2014; Batukaev et al., 2016). The maximum permissible concentration (MPC) of total Cd in the soil is 2 mg kg^{-1} DW in Russia (Maximum permissible concentrations of chemical substances in soil, 2006). Intervention value of Cd in soil is set at 12 mg kg^{-1} DW (Dutch Target and Intervention Values, 2000; NZWWA, 2003; Envirolink 73, 2006). In the world the highest recommended limit of Cd in soil is 5 mg kg^{-1} DW (Snakin et al., 2001).

Anthropogenic pollution with Cd by phosphate fertilizers strongly depends on the origin of phosphate rocks (European Commission, 2016). Phosphogypsum, a waste from phosphate fertilizer production by wet acid digestion of phosphate rock with sulphuric acid, contains more than 60 chemical elements including Cd (Goswami and Nand, 2015). Application of phosphogypsum for soil reclamation is a source of additional HMs input into the soil (Mays and Mortvedt, 1986; Minkin et al., 1992). Potential accumulation of HMs in soil after the application of phosphogypsum was detected by some authors (e.g. Tayibi et al., 2009, 2012), but no significant changes in the natural contents of HMs were observed after the application of phosphogypsum at the recommended doses around 10 t ha^{-1} either immediately after reclamation or in the long-term sequence of soil reclamation (Kalinichenko, 2015; Kalinitchenko, 2016c).

In the Russian Federation, a phosphate fertilizer is produced from apatite of the Kovdor phosphate rock deposit. The Kovdor apatite is of high environmental quality (Lapin and Lyagushkin, 2014), almost nonradioactive (Gázquez et al., 2014), and its ingredients are authorized to be used as feed additives for livestock. Therefore, phosphogypsum is radioactively safe for soil reclamation purposes (Zykov et al., 1966; Azouazi et al., 2001; Casacuberta et al., 2009). An important feature of the Kovdor apatite is its low total Cd content (Lapin and Lyagushkin, 2014).

Phosphogypsum contains many microelements and HMs: Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sb, Cs, Ba, Tl, Pb, Th, U (Enamorado et al., 2014) that cause soil contamination, and these elements have been taken into account for environmentally safe phosphogypsum recycling (Kalinichenko, 2017). On the other hand, it is important to take into account the real danger of contaminants overestimated by the current soil guideline values (Teaf et al., 2010).

In the present article Cd, one of the most hazardous contaminants for the environment (Cichy et al., 2014), is treated in detail. It is important to reveal high concentrations of elements in soil solution, because the degree of HMs inactivation in the form of associated ions increases with increasing elements concentration (Endovitsky et al., 2015, 2017). The danger of HMs contamination for plants depends on the composition of soil solution. The toxic effect of HMs on soil and plants decreases when the milling technology is used during which phosphogypsum is mixed with soil in the 30–60 cm layer as it dissolves in the soil and is passivated by the exclusion of the dangerous aeolian fluxes (Mischenko et al., 2009).

Commonly used models to predict metal bioavailability consider the free ion as the major bioavailable species. Dissolved trace metals are present in the environment as free ions and as complexes. Formation of ion associations and complex ions decrease Cd mobility in soil and thus its availability to the plant root system. The degree of HMs passivation in the soil is connected with their activity of ion association in the soil solution. This circumstance is substantiated on the basis of theoretical thermodynamics of electrolytes (Endovitsky et al., 2014).

Carbonate–calcium equilibrium (CCE) in the soil solution is important for understanding the origin of soil. The process of the formation of the chemical composition of the soil solution is very complex. Variation of the soil solution composition is caused by the destruction and synthesis of organic substances, secondary minerals, and organic–mineral compounds. One of the most important factors of chemical equilibrium in soil solutions is CCE (Minkina et al., 2012a). It depends on the soil chemical composition, pH, redox potential, buffer capacity of the soil solution, precipitation of carbonates in the soil profile, and ion exchange processes at the interface of solid and liquid phases. The knowledge of CCE is a base for the

calculation of CaCO_3 solubility at given conditions (Caldararu et al., 2014; Evans et al., 2014). The mineralization of soil solution varies because of the geological and biological composition of the local biogeosystem, regional and local water mass transfer, wetting and drying cycles of the soil, as well as biological process in the soil. CCE is important for proper modelling of the state and transfer of HMs in soil (Chaplygin et al., 2014; Endovitsky et al., 2014; Anisimov et al., 2015). A solution with a higher ionic strength is able to pass more ions in the form of ions associates. The carbonate system of water solution is under the influence of biological processes, soil–atmosphere gas exchange, partial pressure, and seasonal cycles of CO_2 .

In the present model two phases are considered. The air phase is applied in a common indirect chemical approach of liquid and air phases border representation as a free atmosphere of 25 °C and 0.1 MPa above the solution.

Soil is a heterogeneous (Minkina et al., 2012a) ternary system, involving a solid phase, a water phase, and a soil air phase. Therefore CaCO_3 equilibrium in the ternary heterogeneous system should be taken into consideration (Tenno et al., 2016, 2017), and an additional direct parameter, the air phase, of the model will be the aim of our future research. The water phase will be included into the model by variants of the air pressure on the ‘soil air–soil solution’ border, and by variants of the partial content of CO_2 in the soil air. This approach will allow us to calculate equilibrium constants as well as the whole modelling result. The sedimentation of fresh CaCO_3 on the soil solid phase after the soil solution micro-basin reduction due to the soil water expenditure has to be researched and taken into account concerning the CCE (Batukaev et al., 2016).

The transfer rate of Cd^{2+} to the plant depends on the content of carbonates in the soil as well as on the pH value. The thermodynamic activity of Cd^{2+} free ions decreases as the Cd^{2+} ion is bound into associates with other ions. In the soil solution of alkaline calcareous solonchic soil, the molar fraction of active concentration (activity) of the Cd^{2+} ion does not exceed 4.0%, in water extract the activity of Cd^{2+} is also low: 11.2% (Endovitsky et al., 2014).

The goal of this work was to characterize quantitatively the thermodynamic state of Cd^{2+} in soil solutions of Haplic Chernozem (non-saline ordinary chernozem) before and after the application of different doses of phosphogypsum and to assess based on soil water extract data and extrapolate the level of Cd^{2+} passivation at using phosphogypsum for soil reclamation.

2. MATERIALS AND METHODS

Study area: Krasnodar Krai in the south of the Russian Federation.

Object of research: Haplic Chernozem, the steppe non-saline slightly frozen calcareous carbonate chernozem of the South-European facies of the northern part of the Krasnodar Krai. The climate is continental, semiarid, annual precipitation 500–550 mm. The parent rocks are carbonate and carbonate-sulphate loess-like loam and clay.

Haplic Chernozem is thick, not solonized, humus content 4.2%; particles < 10 μm make up 49.3%, clay (particle size < 1.0 μm) 31.3%, CaCO_3 0.14% (up to 3–6% at a depth of 1.3–1.6 m); pH 7.8, exchangeable cations: Ca^{2+} 342 mmol kg^{-1} , Mg^{2+} 27 mmol kg^{-1} , Na^+ 6 mmol kg^{-1} .

2.1. Sampling and analysis of soil

Soil was sampled in an automorphic landscape from a depth of 20–40 cm. The soil layer was selected in view of the highest need for the reclamation of the illuvial soil horizon. In the preparation procedure, the soil samples were crushed and sieved through a 2 mm sieve. The soil water extract was made in the soil : water ratio of 1 : 5 with digestion for 5 min; the filtered extract volume was 20–60 mL.

Basic physical and chemical properties of the studied soils were determined (Derzhavin and Bulgakov, 2003; Shtiza and Swennen, 2011; Minkina et al., 2012a; Visconti and de Paz, 2012). The pH was determined by potentiometry. The carbonate and bicarbonate anions were titrated directly by 0.01 M hydrochloric acid detenting titration; endpoint on the colour change of indicators – phenolphthalein and

methyl orange. The chloride ion was detected by the argentometric method with potassium chromate. The total content of Ca^{2+} and Mg^{2+} was measured by complexometric titration with EDTA; Ca^{2+} by complexometric titration with another aliquot, Mg^{2+} was calculated as a difference. Other ions were not measured by the complexometric method with EDTA. Calculation of Mg^{2+} content as a difference is accurate enough because in the soil solution of Haplic Chernozem there is no significant amount of any other macro-ions that are determined by a complexometric titration with EDTA and therefore can distort the real content of Mg^{2+} . The sulphate was analysed by the BaSO_4 sedimentation method and Na^+ by flame photometric detection.

The total content of Cd in the soils was determined by the X-ray fluorescence (XRF) method on the scanning spectrometer 'Spectroscan MAKSGV'. This method is included in the register of methods approved for the state and industrial environmental monitoring of the Russian Federation (PND F 16.1.42-04, 2004). Analytical quality of the XRF measurements was checked by analysing reference standard soil sample 'Chernozem' No. 29107. Duplicates and reagent blanks were also used as part of the quality control.

The concentrations of water soluble Cd in the soil solution were determined by atomic absorption spectrophotometry (AAS). The allowed deviation of the XRF and AAS methods for HMs determination in soil is not more than 10–15%.

The thermodynamic state of the main ions of the salt composition of a soil system before and after the application of phosphogypsum neutralized to pH 5.0–5.3 was studied in a model experiment. Phosphogypsum was applied to the soil at rates of 10, 20, and 40 t ha⁻¹. Phosphogypsum is a by-product of the phosphorus fertilizer production by the sulphuric acid technology from the Kovdor apatite raw material deposit at the Belorechensk chemical plant. The total content of Cd²⁺ in this phosphogypsum is 2.76 mg kg⁻¹ and the content of its water-soluble form is 0.33 mg kg⁻¹. The contents of total and water-soluble Cd²⁺ forms in the original soil are 0.240 and 0.0348 mg kg⁻¹ DW, respectively (Endovitsky et al., 2014).

The experiment was performed in triplicate. All statistical calculations were performed using Microsoft Excel 2010.

2.2. Mathematical model of soil solution carbonate–calcium equilibrium

The hydrochemical classification of waters that studies natural waters on the basis of relationships between the macroconcentrations of the main ions of the soil solution was applied. The calculation of ion equilibria in salt solutions was based on the concept of physical chemistry using ion concentrations. The relationship between the equilibria and ions concentrations was calculated by the method of ion pairs presented below (Adams, 1971): the law of initial concentration preservation and the law of the mass action of the chemical equilibrium system.

The presented equations are valid under standard conditions in a binary system 'soil solution – soil air phase': 25 °C and 0.1 MPa (indirect accounting of gaseous phase), soil solution ionic strength range is 0–1.0 mol/L, the solid phase is considered indirectly as a source or sink of ions for soil solution.

The research showed that the main component of the total alkalinity of the soil solution Alk_{Σ} is the alkalinity of carbonates Alk_C . Its share in surface waters is 92–94% and in soil solutions 85–90% (Aleksandrova, 1979). These data make it possible to calculate the carbonate alkalinity of solutions using empirical equations.

The total concentrations of CO_3^{2-} and HCO_3^- were found by calculating from the total alkalinity of soil solution Alk_{Σ} , pH, and the second-step dissociation constant of carbonic acid $K^0(\text{HCO}_3)$, Eqs (1, 2):

$$(\text{CO}_3^{2-})_A = 0.94 Alk_{\Sigma} 10^{-3} / (2 + a\text{H}^+ + y''(K^0(\text{HCO}_3)y')^{-1}), \quad (1)$$

$$(\text{HCO}_3^-)_A = 0.94 Alk_{\Sigma} 10^{-3} - 2(\text{CO}_3^{2-})_A, \quad (2)$$

where A is alkalinity, a is activity, 0.94 is an empirical coefficient accounting for the contribution of carbonate alkalinity to the total alkalinity of soil solution Alk_{Σ} ; y' is the activity coefficient of the singly

charged particle (free ion or its associate); and y'' is the activity coefficient of the doubly charged particle (Minkina et al., 2012a).

After the application of phosphogypsum, the content of Cd^{2+} in soil was determined as the sum of the content of the corresponding metal form in the original soil and the additional content of Cd in phosphogypsum according the applied dose.

The equilibrium compositions of the main ionic forms in the solution of water extract at 25 °C were calculated using ION-2 program (Endovitskii et al., 2009a). The algorithm was realized on the basis of the mass balance equation system for main ions and the concentration stability constants for associates CaCO_3^0 , CaHCO_3^+ , CaSO_4^0 , MgCO_3^0 , MgHCO_3^+ , MgSO_4^0 , NaCO_3^- , and NaSO_4^- (Endovitsky et al., 2014).

The concentration was calculated of free and associated forms of ions according to the sum of ions analytical concentration. Iteration was used to solve the system of algebraic equations of the ions material balance. Linear interpolation was used to calculate the values of tabulated equilibrium constants according to calculated data.

The equations of main ions material balance are as follows, Eqs (3–8):

$$\Sigma\text{Ca}^{2+} = [\text{Ca}^{2+}] + [\text{CaCO}_3^0] + [\text{CaHCO}_3^+] + [\text{CaSO}_4^0], \quad (3)$$

$$\Sigma\text{Mg}^{2+} = [\text{Mg}^{2+}] + [\text{MgCO}_3^0] + [\text{MgHCO}_3^+] + [\text{MgSO}_4^0], \quad (4)$$

$$\Sigma\text{Na}^+ = [\text{Na}^+] + [\text{NaCO}_3^-] + [\text{NaSO}_4^-], \quad (5)$$

$$\Sigma\text{CO}_3^{2-} = [\text{CO}_3^{2-}] + [\text{CaCO}_3^0] + [\text{MgCO}_3^0] + [\text{NaCO}_3^-], \quad (6)$$

$$\Sigma\text{HCO}_3^- = [\text{HCO}_3^-] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+], \quad (7)$$

$$\Sigma\text{SO}_4^{2-} = [\text{SO}_4^{2-}] + [\text{CaSO}_4^0] + [\text{MgSO}_4^0] + [\text{NaSO}_4^-], \quad (8)$$

where $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ denote the equilibrium concentrations of the free forms of the ions, $[\text{CaCO}_3^0]$ and $[\text{MgCO}_3^0]$ are equilibrium concentrations of the ions in the associated forms (ion pairs).

For cations groups the concentration constants of ionic pair dissociation follow the law of mass transfer, Eqs (9–11):

$$K\text{CaSO}_4^0 = [\text{Ca}^{2+}][\text{SO}_4^{2-}]/[\text{CaSO}_4^0], \quad (9)$$

$$K\text{MgSO}_4^0 = [\text{Mg}^{2+}][\text{SO}_4^{2-}]/[\text{MgSO}_4^0], \quad (10)$$

$$K\text{NaCO}_3^- = [\text{Na}^+][\text{CO}_3^{2-}]/[\text{NaCO}_3^-]; \quad K\text{NaSO}_4^- = [\text{Na}^+][\text{SO}_4^{2-}]/[\text{NaSO}_4^-]. \quad (11)$$

The equilibrium concentration of ionic pairs was replaced in Eqs (3–8) with its value according to the relevant dissociation constant from Eqs (9–11). The equations system of the ions material balance was transformed as follows, Eqs (12–17):

$$\Sigma\text{Ca}^{2+} = [\text{Ca}^{2+}] \left(1 + \frac{[\text{CO}_3^{2-}]}{K_{\text{CaCO}_3}} + \frac{[\text{HCO}_3^-]}{K_{\text{CaHCO}_3}} + \frac{[\text{SO}_4^{2-}]}{K_{\text{CaSO}_4}} \right), \quad (12)$$

$$\Sigma\text{Mg}^{2+} = [\text{Mg}^{2+}] \left(1 + \frac{[\text{CO}_3^{2-}]}{K_{\text{MgCO}_3}} + \frac{[\text{HCO}_3^-]}{K_{\text{MgHCO}_3}} + \frac{[\text{SO}_4^{2-}]}{K_{\text{MgSO}_4}} \right), \quad (13)$$

$$\Sigma\text{Na}^+ = [\text{Na}^+] \left(1 + \frac{[\text{CO}_3^{2-}]}{K_{\text{NaCO}_3}} + \frac{[\text{SO}_4^{2-}]}{K_{\text{NaSO}_4}} \right), \quad (14)$$

$$\Sigma\text{CO}_3^{2-} = [\text{CO}_3^{2-}] \left(1 + \frac{[\text{Ca}^{2+}]}{K_{\text{CaCO}_3}} + \frac{[\text{Mg}^{2+}]}{K_{\text{MgCO}_3}} + \frac{[\text{Na}^+]}{K_{\text{NaCO}_3}} \right), \quad (15)$$

$$\Sigma\text{HCO}_3^- = [\text{HCO}_3^-] \left(1 + \frac{[\text{Ca}^{2+}]}{K_{\text{CaHCO}_3}} + \frac{[\text{Mg}^{2+}]}{K_{\text{MgHCO}_3}} \right), \quad (16)$$

$$\Sigma\text{SO}_4^{2-} = [\text{SO}_4^{2-}] \left(1 + \frac{[\text{Ca}^{2+}]}{K_{\text{CaSO}_4}} + \frac{[\text{Mg}^{2+}]}{K_{\text{MgSO}_4}} + \frac{[\text{Na}^+]}{K_{\text{NaSO}_4}} \right). \quad (17)$$

According to the Davies equation (Sposito, 1989) for constants, the concentration constant of dissociation in Eqs (12–17) was recalculated, Eq. (18):

$$\text{p}K = \text{p}K^0 - A\Delta Z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.1I \right), \quad (18)$$

where $\text{p}K$ is the concentration constant of ionic couple dissociation, $\text{p}K^0$ is the corresponding thermodynamic constant, A is Debye–Hückel constant 0.5042 at 25 °C; ΔZ^2 is the algebraic sum of the particles charge squares in the equation of dissociation constant, and I is the ionic strength of the solution.

The value of $\text{p}K$ calculated with Eq. (18) corresponds to (Zykov et al., 1966; Sposito, 1989):

$$\begin{aligned} \text{p}K^0(\text{CaCO}_3) &= 3.2; \text{p}K^0(\text{CaHCO}_3) = 1.26; \text{p}K^0(\text{CaSO}_4) = 2.31; \\ \text{p}K^0(\text{MgCO}_3) &= 3.4; \text{p}K^0(\text{MgHCO}_3) = 1.16; \text{p}K^0(\text{MgSO}_4) = 2.36; \\ \text{p}K^0(\text{NaCO}_3) &= 1.27; \text{p}K^0(\text{NaSO}_4) = 0.72. \end{aligned}$$

The formal ionic strength (I) of the soil solution was calculated on the data of the analytical ion concentration, Eq. (19), mol/L:

$$I = 0.5(2^2[\text{Ca}^{2+}] + 2^2[\text{Mg}^{2+}] + [\text{Na}^+] + 2^2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + 2^2[\text{SO}_4^{2-}] + [\text{Cl}^-]). \quad (19)$$

The equilibrium concentrations of ions free forms were designated as unknown values of the equation system. The analytical concentration of all ion forms was used as a total value of every compound. The system was obtained of six equations with six unknowns.

Iteration was used to find out the value of the equilibrium concentrations of free ions. The equilibrium concentrations of ion pairs were determined for dissociation constants, Eqs (9–11).

The effective ionic strength (I^* , in mol/L) of the solution was calculated by Eq. (20) taking into account the values of equilibrium concentrations of all ion forms:

$$\begin{aligned} I^* &= 0.5(2^2[\text{Ca}^{2+}] + 2^2[\text{Mg}^{2+}] + [\text{Na}^+] + 2^2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + 2^2[\text{SO}_4^{2-}] + [\text{CaHCO}_3^-] \\ &+ [\text{MgHCO}_3^-] + [\text{NaCO}_3^-] + [\text{NaSO}_4^-] + [\text{Cl}^-]). \end{aligned} \quad (20)$$

As a result of the first step of the iteration procedure, the concentration constants of dissociation were calculated, Eq. (18). A new system of material balance equations was obtained. In the new system, ingredients made the next iteration of Eqs (12–17). By the iteration, the sequence of the ion forms in the soil solution was calculated.

The coefficient of ion association γ_e as a ratio of the ion free form to its analytical content was proposed, Eq. (21):

$$\gamma_e = C_{\text{ass}} / C_{\text{an}}, \quad (21)$$

where C_{ass} is the calculated ion content in the solution taking into account its association with other ions and C_{an} is the analytical concentration of an ion.

The thermodynamic equilibrium constants were converted to the corresponding concentration constants using the activity coefficients (γ) of free ions and associates. The activity coefficients were determined by the Davies equation (Sposito, 1989):

$$-\lg y = AZ^2 \left(\frac{\sqrt{\mu^*}}{1 + \sqrt{\mu^*}} - 0.2\mu^* \right), \quad (22)$$

where $A = 0.5085$ at 25 °C, Z is the charge of the particle (ion or associate), and μ^* is the effective ionic strength of the solution.

In natural waters and in soil the HMs bind in associates and hydroxo complexes (Sposito, 1989; Endovitskii et al., 2009b; Endovitsky et al., 2014). The degree of an ion's binding depends on the values of the thermodynamic instability constant of the compound and the concentration of the main ions. In general, an ion's binding can be characterized by the ratio of the HM ion's association degree by the following formula:

$$k_{\text{as(HM)}} = \sum_{i=1}^n [An_i] (K_{\text{HM}An_i})^{-1}. \quad (23)$$

The essence of the term 'coefficient of association k_{as} ' is considered in a framework of the thermodynamics of electrolytes and surface waters on the basis of vast objective data of experiments in vitro and in situ (Endovitsky et al., 2014).

Given the $k_{\text{as(HM)}}$, the final version of the HM model (23) is as follows:

$$C_{\text{(HM)}} = (1 + k_{\text{as(HM)}}) [C_{\text{(HM)}}], \quad (24)$$

where $C_{\text{(HM)}}$ is the total concentration of a microelement in the solution, and $[C_{\text{(HM)}}]$ is the equilibrium concentration of a free microelement ion.

The value of the HM ions association degree for Cd^{2+} was calculated from the equation

$$k_{\text{as(Cd)}} = [\text{CO}_3^{2-} (K(\text{CdCO}_3))^{-1} + [\text{HCO}_3^-] (K(\text{CdHCO}_3))^{-1} + [\text{SO}_4^{2-}] (K(\text{CdSO}_4))^{-1} + [\text{Cl}^-] (K(\text{CdCl}))^{-1} + [\text{OH}^-] (K(\text{CdOH}))^{-1}]. \quad (25)$$

Using the coefficient of ion association, the molar fractions of free and bounded Cd^{2+} can be calculated as follows:

$$\nu_{\text{free}} = 1/(1 + k_{\text{as(HM)}}) \times 100\%, \quad (26)$$

$$\nu_{\text{bound}} = 100 - \nu_{\text{free}}, \quad (27)$$

$$\nu_{\text{Cd}} = 100/(1 + k_{\text{as(Cd)}}), \quad (28)$$

$$\nu_{\text{Cd(as)}} = 100 - \nu_{\text{Cd}}, \%. \quad (29)$$

3. RESULTS AND DISCUSSION

The original soil, Haplic Chernozem, has a calcium chloride composition of soil solution (Table 1). The composition of the water extract $\text{Ca} > \text{Mg} > \text{Na}$ (calcium water group) is the same both before and after

Table 1. Analytical composition of main ions of soil water extract (in the ratio 1 : 5) before and after phosphogypsum application

| Treatment | pH | Total alkalinity (Alk_{Σ}), cmol (+/-)/L | Ca^{2+} | Mg^{2+} | Na^+ | SO_4^{2-} | Cl^- | $(\text{CO}_3^{2-})_A$ | $(\text{HCO}_3^-)_A$ |
|-------------------------------------|------|---|------------------|------------------|---------------|--------------------|---------------|------------------------|----------------------|
| | | | $\times 10^{-1}$ | | | | | $\times 10^{-4}$ | $\times 10^{-2}$ |
| Control (original soil) | 7.89 | 44 | 0.35 | 0.10 | 0.012 | 0.086 | 0.30 | 1.492 | 4.106 |
| 10 t ha ⁻¹ phosphogypsum | 7.72 | 40 | 1.90 | 0.45 | 0.013 | 2.005 | 0.30 | 1.217 | 3.736 |
| 20 t ha ⁻¹ phosphogypsum | 7.61 | 36 | 2.75 | 0.50 | 0.013 | 2.880 | 0.35 | 0.885 | 3.366 |
| 40 t ha ⁻¹ phosphogypsum | 7.63 | 36 | 4.50 | 0.75 | 0.013 | 4.925 | 0.30 | 0.877 | 3.366 |

the phosphogypsum application. After the application of neutralized phosphogypsum, the pH of water extracts decreases by 0.23–0.26 units, the soil solution changes to the sulphate class, with prevalence of Ca^{2+} and SO_4^{2-} ions. The real state of the main ions in soil solutions was determined on the basis of ionic strength and ions association in the soil solution according to the model of soil solution equilibrium (Endovitskii et al., 2009b).

The thermodynamic properties of a soil solution depend on the association of its main ions. The result of ion association is a significant decrease of the concentration of ion free forms and ionic strength of the solution (μ). The activity coefficients of singly charged (γ') and doubly charged (γ'') ions increase. As a result, the stability constants of associates and complexes in the soil solution also change.

On the basis of analytical data (Table 1), the forms of the main ions in the soil solution were calculated according to the thermodynamic model, Eqs (1–22). In chernozem the main ions forms in the soil solution are to a significant degree less bound into associates than those in solonetzic soil (Table 2). In the considered soils, the molar fractions of calcium and magnesium associates are 2.0–6.1% [Ca^{2+}] and 1.4–6.6% [Mg^{2+}] against 13.1–19.2% and 15.7–23.5%, respectively, in solonetz (Endovitskii et al., 2009b).

The degree of association of the anions in chernozem is significantly higher than that of the cations. In particular, the molar fraction of associated carbonate ion is 27.7–57.7% (in solonetz, 31.0–38.6%), and that of associated sulphate ion is 6.3–12.9% (in solonetz, 5.6–7.9%) (Endovitskii et al., 2009b).

For calcium and magnesium, the molar fractions of associates in the soil solution of chernozem increase up to 21.8–20.6% [Ca^{2+}] and 18.5–22.4% [Mg^{2+}] according to the increasing of the phosphogypsum dose. The fractions of carbonate associates increase up to 64.7–78.2%, sulphate associates up to 22.5–29.2%.

Along with the main ions, soil contains different microelements, including potentially harmful HMs (Alloway, 2013; Cichy et al., 2014; Enamorado et al., 2014; Minkina et al., 2014; Anisimov et al., 2015; European Commission, 2016). The total background content of Cd^{2+} in soil is 0.24 mg kg⁻¹ DW. Considering the available data, in the calculation of the Cd^{2+} forms the content of total Cd^{2+} in soil is taken as 0.22–0.24 mg kg⁻¹ DW. The molar fractions of free and associated ions are universal characteristics of the thermodynamic state of a microelement or HM in the soil solution. For adequate model synthesis of the thermodynamic state of the soil solution required for analytical quantification of the main ions in the solution, the data of water extracts were used. The weight fraction of water-soluble Cd^{2+} in the model approximation was taken as 14.5%.

The content of Cd in soil is many times less than the contents of macro-ions. As this content has a weak influence on the soil solution ionic strength and the values of thermodynamic constants, there is no need to include the equation for Cd into the system of equations for macro-ions. The obtained equilibrium concentrations of free anions [CO_3^{2-}], [HCO_3^-], [SO_4^{2-}], [Cl^-], and [OH^-] were used for the calculation of the contents of soluble Cd^{2+} forms in water extracts from the mass balance equations (Endovitsky et al., 2014; Batukaev et al., 2016).

Table 2. Equilibrium concentrations of main ions, cmol (+/–) L⁻¹ (above) and molar fractions, % (below), of free forms of the main ions in the soil solution

| Treatment | Effective ionic strength, μ^* | Activity coefficient of ion γ'/γ'' | [Ca ²⁺] | [Mg ²⁺] | [Na ⁺] | [SO ₄ ²⁻] | [Cl ⁻] | [CO ₃ ²⁻] _f | [HCO ₃ ⁻] _f | [OH ⁻] _f |
|-------------------------------------|-----------------------------------|--|---------------------|---------------------|--------------------|----------------------------------|--------------------|---|---|---------------------------------|
| | | | ×10 ⁻¹ | | | | | | ×10 ⁻⁴ | ×10 ⁻² |
| Control (original soil) | 0.001814 | 0.9537 | 0.343 | 0.0986 | 0.01199 | 0.0806 | 0.30 | 1.079 | 4.081 | 8.141 |
| | | 0.8272 | 98.00 | 98.60 | 99.92 | 93.72 | 100.00 | 72.32 | 99.39 | |
| 10 t ha ⁻¹ phosphogypsum | 0.007702 | 0.9115 | 1.627 | 0.380 | 0.01292 | 1.672 | 0.30 | 0.454 | 3.648 | 5.759 |
| | | 0.6902 | 85.63 | 84.44 | 99.38 | 83.39 | 100.00 | 37.30 | 97.64 | |
| 20 t ha ⁻¹ phosphogypsum | 0.01036 | 0.8997 | 2.277 | 0.4065 | 0.01292 | 2.324 | 0.35 | 0.296 | 3.265 | 4.292 |
| | | 0.6551 | 82.80 | 81.30 | 99.38 | 80.69 | 100.00 | 33.45 | 97.00 | |
| 40 t ha ⁻¹ phosphogypsum | 0.01715 | 0.8826 | 3.518 | 0.6111 | 0.01289 | 3.818 | 0.30 | 0.309 | 3.235 | 4.833 |
| | | 0.6069 | 78.18 | 81.48 | 99.15 | 77.52 | 100.00 | 35.23 | 96.11 | |

The mobile fractions of free and associated Cd^{2+} forms in the soil water extracts are calculated applying Eq. 30:

$$\text{Cd}^{2+} = [\text{Cd}^{2+}] \{ 1 + [\text{CO}_3^{2-}] (K(\text{CdCO}_3))^{-1} + [\text{HCO}_3^-] (K(\text{CdHCO}_3))^{-1} + [\text{SO}_4^{2-}] (K(\text{CdSO}_4))^{-1} + [\text{Cl}^-] (K(\text{CdCl}))^{-1} + [\text{OH}^-] (K(\text{CdOH}))^{-1} \}. \quad (30)$$

The thermodynamic equilibrium constants of the associates CdCO_3^0 and CdHCO_3^+ were determined according to Zykov et al. (1966) and Sposito (1989) as follows:

$$\begin{aligned} pK^0(\text{CdCO}_3) &= 4.23, pK^0(\text{CdHCO}_3) = 2.261, pK^0(\text{CdSO}_4) = 2.11; \\ pK^0(\text{CdCl}) &= 2.05, pK^0(\text{CdOH}) = 6.08. \end{aligned}$$

The set of associates was selected considering the inorganic part of the soil solution composition determined on the basis of data obtained from the soil water extracts. The instability constants of chemical compounds from (Zykov et al., 1966; Sposito, 1989) were used.

The unstable associates were not considered. The forms of the soil organic matter in the soil solution are protonic complexes with salt cations, but these complexes are significant only in the case of a high level of organic matter in the soil under specific conditions such as a high water supply and organic matter content in fluvic soils (Minkin et al., 1979). The complexes of organic matter with salt cations are not significant for soil consideration (Minkin et al., 1979). Moreover, being taken into account in Eq. (30), the organic complexes in the soil solution will cause a reduction of calculated concentrations of the free Cd^{2+} ions. Thus, Cd^{2+} association and complexation will be even lower than those obtained using the proposed model. The information about unstable associates is not presented in the article because the content of these associates in the solution is negligible, and their influence on the soil solution equilibrium is weak.

The total concentration of Cd^{2+} is given in the left part of Eqs (31–34). When phosphogypsum is applied, the concentrations of the main ions and (hence of Cd^{2+}) in Eqs (32–34) will change accordingly, and equilibrium of Cd^{2+} will form as well.

Water extract before the application of phosphogypsum:

$$\begin{aligned} 6.192 \times 10^{-6} &= [\text{Cd}^{2+}] (1 + 10^5 [\text{CO}_3^{2-}] / 8.5567 + 10^3 [\text{HCO}_3^-] / 6.6308 + 10^3 [\text{SO}_4^{2-}] \\ &/ 11.3436 + 10^3 [\text{Cl}^-] / 10.7749 + 10^7 [\text{OH}^-] / 10.0556). \end{aligned} \quad (31)$$

After the application of 10 t ha^{-1} of phosphogypsum:

$$\begin{aligned} 6.415 \times 10^{-6} &= [\text{Cd}^{2+}] (1 + 10^5 [\text{CO}_3^{2-}] / 12.2907 + 10^3 [\text{HCO}_3^-] / 7.9470 + 10^3 [\text{SO}_4^{2-}] \\ &/ 16.2938 + 10^3 [\text{Cl}^-] / 12.9136 + 10^7 [\text{OH}^-] / 12.0516). \end{aligned} \quad (32)$$

After the application of 20 t ha^{-1} of phosphogypsum:

$$\begin{aligned} 6.639 \times 10^{-6} &= [\text{Cd}^{2+}] (1 + 10^5 [\text{CO}_3^{2-}] / 13.6431 + 10^3 [\text{HCO}_3^-] / 8.3728 + 10^3 [\text{SO}_4^{2-}] / 18.0867 \\ &+ 10^3 [\text{Cl}^-] / 13.6056 + 10^7 [\text{OH}^-] / 12.6973). \end{aligned} \quad (33)$$

After the application of 40 t ha^{-1} of phosphogypsum:

$$\begin{aligned} 7.085 \times 10^{-6} &= [\text{Cd}^{2+}] (1 + 10^5 [\text{CO}_3^{2-}] / 15.8962 + 10^3 [\text{HCO}_3^-] / 9.0377 + 10^3 [\text{SO}_4^{2-}] / 21.0736 \\ &+ 10^3 [\text{Cl}^-] / 14.6861 + 10^7 [\text{OH}^-] / 13.7057). \end{aligned} \quad (34)$$

The contents of total and water-soluble Cd^{2+} forms in soils were calculated with Eqs (23–34) (Tables 3, 4). At the application of phosphogypsum the contents of Cd^{2+} total and water-soluble forms in soil

Table 3. Contents of total and water-soluble Cd²⁺ forms in soils, mg kg⁻¹ DW

| Treatment | Total | Water-soluble form | Weight fraction of water-soluble form of Cd ²⁺ , % of total content of Cd ²⁺ |
|-------------------------------------|--------|--------------------|--|
| Control (original soil) | 0.240 | 0.0348 | 14.500 |
| 10 t ha ⁻¹ phosphogypsum | 0.2505 | 0.03605 | 14.392 |
| 20 t ha ⁻¹ phosphogypsum | 0.2610 | 0.0373 | 14.296 |
| 40 t ha ⁻¹ phosphogypsum | 0.2819 | 0.0398 | 14.123 |

Table 4. Concentration and forms of water-soluble Cd in water extract form soil

| Treatment | Concentration, cmol (+/-)L ⁻¹ × 10 ⁻⁶ | | | Molar fraction, % | | | | | | | Association coefficient |
|-------------------------------------|---|----------------------------------|------------------------------|----------------------|---------------------|-----------------------------------|------------------------------------|-----------------------------------|----------------------|----------------------|-------------------------|
| | Total, Cd ²⁺ | Equilibrium, [Cd ²⁺] | Active, α[Cd ²⁺] | α[Cd ²⁺] | [Cd ²⁺] | [CdCO ₃ ⁰] | [CdHCO ₃ ⁺] | [CdSO ₄ ⁰] | [CdCl ⁺] | [CdOH ⁺] | |
| Control (original soil) | 6.192 | 3.2272 | 2.6695 | 43.118 | 52.119 | 0.657 | 3.208 | 0.370 | 1.451 | 42.195 | 0.919 |
| 10 t ha ⁻¹ phosphogypsum | 6.415 | 3.8801 | 2.6780 | 41.746 | 60.485 | 0.223 | 2.776 | 6.207 | 1.405 | 28.904 | 0.656 |
| 20 t ha ⁻¹ phosphogypsum | 6.639 | 4.3296 | 2.8363 | 42.722 | 65.214 | 0.142 | 2.543 | 8.379 | 1.678 | 22.044 | 0.533 |
| 40 t ha ⁻¹ phosphogypsum | 7.085 | 4.4505 | 2.7010 | 38.123 | 62.815 | 0.122 | 2.248 | 11.380 | 1.283 | 22.150 | 0.592 |

increased following the phosphogypsum dose (Table 4). The maximum values of total and water-soluble forms of Cd²⁺ were observed at a dose of 40 t ha⁻¹.

The maximum coefficient of association of Cd²⁺ is 0.919 in the original soil. Most of the Cd²⁺ ion is bound into hydroxo-complexes CdOH⁺ (molar fraction 42.2–46.4%). Smaller amounts of the Cd²⁺ ion are bound into hydrocarbonate associates CdHCO₃⁺ (3.2%) or chloride associates CdCl⁺ (4.5%). The molar fraction of the active concentration of free Cd²⁺ ions is 38.3% (Endovitsky et al., 2014). Compared to the original soil, application of phosphogypsum reduces the molar fractions of associates of Cd²⁺, and other forms of associates are observed. At the phosphogypsum dose of 20 t ha⁻¹, the molar fraction of free Cd²⁺ increases by 13.1%, and the fraction of its active concentration decreases by 2.0%.

The most mobile form of Cd available for plants uptake is the Cd²⁺ free form (Amari et al., 2017). Ion associates are difficult to absorb by the plant roots, and therefore are less available for plants. Establishing a favourable ratio of the forms CdOH⁺, CdHCO₃⁺, and CdCl⁺ for plant roots uptake is the aim of future research.

At the maximum dose of phosphogypsum, the hydroxo complexes are the prevailing Cd²⁺ compounds with 23.4% and sulphate associates make up 9.8%. The association coefficient is 0.533. At the application of phosphogypsum, the association coefficient of Cd²⁺ decreased 1.43 times.

Neither the total content of Cd²⁺ nor the content of its water-soluble form in the original soil and in the soil at the phosphogypsum application (10–40 t ha⁻¹) exceeded the Cd content limits. This indicates that soil reclamation with phosphogypsum had no hazard for the soil and the ecosystem.

Chernozem is not saline; so the solution is extremely diluted and its ionic strength is low (Table 1). It was shown before that in the soil solution extracted from wet soil the ionic strength is higher than in the water extract from the same soil, and the real degree of Cd²⁺ passivation is also higher (Endovitskii et al., 2009b). Moreover, the moisture in vitro of both the water extract and the soil solution extracted from soil by the standard method is higher than the typical in situ water content of steppe soil. For the typical low water content of 9–16% DW in the period of organogenesis of plants, the real concentration of the soil solution is 30–100 times higher than the data shown in Table 1. At this in situ concentration, the effective

ionic strength of the soil solution can be assessed at a high level, up to $\mu^* = 0.2\text{--}0.6$. The coefficient of Cd^{2+} association can be extrapolated as 10–30 units at the effective ionic strength. This means that in the Krasnodar Krai, in their period of organogenesis the plants are reliably defended from Cd^{2+} transfer through their root system because Cd^{2+} ions passivation is observed in the soil solution according to the laws of soil solution thermodynamics.

The proposed ION-2 program (Endovitskii et al., 2009a) does not consider the time pattern of the chemical reaction rate; the current soil solution equilibrium at the specific soil moisture content is represented. The time pattern of soil solution depends on the soil moisture, and its dynamics is an important factor, which a program can help to take into account by calculating equilibriums by the steps of the increase of the concentration of the soil solution while the soil is drying under different weather conditions.

The Cd activity coefficient was calculated for a rather low soil solution concentration, but even at this concentration of the solution the influence of the ion association was significant. The role of the ion association is more important at higher ionic strengths, and the Cd activity coefficient gradually decreases at the high level of soil solution concentration (Batukaev et al., 2016).

The more hydromorphous the landscape and the higher the soil humidity, the higher is the danger of Cd^{2+} and other HMs for the plants and the environment (Kalinichenko, 2014; Kwasniewska, 2014). The problem of Cd^{2+} in soil is closely linked to the problem of leaching. The landscape of the Krasnodar Krai is automorphic. It is an additional reason for using phosphogypsum for the reclamation of chernozem without ecological adverse effects of Cd^{2+} because of rather high ionic strength and the corresponding ions association of a concentrated soil solution (Visconti and de Paz, 2012; Amakor et al., 2013).

The highest dose of phosphogypsum in our research was 40 t ha^{-1} . The most optimum dose of phosphogypsum for soil restoration depends on the HMs content, radioactivity, the Na content in the soil for displacement by Ca, and some other factors specific to different soil types. Doses up to 100 t ha^{-1} are proposed as environmentally safe (Mays and Mortvedt, 1986; Endovitsky et al., 2017; Kalinichenko, 2017).

At the reclamation of Haplic Chernozem with phosphogypsum, Cd is uniformly distributed throughout the soil continuum at concentrations lower than the clark value (Rules and Regulations, 2001). The studied doses of phosphogypsum from 10 to 40 t ha^{-1} applied to the soil layer of 20–40 cm are environmentally substantiated from the thermodynamic point of view. This finding gives a possibility of utilizing phosphogypsum safely, improving soil fertility, and ensuring the ecological stability of the landscape. On the basis of the research, new technical solutions and technology of soil reclamation were proposed (Kalinichenko, 2015).

4. CONCLUSIONS

- According to the equivalent concentrations of calcium, magnesium, and sodium cations in the soil solution, Haplic Chernozem (non-saline calcareous carbonate chernozem) of the northern part of the Krasnodar Krai (Russia) has the ion composition $\text{Ca} > \text{Mg} > \text{Na}$ of the calcium water group. The composition is the same both before and after the phosphogypsum application for soil melioration. Solutions of the original soil had a calcium chloride composition; after adding phosphogypsum, calcium sulphate became dominant.
- The degree of anions binding into associates in non-saline Haplic Chernozem is significantly higher than that of cations: the molar fraction of associates is 27.7–57.7% for carbonate ion and 6.3–12.9% for sulphate ion. The application of phosphogypsum increased the associated form of cations and anions in the soil solution. For calcium and magnesium, the molar fractions of associates in the soil solution of chernozem increased up to 21.8–20.6% for Ca^{2+} and 18.5–22.4% for Mg^{2+} at high phosphogypsum doses. The fractions of carbonate associates increased up to 64.7–78.2%, and those of sulphate associates increased to 22.5–29.2%.
- At the application of phosphogypsum to Haplic Chernozem, the content of the total and water-soluble forms of Cd^{2+} in the soil increased at the phosphogypsum dose of 40 t ha^{-1} by 19.8% and 16.6%, respectively.

- The calculated equilibrium concentrations and molar fractions of Cd^{2+} in soil solutions of the original soil showed that Cd^{2+} was predominantly binding into associates with hydroxo complexes CdOH^+ ; the association coefficient of Cd^{2+} ion was 0.919.
- Compared to the original soil, after the phosphogypsum applications, the content of molar fractions of Cd^{2+} associates was reduced. At the phosphogypsum dose of 40 t ha^{-1} the content of Cd^{2+} molar fractions bounded into associates with hydroxo complexes CdOH^+ and $\text{Cd}(\text{OH})_2^0$ was lower, while the content of Cd^{2+} sulphate associates with the CdSO_4^0 fraction as well as the quantity of free Cd^{2+} ions were higher; the association coefficient of Cd^{2+} ion was 0.533.
- The application of phosphogypsum to Haplic Chernozem, initially uncontaminated with heavy metals, is environmentally permissible. The total content of Cd^{2+} in soil increased by 14.4% at the application of 40 t ha^{-1} phosphogypsum, but it did not reach the maximum permissible concentration of Cd in soil of 2 mg kg^{-1} DW or the soil guideline value of 1.0 mg kg^{-1} DW.
- The application of phosphogypsum in the chernozem of southern Russia allows utilizing the by-products, increasing soil fertility, and ensuring the environmental stability of the soil and landscape.
- The proposed model helps to obtain an adequate assessment of highly concentrated soil solution, which is inaccessible for direct analytical determination through the reasonable variation of model ingredients, based on some indirect resultant data on the soil solid phase and soil solution composition. This possibility is significant in terms of the soil quality and environmental safety, especially for Cd as a most dangerous heavy metal.

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**Kaadmiumi tasakaal fosfokipsi kasutamisel Krasnodari krai (Venemaa)
chernozem-muldades**

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Fosforväetise tootmisel tekkivat fosfokipsi kasutatakse sageli mullaparandusainena. Samas sisaldavad need väetisetööstuse jäätmed raskmetalle. Artiklis on käsitletud fosfokipsi kasutamist väetisena suure orgaanilise aine sisaldusega *chernozem*-muldade puhul ja väetises sisalduva kaadmiumi tasakaalu mullas. On analüüsitud fosfokipsi kasutamisel CD^{2+} iooni tasakaalu muldades ja koostatud keemilisi tasakaale hõlmav matemaatiline mudel.