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### Carbonate Calcium Equilibrium in Soil Solution as a Driver of Heavy Metals Mobility

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#### Abstract

The thermodynamic model is proposed of heavy metals state in nosaline chernozem common carbonate of steppe zone of South Russia.

The climate is continental semiarid, annual precipitation of 500–550 mm. The parent rocks are Carbonate and Carbonate-sulfate loess-like loam and clay. The chernozem common is thick, not solonized, humus 4.2%, physical clay 49.3%, clay 31.3%, CaCO<sub>3</sub> 0.14% (up to 3–6% at the depth of 1,3–1,6 m), pH = 7.8, exchangeable cations: Ca<sup>2+</sup> – 342 mmol kg<sup>-1</sup>, Mg<sup>2+</sup> – 27 mmol kg<sup>-1</sup>, Na<sup>+</sup> – 6 mmol kg<sup>-1</sup>. The soil section in autoromorphic landscape. The soil solution water extract analyzed by standard methods.

The state of ions in soil solution is influenced by ion association. The method of ion pairs in water solution is used. At high ionic force in soil solution are formed electrically neutral ion pairs CaCO<sub>3</sub><sup>0</sup>; CaSO<sub>4</sub><sup>0</sup>, MgCO<sub>3</sub><sup>0</sup>, MgSO<sub>4</sub><sup>0</sup>, charged ion pairs CaHCO<sub>3</sub><sup>+</sup>, MgHCO<sub>3</sub><sup>+</sup>, NaCO<sub>3</sub><sup>-</sup>, NaSO<sub>4</sub><sup>-</sup>, CaOH<sup>+</sup>, MgOH<sup>+</sup>.

On the basis of of ion pair's method the algorithms and computer programs were developed to calculate the real equilibrium forms of ions in the soil solution. The concentration of free and associated macro-ion's forms were calculated by iteration procedure according to analytical ion concentration considering ion material balance, linear interpolation of equilibrium constants, Method of ionic pairs, laws of: initial concentration preservation, operating masses of equilibrium system. Concentration constants of ion pair dissociation were calculated following the law of operating masses. Were determined the quantity of macro-ion free form and coefficient of ion association  $\gamma_e$  as a ratio of ions free form to its analytical content  $\gamma_e = C_{ass} / C_{an}$ .

To interpret a behavior of heavy metal in soil solution two approaches are proposed: an additional equation for microelement to the mathematical model of macro-ions; an individual

equation for microelement based on calculated quantities of macro-ions and their forms after the solution of mathematical model equations for macro-ions. The latter approach is reasonable because the quantity of microelement is for 100–1000 times less of quantity of macro-ions, and on this reason the contribution of microelement into the value of soil solution ionic strength is negligible. Besides, the latter approach help to reduce the number of equations in the system of equation, thus the calculation procedure is simpler, reliability of calculation is higher.

To characterize  $\text{Cd}^{2+}$   $\text{Pb}^{2+}$  ion's binding was proposed the ratio of heavy metal ion's association degree – the coefficient of association  $k_{\text{as Me}}$ . To To characterize  $\text{Sr}^{2+}$  ion association an additional equation for  $\text{Sr}^{2+}$  was included to material balance equation system.

The models were tested on the data of laboratory and field experiment in Krasndar krii, chernozem common, phosphogypsum utilization at dose of 10–40 t ha<sup>-1</sup> in the soil layer of 20–50, 30–60 cm. According to the model, the molar fractions of associated calcium and magnesium are 2.0–6.1% ( $\text{Ca}^{2+}$ ) and 1.4–6.6% ( $\text{Mg}^{2+}$ ), carbonate and sulfate – 27.7–57.7%, 6.3–12.9%. The  $\text{Cd}^{2+}$  association coefficient is of 0.919–1.243. The association coefficient of  $\text{Pb}^{2+}$  is 25.193–31.207. At the phosphogypsum dose of 40 t/ha the molar fraction of the active concentration of free ions is:  $\text{Cd}^{2+}$  – 28.0–38.1%;  $\text{Pb}^{2+}$  – 3.66–5.06. The level of the  $\text{Sr}^{2+}$  ion binding into associates in original soil is 1.5%, after apply of phosphogypsum increases respectively to dose for 12.5; 15.0; 19.3%. The activity of the  $\text{Sr}^{2+}$  ion in the control variant is 83.3%, after apply of phosphogypsum it is of 60.4%; 55.6%; 48.4% respectively.

The recycling of phosphogypsum in soil is ecology safe, concentration of heavy metals supplied to the soil with phosphogypsum are lower than Clark. Utilization of pollutant increases the soil fertility, ensures the environmental stability of soil and landscape, gives high biological production of soil and recreational result.

**Keywords:** soil solution, ion's association, heavy metals, mathematical model, phosphogypsum, utilization, soil reclamation.

### Introduction

The anthropogenic impact causes different adverse effects on environment (1, 2, 3). The natural and anthropogenic heavy metals (HMs) badly influence the biosphere (4–6). It is important cause, which leads to conflicts of biosphere and agroecosystems (7). There are direct and comparative expert (estimated) approach to HMs limitation in soil. HM is most dangerous in water-diluted form. Maximum permissible concentrations are: for drinking water the Cd (MPC) is 0.001 mg l<sup>-1</sup> (8), Pb in soil 32 mg kg<sup>-1</sup> soil dry weight (DW) [9]; Sr in water 7 mg l<sup>-1</sup> [10]. Of great Importance is aspect of drivers of HMs and another chemicals water transfer in soil, vadose zone, aquifers, landscape, catchment basin [11–29], even selective chemical extraction of HMs from soil [30]. The contents of total and water-soluble HMs forms in the original soil are linked to its geographical location, ionic composition of soil solution, genesis. The distribution of Cd was found in the UK by Soil and Herbage Survey (SHS) for urban soils, with a range of 0.1 to 2.39 mg kg<sup>-1</sup> soil dry weight (DW) and a mean of 0.44 mg kg<sup>-1</sup> soil DW [31]. Limits of the total and water-soluble HMs content in soil differs in the world. In Russia they are most strict [32]. Usually, the content of total and water-soluble HMs in Russia does not exceed the limits [33–37]. For example, limit for  $\text{Cd}^{2+}$  in soil are 0.8–5.0 mg kg<sup>-1</sup> soil dry weight (DW), including MPC or soil limit of 0.8–1.0 mg kg<sup>-1</sup> soil DW [10, 15, 38–41]. The maximum in the world recommended (MPC) of Cd in the soil is 5 mg kg<sup>-1</sup> DW [42]. The limit of Cd for Residential Land use is 10 mg kg<sup>-1</sup> DW [31]. Intervention value of Cd in the soil is set of 12 mg kg<sup>-1</sup> DW [38]. The limit of Cd for commercial purposes of land use is 230 mg kg<sup>-1</sup> DW [31]. The same is approach to limiting the Pb, Sr. Higher values of HMs content may reflect anthropogenic influences. The average content of Cd has been estimated to be 0.53 mg kg<sup>-1</sup>, range varies from < 0.01 to 14.2 mg kg<sup>-1</sup>. According to EU recommendations, soil treated with sewage sludge should not contain more than 3 mg kg<sup>-1</sup> Cd. The median total Pb content (ICP-MS analysis) in soil is 41.0 mg kg<sup>-1</sup>, the range varies from 0.80 to 536 mg kg<sup>-1</sup>. The Sr content in soil is highly controlled by parent rocks and climate and, therefore, its concentrations is 89 mg kg<sup>-1</sup>, range from 6 to 3120 mg kg<sup>-1</sup> [43]. Limits of detection and quantification of HMs can vary due to the sample matrix and the range, sensitivity, set-up of the instrumentation being used [3].

In biosphere the need is strong for HMs passivation and removing [44, 45]. Minerals can passivate HMs [46]. The technology increases the level, uncertainty and danger of HMs for

biosphere. Anthropogenic pollution of Cd in fertilizers strongly depends on the origin of phosphate rock [47].

The anthropogenic pollutant phosphogypsum, the waste of most common production process of phosphate fertilizer production based on wet acid digestion of the phosphate rock with sulphuric acid technology, contains more than 60 chemical elements, including HMs as well. In the Russian Federation a phosphate fertilizer is produced from apatite of the Kovdor phosphate rock deposit. The practice of phosphogypsum utilization is the same to the every chemical plant in the world – in concentrated waste repository, tailing of the chemical plant. This is hazardous in terms of further ingress of pollutants into the soils, waters, landscapes and biosphere as a whole. Phosphogypsum terricones unfavorably affect the vast adjacent areas because of aeolian transfer; they abruptly deteriorate the areas for habitation, violate its attractiveness, It causes a long-term pollution of air, land and water systems. Ecology, health and recreational quality of landscape reduced.

The Kovdor apatite is almost nonradioactive, and its ingredients are authorized to be used as the feed additives for livestock, therefore, phosphogypsum is radioactively safe for soil reclamation purposes [48, 49]. Worldwide phosphogypsum generation is estimated to be around 100–280 Mt per year. Applying for soil reclamation the phosphogypsum is a source of additional HM input into the soil. Potential accumulation of HMs in the soil after application of phosphogypsum was noted but significant changes in the natural contents of HMs were not observed at application of phosphogypsum at recommended doses around 10 t ha<sup>-1</sup> both immediately after reclamation, and in the long-term sequence of soil reclamation [50–53].

At the Belorechensk chemical plant the phosphogypsum is a by-product. The water version of end-of-pipe technology is used for waste utilization: removal of phosphogypsum includes neutralization of its acid residue with lime milk, transportation of pulp to open sludge collectors. It constitutes an environmental danger as a source of surface and soil – vadoze zone runoff of pollutants to the Belaya River basin.

The HMs transfer into the plant through the trophic chains is important task. The studies were performed using methods of soil science, hydrochemistry, and physical chemistry.

Commonly used models to predict HMs bioavailability consider the free ion as the major bioavailable species. But dissolved trace metals are present in the environment as free ions and as complexes. HMs mobility in soil and thus its availability to enter the plant root system is decreased by ion association and complex ions formation. The degree of HMs passivation into the soil is conjugated to its activity in the process of ion association in soil solution. It is substantiated on the base of theoretical thermodynamics of electrolytes [54–72].

In our previous research environmentally safe application rates 10 t ha<sup>-1</sup> of phosphogypsum to solonchic soils were experimentally determined, theoretically substantiated, and recommended for practice [33, 73]. At the same time, the practice of phosphogypsum application to chernozems for solving the problem of phosphogypsum's utilization is still of no wide use. In particular, it is because of the possible contamination of agricultural products with potentially hazardous elements, especially at high application rates of phosphogypsum to the chernozem soil.

It was found that the pH of the soil higher than 7 units reduces the transfer of HMs to plant significantly. The possibilities of biological barriers for HMs can be strengthened by the methods of HMs passivation into the soil. Exclusion of HMs transfer to plants is linked to biological barriers – the content of HMs in plant's biomass is as a rule low, even at high total content in the soil [74, 75].

One of the factors is most important chemical equilibrium in soil solutions – carbonate calcium equilibrium (CCE) [61]. CCE depend on, and, in its turn, influences the chemical composition, pH, Eh, buffering properties of liquid phase, dissolution, migration, precipitation of carbonates in the soil profile and landscape, ion exchange processes at the interface of solid and liquid phases. The carbonate system of water solution is under the influence of biological process, soil-atmosphere gas exchange, partial pressure and seasonal cycles of CO<sub>2</sub> [76]. The mineralization of soil solution varies because of geological and biological composition of the local biogeosystem, regional and local water-mass-transfer, wetting and drying circles of the soil, biological process in the soil. Carbonate calcium equilibrium is important for proper modeling of the HMs state and transfer in soil [77–79]. The higher is ionic strength of solution, the more ions pass to form of ion's associates.

In the soil solution are formed electrically neutral ion pairs  $\text{CaCO}_3^\circ$ ;  $\text{CaSO}_4^\circ$ ,  $\text{MgCO}_3^\circ$ ,  $\text{MgSO}_4^\circ$ , charged ion pairs  $\text{CaHCO}_3^+$ ,  $\text{MgHCO}_3^+$ ,  $\text{NaCO}_3^-$ ,  $\text{NaSO}_4^-$ ,  $\text{CaOH}^+$ ,  $\text{MgOH}^+$ . The interrelation between associated ions in soil solution is much more diverse comparing to water systems [80–86].

Carbonate-calcium equilibrium of the soil solution is important for understanding the origin of soil pollution. The soil solution is the most mobile, volatile and active part of the Pedosphere. Soil solution composition varies. In the soil solution are observed the destruction and synthesis of secondary minerals, organic substances, organomineral compounds [87–89].

CCE system of soil solution is an adsorption-hydration balance between solution, gas phase, bioorganic phase. This balance includes step dissociation of carbonic acid; calcium carbonate-equilibrium between solution, soil absorbing complex, sediments of  $\text{CaCO}_3$  and solid phase, the ion equilibrium of water. An important characteristic of the CCE is a degree of saturation of solution with  $\text{CaCO}_3$ . The deposition or dissolution of  $\text{CaCO}_3$  caused by receipt or removal of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  from solution, as well as carbonate equilibrium shift, influence the ionic composition of the soil solution and determine the type of migration and accumulation of various forms of carbonate forms through the soil profile.

The analytical composition of solution rather adequately characterizes the chemical system at a low concentration of the main ions in diluted solution. The measure of real participation of salts and separate ions in soil chemical reactions is their activity.

The transfer rate of HMs to the plant depends on the content of carbonates in the soil as well as on the pH value. The thermodynamic activity of HM free ion decreases because the HM ion bound into associates with other ions.

The goal of this work is to characterize quantitatively the thermodynamic state of HMs in soil solutions of not saline ordinary chernozem before and after application of different doses of phosphogypsum, to assess on the basis of soil water extract data and extrapolate the degree of HMs passivation at utilization of phosphogypsum for soil reclamation.

### Objects and Methods

Study Area – the South of the Russian Federation, Krasnodar krai, Rostov oblast.

Object of research – the steppe non-saline slightly frozen chernozem calcareous ordinary of the south-European facies of the northern zone of the Krasnodar krai and frozen chernozem calcareous ordinary of the south-European facies of the Rostov oblast.

Krasnodar krai: the climate is continental, semiarid, 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%, physical clay 49.3%, clay 31.3%,  $\text{CaCO}_3$  0.14% (up to 3–6% at the depth of 1,3–1,6 m), pH = 7.6, exchangeable cations:  $\text{Ca}^{2+}$  – 342 mmol  $\text{kg}^{-1}$ ,  $\text{Mg}^{2+}$  – 27 mmol  $\text{kg}^{-1}$ ,  $\text{Na}^+$  – 6 mmol  $\text{kg}^{-1}$ .

Rostov oblast: the climate is continental, arid, annual precipitation of 350–450 mm, the parent rocks are Carbonate and Carbonate-sulfate loess-like loam and clay. The chernozem common is moderately thick, low solonized, humus 3.6%, physical clay 47.7%, clay 29.5%,  $\text{CaCO}_3$  0.15% (up to 3–10% at the depth of 0,8–1,5 m), pH = 7.8, exchangeable cations:  $\text{Ca}^{2+}$  – 282 mmol  $\text{kg}^{-1}$ ,  $\text{Mg}^{2+}$  – 55 mmol  $\text{kg}^{-1}$ ,  $\text{Na}^+$  – 14 mmol  $\text{kg}^{-1}$ .

### Sampling and Analysis of Soil

The soil sections have been made in autoromorphic landscape. Soil species were sampled from the soil profile section wall.

Soil solution from chernozem was obtained by water extracts (soils 1: water 5). Chemical elements in soil solution were determined by conventional widely accepted analytic methods To determine the content of macro-ions and microelements were used the most common soil sampling and analytical procedures for measuring concentrations of elements in biological samples by standard chemical methods and atomic absorption spectroscopy (AAS) and inductively coupled plasma atomic emission spectroscopy (ICP/AES) [12, 14, 34, 91–93].

The thermodynamic state of the main ions of salt composition of a soil system before and after apply of phosphogypsum neutralized to pH 5.0–5.3 was studied in a model experiments. Phosphogypsum was applied to the soil at rates of 10, 20, and 40 t/ha. Phosphogypsum is a by-product of the phosphorus fertilizer production by sulfuric acid technology from the Kovdor apatite

raw material deposit at the Belorechensk chemical plant in accord to Russian state standards [94, 95]. The total content of Cd, Pb, Sr in phosphogypsum is lower of every kind of limitations [36]

The experiments were performed in triplicate.

### Mathematical models

The calculation of ion equilibriums in salt solutions was based on the concepts of physical chemistry using ion concentrations by the presented below method of ion pairs.

To interpret a behavior of HMs in soil solution the two approaches are proposed: an additional equation for microelement to the mathematical model of macro-ions; an individual equation for microelement based on calculated quantities of macro-ions and their forms after the solution of mathematical model equations for macro-ions. The latter approach is reasonable because the quantity of microelement is for 100–1000 times less of quantity of macro-ions, and on this reason the contribution of microelement into the value of soil solution ionic strength is negligible. Besides, the latter approach help to reduce the number of equations in the system of equation, thus the calculation procedure is simpler, reliability of calculation is higher.

#### Approach 1

The determination of concentrations of  $CO_3^{2-}$  and  $HCO_3^-$  in soil is linked to the alkalinity effects of other ingredients of solution. It is a cause of analytical distortion. The total concentrations of ions  $CO_3^{2-}$  and  $HCO_3^-$  can be found by calculation from the total alkalinity  $Alk_{\Sigma}$ ,  $pH$ , and the second-step dissociation constant of carbonic acid  $K^o(HCO_3)$ . Equations (1), (2):

$$\begin{aligned}(CO_3^{2-})_A &= 0,94Alk_{\Sigma}10^{-3}/(2+aH^+ + y''(K^o(HCO_3) y')^{-1}), & (1) \\ (HCO_3^-)_A &= 0,94Alk_{\Sigma}10^{-3} - 2(CO_3^{2-})_A, & (2)\end{aligned}$$

where 0.94 is the coefficient accounting the contribution of carbonate alkalinity to the total alkalinity [34];  $y'$  is the activity coefficient of the singly-charged particle (free ion or its associate); and  $y''$  is the activity coefficient of the double-charged particle.

After phosphogypsum apply, the content of  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Sr^{2+}$  in soil were determined as the sum of contents of corresponding metal forms in original soil and the addition content of HMs in phosphogypsum according the application dose.

The equilibrium compositions of the main ionic forms in solution of water extract at 25°C were calculated using ION–2 program [96–99]. The algorithm was realized on the basis of the mass balance equation system for main ions and the concentration stability constants for associates  $CaCO_3^o$ ,  $CaHCO_3^+$ ,  $CaSO_4^o$ ,  $MgCO_3^o$ ,  $MgHCO_3^+$ ,  $MgSO_4^o$ ,  $NaCO_3^-$ , and  $NaSO_4^-$ .

On the basis of analytical data were calculated the forms of main ions in the soil solution according the Method of Ionic Pairs (MIP) [54–72, 100–102]: the law of initial concentration preservation, the law of the operating masses of chemical equilibrium system.

The concentration was calculated of free and associated forms of ions according to the sum of ion's analytical concentration. To carryout the calculation were used: iteration to solve the system of algebraic equations of the material balance of ions; linear interpolation to calculate the values of tabulated equilibrium constants according calculated data.

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

$$\Sigma Ca^{2+} = [Ca^{2+}] + [CaCO_3^o] + [CaHCO_3^+] + [CaSO_4^o] \quad (3)$$

$$\Sigma Mg^{2+} = [Mg^{2+}] + [MgCO_3^o] + [MgHCO_3^+] + [MgSO_4^o] \quad (4)$$

$$\Sigma Na^+ = [Na^+] + [NaCO_3^-] + [NaSO_4^-] \quad (5)$$

$$\Sigma CO_3^{2-} = [CO_3^{2-}] + [CaCO_3^o] + [MgCO_3^o] + [NaCO_3^-] \quad (6)$$

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

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

where,  $[\text{Ca}^{2+}]$ ,  $[\text{Mg}^{2+}]$  – the equilibrium concentration of the free form of ion,  $[\text{CaCO}_3^0]$ ,  $[\text{MgCO}_3^0]$ , – equilibrium concentration of ion in associated form (ion pair).

For groups of cation the concentration constants of ionic pair dissociation follow the law of operating masses. Equations (9–11):

$$K_{\text{CaCO}_3} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3^0]}; \quad K_{\text{CaHCO}_3} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{CaHCO}_3^+]} \quad (9)$$

$$; \quad K_{\text{CaSO}_4} = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{[\text{CaSO}_4^0]}$$

$$K_{\text{MgCO}_3} = \frac{[\text{Mg}^{2+}][\text{CO}_3^{2-}]}{[\text{MgCO}_3^0]}; \quad K_{\text{MgHCO}_3} = \frac{[\text{Mg}^{2+}][\text{HCO}_3^-]}{[\text{MgHCO}_3^+]} \quad (10)$$

$$K_{\text{MgSO}_4} = \frac{[\text{Mg}^{2+}][\text{SO}_4^{2-}]}{[\text{MgSO}_4^0]}$$

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

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

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

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

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

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

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

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

According to Davies equation for constant the concentration constant of dissociation in equations (12–17) was recalculated. Equation (18):

$$pK = pK^0 - A\Delta Z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0,11 \right) \quad (18)$$

where in  $K$  – concentration constant of dissociation of ionic couple;  $K^0$  – the corresponding thermodynamic constant;  $A$  – Debye-Huckel constant 0,5042 at 20°C;  $\Delta Z^2$  – the algebraic sum of squares of a charge of the particles in the equation of dissociation constant;  $I$  – ionic strength of solution.

The calculated with equation (18) value of  $pK$  corresponds to [55, 56, 58, 62]. Thermodynamic equilibrium constants of dissociation as follows [56, 102]:

$$\begin{aligned} pK^0(\text{CaCO}_3) &= 3,2; pK^0(\text{CaHCO}_3) = 1,26; pK^0(\text{CaSO}_4) = 2,31; \\ pK^0(\text{MgCO}_3) &= 3,4; pK^0(\text{MgHCO}_3) = 1,16; pK^0(\text{MgSO}_4) = 2,36; \\ pK^0(\text{NaCO}_3) &= 1,27; pK^0(\text{NaSO}_4) = 0,72. \end{aligned}$$

The formal ionic strength of soil solution was calculated on the data of analytical ion concentration. Equation (19):

$$\begin{aligned} I &= 0,5[2^2(\text{Ca}^{2+}) + 2^2(\text{Mg}^{2+}) + (\text{Na}^+) \\ &+ 2^2(\text{CO}_3^{2-}) + (\text{HCO}_3^-) + \\ &+ 2^2(\text{SO}_4^{2-}) + (\text{Cl}^-)], \text{mol / l} \end{aligned} \quad (19)$$

The equilibrium concentrations of ion's free forms were designated as unknown values of the equations system. The analytical concentration of all ion forms was used as a total value of every chemical element. The system was obtained of six equations with six unknown.

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

The effective ionic force of solution was calculated taking according the values of equilibrium concentration of all ion forms. Equation (20):

$$\begin{aligned} I^* &= 0,5 \left\{ 2^2[\text{Ca}^{2+}] + 2^2[\text{Mg}^{2+}] + [\text{Na}^+] \right. \\ &\left. + 2^2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + 2^2[\text{SO}_4^{2-}] + \right. \\ &+ [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+] + [\text{NaCO}_3^-] \\ &\left. + [\text{NaSO}_4^-] + [\text{Cl}^-] \right\}, \text{mol / l} \end{aligned} \quad (20)$$

As a result of the first step of iteration procedure were calculated the concentration constants of dissociation (18). The new system was obtained of equations of material balance. On the new set of the system ingredients made the next iteration of (12–17).

By the iteration sequence calculated the ion forms in soil solution.

The coefficient of ion association  $\gamma_e$  proposed as a ratio of ion free form to its analytical content. Equation (21):

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

where,  $C_{\text{ass}}$  – calculated ion content in solution taking into account its association with another ions,  $C_{\text{an}}$  – analytical concentration of an ion.

The thermodynamic equilibrium constants were converted to the corresponding concentration constants using the activity coefficients ( $\gamma$ ) of free ions and associates. The activity coefficients were determined by Davis equation [57]:

$$-\lg \gamma = Az^2 \left( \frac{\sqrt{\mu^*}}{1 + \sqrt{\mu^*}} - 0,2\mu^* \right) \quad (22)$$

where the coefficient  $A$  depends on temperature; at 25°C,  $A = 0.5085$ ;  $z$  is the charge of the particle (ion or associate);  $\mu^*$  is the effective ionic strength of the solution.

The total and water-soluble forms contents of the  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$  in original soil were taken using the reported data as an upper limit of variation ranges [1, 5, 13]. The molar fractions of free and associated ions are the universal characteristics of the thermodynamic state of a microelement (or HM) in soil solution. The adequate model synthesis of thermodynamic state of soil solution requires for analytical quantification of the main ions in the solution, the data of water extracts were used for calculation in the considered model approximation.  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$  compounds in soil are of rather high solubility. The solubility of  $\text{Cd}^{2+}$  less depends on the pH of solution than solubility of  $\text{Pb}^{2+}$  [35].

The content of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$  in soil is less than contents of macro-ions, so there is no need to include the equation for microelement into the system of equations for macroions. The obtained equilibrium concentrations of free anions  $[\text{CO}_3^{2-}]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{SO}_4^{2-}]$ ,  $[\text{Cl}^-]$ , and  $[\text{OH}^-]$  were used for the calculation of soluble  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  forms contents in water extracts from the mass balance equations [35]:

$$\text{Cd}^{2+} = [\text{Cd}^{2+}] \{ 1 + [\text{CO}_3^{2-}] (\text{K}(\text{CdCO}_3))^{-1} + [\text{HCO}_3^-] (\text{K}(\text{CdHCO}_3))^{-1} + [\text{SO}_4^{2-}] (\text{K}(\text{CdSO}_4))^{-1} + [\text{Cl}^-] (\text{K}(\text{CdCl}))^{-1} + [\text{OH}^-] (\text{K}(\text{CdOH}))^{-1} \} \quad (23)$$

$$\text{Pb}^{2+} = [\text{Pb}^{2+}] \{ 1 + [\text{CO}_3^{2-}] (\text{K}(\text{PbCO}_3))^{-1} + [\text{CO}_3^{2-}]^2 (\text{K}(\text{Pb}(\text{CO}_3)_2))^{-1} + [\text{HCO}_3^-] (\text{K}(\text{PbHCO}_3))^{-1} + [\text{SO}_4^{2-}] (\text{K}(\text{PbSO}_4))^{-1} + [\text{Cl}^-] (\text{K}(\text{PbCl}))^{-1} + [\text{OH}^-] (\text{K}(\text{PbOH}))^{-1} + [\text{OH}^-]^2 (\text{K}(\text{Pb}(\text{OH})_2))^{-1} \} \quad (24)$$

The thermodynamic equilibrium constants of the associates  $\text{CdCO}_3^0$  and  $\text{CdHCO}_3^+$  were determined according to Sposito [62, 100]:

$$\text{pK}^0(\text{CdCO}_3) = 4,23; \text{pK}^0(\text{CdHCO}_3) = 2,261,$$

and according to [48, 102]:

$$\text{pK}^0(\text{CdSO}_4) = 2,11; \text{pK}^0(\text{CdCl}) = 2,05 \text{ и } \text{pK}^0(\text{CdOH}) = 6,08$$

The transformation of Eqs. (23), (24) gives the equations for calculation of the mobile fractions of free and associated  $\text{Cd}^{2+}$  forms in the soil water extracts. The transformations allow increasing the model of HM behavior in soil approach to local pedogenesis conditions.

The set of associates was selected considering the inorganic part of soil solution composition determined on the data of the soil water extracts. The instability constants of chemical compounds were used from [48, 56, 57, 100, 102].

The unstable associates were not considering. In the soil solution, the organic matter of soil forms the protonic complexes with salt cations, but these complexes are significant only at high content of organic matter in the soil under specific conditions. For the soil considered the complexes of organic matter with salt cations are not significant. Moreover – being taken into account in the Eqs. (5), the organic complexes in soil solution cause a reduced calculated concentrations of the free  $\text{Cd}^{2+}$  ions, so  $\text{Cd}^{2+}$  association and complexation will be even lower than those obtained from our model.

Using Eqs. (23) the total concentrations of Cd<sup>2+</sup> were calculated by Eqs. (24)–(27) for the studied object. In Eqs. (24)–(27) the total concentrations of Cd<sup>2+</sup> are given. When phosphogypsum application, the concentrations of the main ions and (hence - Cd<sup>2+</sup>) in Eqs. (25)–(27) change.

The trace element at comparatively high concentration in soil is potentially hazardous HM. At low concentration it can be considered as a microelement. In natural waters the HMs are binding in associates and hydroxocomplexes.

The degree of ion's binding depends on the values of thermodynamics instability constant of compound and concentration of main ions. In general, ion's binding can be characterized with ratio of heavy metal ion's association degree by the formula:

$$k_{as(TM)} = \sum_{i=1}^n [An_i] (K_{TMAn_i})^{-1} \quad (25)$$

The essence of term “coefficient of association  $k_{as}$ ” is considered in a framework of electrolytes and surface waters thermodynamics on the vast basis of objective data of experiments in vitro and in situ [36].

Given the  $k_{as(ME)}$  the final version of the HM model – Eqs. (5) could be written as  $C_{(M\Theta)} = (1 + k_{as(M\Theta)}) [C_{(M\Theta)}]$ , (26)

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

In our research the value of heavy metal ion's association degree ratio for Cd<sup>2+</sup> was calculated from equation:

$$k_{as(Cd)} = [\text{CO}_3^{2-}](K_{Cd\text{CO}_3})^{-1} + [\text{HCO}_3^-](K_{Cd\text{HCO}_3})^{-1} + [\text{SO}_4^{2-}](K_{Cd\text{SO}_4})^{-1} + [\text{Cl}^-](K_{Cd\text{Cl}})^{-1} + [\text{OH}^-](K_{Cd\text{OH}})^{-1}; \quad (27)$$

Using coefficient of ion association, the molar fractions of free and bounded Cd<sup>2+</sup> can be calculated as follows:

$$v_{\text{free}} = 1/(1 + k_{as(ME)}) \cdot 100, \%, \quad v_{\text{bound}} = 100 - v_{\text{free}}. \quad (28)$$

$$v_{Cd} = 100/(1 + k_{as(Cd)}), \%; \quad v_{Cd(as)} = 100 - v_{Cd}, \%; \quad (29)$$

### Approach 2

The model for the Sr is the same to the above interpreted model from the chemical thermodynamic point of view. The difference is in calculation procedure only. In the model for Cd and Pb the equation for macro elements is used. In the model for the Sr a cooresponding equation is included into the system of chemical material balance equation. The model for the Sr is as follows:

$$(\text{Ca}^{2+}) = [\text{Ca}^{2+}] [1 + [\text{CO}_3^{2-}][K(\text{CaCO}_3^0)]^{-1} + [\text{HCO}_3^-][K(\text{CaHCO}_3^+)]^{-1} + [\text{SO}_4^{2-}][K(\text{CaSO}_4^0)]^{-1}, \quad (30)$$

$$(\text{Mg}^{2+}) = [\text{Mg}^{2+}] [1 + [\text{CO}_3^{2-}][K(\text{MgCO}_3^0)]^{-1} + [\text{HCO}_3^-][K(\text{MgHCO}_3^+)]^{-1} + [\text{SO}_4^{2-}][K(\text{MgSO}_4^0)]^{-1}, \quad (31)$$

$$(\text{Sr}^{2+}) = [\text{Sr}^{2+}] [1 + [\text{CO}_3^{2-}][K(\text{SrCO}_3^0)]^{-1} + [\text{HCO}_3^-][K(\text{SrHCO}_3^+)]^{-1} + [\text{SO}_4^{2-}][K(\text{SrSO}_4^0)]^{-1}, \quad (32)$$

$$(\text{CO}_3^{2-}) = [\text{CO}_3^{2-}] [1 + [\text{Ca}^{2+}][K(\text{CaCO}_3^0)]^{-1} + [\text{Mg}^{2+}][K(\text{MgCO}_3^0)]^{-1} + [\text{Sr}^{2+}][K(\text{SrCO}_3^0)]^{-1} + [\text{Na}^+][K(\text{NaCO}_3^-)]^{-1}, \quad (33)$$

$$(\text{HCO}_3^-) = [\text{HCO}_3^-] [1 + [\text{Ca}^{2+}][K(\text{CaHCO}_3^+)]^{-1} + [\text{Mg}^{2+}][K(\text{MgHCO}_3^+)]^{-1} + [\text{Sr}^{2+}][K(\text{SrCO}_3^0)]^{-1}, \quad (34)$$

$$(\text{SO}_4^{2-}) = [\text{SO}_4^{2-}] [1 + [\text{Ca}^{2+}] [\text{K}(\text{CaSO}_4^0)]^{-1} + [\text{Mg}^{2+}] [\text{K}(\text{MgSO}_4^0)]^{-1} + [\text{Sr}^{2+}] [\text{K}(\text{SrSO}_4^0)]^{-1} + [\text{Na}^+] [\text{K}(\text{NaSO}_4^-)]^{-1}, \quad (35)$$

where  $(\text{Sr}^{2+})$  – the total concentration of ion,  $[\text{Sr}^{2+}]$  – the equilibrium concentration of the free form of ion, other ingredients of equations (30–35) are the same to (3–24).

Other equations and a method of constant's determining for the equation system (30–35) are the same to the text hereinabove.

The weight fractions of the water-soluble  $\text{Pb}^{2+}$  forms of 5.6% of its total content in the chernozem from the Krasnodar krai, of 4.2% in the chernozem from the Rostov oblast, weight fraction of water-soluble  $\text{Cd}^{2+}$  14.5 and 14.0%, respectively, were taken to carry out the calculations.

The thermodynamic properties of soil solutions depend on association of ions, prematurely, association of the main ions (macroions) because these ions give the most contribution to the value of solution's ionic force. In result of ion association, is observed a decrease of ion free forms concentration, the real ionic strength of soil solution becomes less, the activity coefficients of singly-charged ( $y'$ ) and double-charged ( $y''$ ) ions is higher comparing the state of solution when all ions are in free form. The stability constants of associates and complexes in the soil solution change in their turn. In general, we should expect that the solubility of solution's components at ionic strength of 0.01–1.0 do not matches the thermodynamic solubility product for ideal solution. The elements remain in solution in soluble form of free and associated ions. But, nevertheless, despite of relatively reduced rate of ionic strength growth, its value and ion's activity coefficients reduce. Simultaneously, the mobility of ions reduced too, but remains much higher comparing assessment not accounting the association of ions.

### Results and discussion

The chernozem soil both of Krasnodar krai and of Rostov oblast before the application of phosphogypsum has a calcium chloride composition of soil solution.

The composition of water extract  $\text{Ca} > \text{Mg} > \text{Na}$  (calcium water group) is the same both before and after the phosphogypsum application. After the application of neutralized phosphogypsum, the pH of water extracts decreases by 0.23–0.26 units, the soil solution become calcium sulfate.

On the basis of analytical data the forms were calculated of main ions in soil solution according the thermodynamical model, Equations (1–22). The result of calculation shows that in native chernozem calcareous ordinary the forms of main ions in soil solution are bound into associates at low degree according the effective ionic strength of solution only 0,001814. The activity coefficient of single-charged ion is 0.9537 – close to 1. The activity coefficient of double-charged ion is 0.8272. The molar fractions of calcium and magnesium associates are low: 2.0–6.1% ( $\text{Ca}^{2+}$ ) and 1.4–6.6% ( $\text{Mg}^{2+}$ ).

Even at low ionic strength of solution, the association of the anions in chernozem is significant comparing cations. The molar fraction of associated carbonate ion is 27.7–57.7%, associated sulfate ion – 6.3–12.9%.

According to increase of phosphogypsum dose, the ionic strength of solution become higher (10 t/ha phosphogypsum –  $\mu^* = 0,007702$ ;  $y' = 0,9115$ ;  $y'' = 0,6902$ ; 20 t/ha phosphogypsum –  $\mu^* = 0,01036$ ;  $y' = 0,8997$ ;  $y'' = 0,6551$ ; 40 t/ha phosphogypsum –  $\mu^* = 0,01715$ ;  $y' = 0,8826$ ;  $y'' = 0,6069$ ) the molar fractions of associated ions in the soil solution of chernozem increase. The cation associates are up to 21.8–20.6% ( $\text{Ca}^{2+}$ ) and 18.5–22.4% ( $\text{Mg}^{2+}$ ). The carbonate associates increase up to 64.7–78.2%, sulfate associates – up to 22.5–29.2%.

At application of maximum phosphogypsum dose of 40 t ha<sup>-1</sup> was observed the maximum increase of total contents Pb by 4.9%, Cd by 19.8%, and of the water-soluble forms – 4.2; 16.6% respectively.

The maximum coefficient of association of  $\text{Cd}^{2+}$  is of 0.919 in original soil of Krasnodar krai, 1.243 in original soil of Rostov oblast. The association of  $\text{Cd}^{2+}$  is obvious. The association coefficient of  $\text{Pb}^{2+}$  ions is 25.193 for the chernozem from the Krasnodar krai and 31.207 for the chernozem from the Rostov oblast.

Mostly,  $\text{Cd}^{2+}$  ion is bound into hydroxo-complexes  $\text{CdOH}^+$ , molar fraction 42.2 for Krasnodar krai, 46.4% for Rostov oblast. Smaller amount of  $\text{Cd}^{2+}$  ion is bound into hydrocarbonate associates  $\text{CdHCO}_3^+$  (3.2%) or chloride associates  $\text{CdCl}^+$  (4.5%). The molar fraction of the active concentration

of free  $\text{Cd}^{2+}$  ions at the phosphogypsum dose 40 t/ha is 38.1 for Krasndar krai, 28.0% for Rostov oblast. The major part of the bound ions  $\text{Pb}^{2+}$  occurs in the form of  $\text{PbOH}^+$  and  $\text{Pb}(\text{OH})_2^0$  hydroxo complexes, molar fraction 85.2 for Krasndar krai, 89.0% for Rostov oblast. The carbonate associates  $\text{PbCO}_3^0 + \text{Pb}(\text{CO}_3)_2^{2-}$  and the hydrocarbonate associates  $\text{PbHCO}_3^+$  are less in quantity 8.7, 5.9; 2.1, 1.6, accordingly, their content is lower than that of hydroxo complexes by 9.8–15.2 times. The molar fraction of the active concentration of free  $\text{Pb}^{2+}$  ions at the phosphogypsum dose 40 t/ha is 5.06 for Krasndar krai, 3.66% for Rostov oblast.

The mathematic thermodynamical model for Sr in small details differs from the model for Cd and Pb. But the thermodynamic approach is the same, as well as a thermodynamic essence of result. The model was tested on the data of field experiment in Krasndar krai, chernozem common. The calculated level of the  $\text{Sr}^{2+}$  ion binding into associates in the original soil is 1.5%, after apply of phosphogypsum increases respectively to dose for 12.5; 15.0; 19.3%. The calculated activity of the  $\text{Sr}^{2+}$  ion in the control variant is 83.3%, after apply of phosphogypsum it is of 60.4%; 55.6%; 48.4% respectively.

The environment risk of soil conditioners is linked to origin of the rock deposit. Some of the worst deposits of phosphate rock are Morocco, North Caroline, Florida, Negev Dessert. The higher is technological degree of purification of phosphate-based products such as dicalcium phosphate, monocalcium phosphate) and tricalcium phosphate, the worse is by-product environmental quality [49, 103, 104].

An important feature of Kovdor apatite is the lowest Cd total content [104]. The excellent from the environmental point of view properties of Kovdor apatite are reducing to the great extend the danger of soil pollution with phosphorus fertilizers or phosphogypsum. No the total content, nor content of water soluble form of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$  in original soil, and in the soil at the doses of phosphogypsum of 10–40 t/ha do not exceed the MPC, APC, SGVs, limits of national and international content, and are not of any hazard for soil and ecosystem.

An additional confirmation of this statement has been made in the field experiment. Presented in this paper model and result of calculations according the soil solution and water extract data were used as a base of experiment. In not saline soil solution is deluted – ionic force is low. But it was that even in this case a real degree of  $\text{Cd}^{2+}$ ,  $\text{Sr}^{2+}$  passivation is significant, of  $\text{Pd}^{2+}$  is high [33]. The moisture in vitro of both, soil solution extracted from soil by standard method and water extract, is higher than typical water content of steep soil in situ. For low typical water content 9–16% DW in period of plat's organogenesis, the real concentration of soil solution is higher than in used in the model. At this concentration the effective ionic force of soil solution can be assessed at the high level of up to  $\mu^* = 0.2-0.8$ . At this effective ionic force the coefficient of  $\text{Cd}^{2+}$  association can be extrapolated as 10–30 units. The value for  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$  will be higher too. It means that plats in period of organogenesis are reliably defended from  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sr}^{2+}$  transfer due to passivation in soil solution according to the laws of soil solution thermodynamics.

The problem of HMs in soil is closely linked to the leaching. The more hydromorphous is landscape, the higher the danger of HMs for environment. The landscapes of Krasnodar krai and Rostov oblast are automorphic. It is additional reason to utilize the phosphogypsum for reclamation of chernozem soil without ecological adverse HMs effects. For example, if assigned dose of phosphogypsum is higher 20–30 t/ha, there is a risk of Kashin-Beck Disease [52].

At recycling of phosphogypsum in calcareous ordinary chernozems the Cd, Pb, Sr are uniformly distributed throughout the soil continuum at concentrations lower than Clark. The doses of phosphogypsum are substantiated environmentally from the thermodynamic point of view. Utilization of pollutant is safe, improves the soil fertility, ensure the ecological stability of the landscape.

## Conclusions

The degree of binding of anions into associates in 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 sulfate ion. The application of phosphogypsum increases 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 increase up to 21.8–20.6% for  $\text{Ca}^{2+}$  and 18.5–22.4% ( $\text{Mg}^{2+}$ ) at high phosphogypsum doses. The fractions of carbonate associates increase up to 64.7–78.2%, and those of sulfate associates increase to 22.5–29.2%.

The application of neutralized phosphogypsum from the Belorechensk chemical plant to the ordinary chernozem initially uncontaminated with heavy metals is environmentally permissible. Although the total content of HMs in soils increases by 10–20% at the of 40 t/ha phosphogypsum, the content of Cd, Pb, Sr does not reach adopted in different countries direct or estimated values of all existing limitation criteria: MPC, APC, SGV, soil limits and other.

Recycling of phosphogypsum in the calcareous ordinary chernozem of the southern Russia allows utilization of pollutant, increase of soil fertility, environmental stability of the soil and landscape, recreational effect.

Despite sufficient ecological safety of fertilizers and ameliorants derived from high-quality raw material – Kovdor apatite, a cumulative effect of HMs should be beared in mind.

The study of most important chemical equilibria and ionic structure of soil solution help to determine the formation and nature of chemical composition of soil.

The shortcoming of research fulfilled is the operation under the individual soil solutions from the layers of soil section. But soil continuum consists of series of vertical sections – one-dimension profiles. The layers of section and individual sections are interacting. The key problem of future research is not only to describe the state of soil solution system in individual part of soil volume at a particular moment of time but to explain the origin of metamorphisation of soil solution in time and through the soil continuum in accord to water-salt-mass transfer, concerning high soil concentration of CO<sub>2</sub> in situ. On this foundation the prediction of soil evolution will be proper, soil management will be better and stable.

Next problem is modeling not only the soil solution macrosystem but taking into account disperse origin of the soil and soil solution. It is because the state of water in soil is not a continuous water amount crossed by solid soil phase continuum. It is a system of discreet insulated form one another micro-water-basins on the internal surfaces of soil. This approach gives the new understanding of water-salt transfer, geochemical barrier functions and ecological properties of soil.

The idea of ions association in the soil solution helps to obtain a new glance on the processes in soil solution, soil and landscape, to consider quantitatively the equilibria model and its options for soil in vivo, undisturbed by procedures of physical modeling. The research fulfilled on example of dry steppe chestnut saline solonchic soil of Southern Russia shows dangerous for biosphere uncertainty of terrestrial carbon sink from soil to the great extend is linked to high mobility of carbon in form of carbonates in the soil solution. Concerning preferable water flows, the soil geochemical barriers for carbonates are probably less stable than in was known before.

The association of ions in soil solutions is one of the geochemical drivers promoting transformation of solution, salt and heavy metal migration and accumulation in soil disperse system, lithosphere and other geospheres. According to the mathematical model of thermodynamic state of soil solution, the HMs are to the great extend passivated in result of ion association. HMs availability for plants reduces. On the other hand, the excessive HMs sink from the soil to other parts of biosphere and geospheres is of high probability. On the base of research fulfilled it is obvious that correction of phases and stages of HMs in soil in a view of ion's association is a challenging task to stabilize the soil and landscape. Problem of the new methods of HMs passivation in a view of ion's association in soil solutions is vital [105–108].

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