Lead Status in Chernozem of the Krasnodar Krai After the Application of Phosphogypsum

^{1}A.P. Endovitskii, ^{1}V.P. Kalinichenko, ^{2}T.M. Minkina, ^{2}S.S. Mandzhieva,
^{2}S.N. Sushkova and ^{2}T.I. Abramova

^{1}Institute of Soil Fertility of South Russia, Ul. Krivoshlykova 2,
Persianovka, Oktyabr'skii Raion, Rostov oblast, 346493 Russia
^{2}Southern Federal University, Prosp. Stachki 194/1, Rostov-on-Don, 344090 Russia

Abstract: The thermodynamic state of Pb^{2+} in calcareous ordinary chernozem of the northern zone of the Krasnodar krai at the application of phosphogypsum for soil reclamation and utilization has been evaluated. Standard and increased application rates of phosphogypsum @ 10, 20 and 40 t/ha) have been studied. Results showed that application of the maximum phosphogypsum dose has increased the contents of total Pb^{2+} by 4.9; their water-soluble forms increased by 21.0 and 16.6%, respectively. Because of ion association, the average molar fractions of the Pb^{2+} free (not associated) forms in the water extract from the original soil make up 3.5 and 48.4% of the total water-soluble form, respectively. The application of phosphogypsum to the soil increases their contents to 7.4 and 57.1%, respectively. It has been found that Pb^{2+} added to the soil together with phosphogypsum do not hazard the soil and ecosystem.

Key words: Heavy Metals · Ion Association · Phosphogypsum · Reclamation · Soil Solution · Utilization

INTRODUCTION

It was found that t he liming increases of the soil pH and reduces the content of heavy metals (HM) in plants significantly. Pb^{2+} in calcareous soils is weakly transferred to plants, even at a high total content in the soil [1].

This dependence of Pb^{2+} input into plant on the content of carbonates in the soil and the pH value is primarily proved by the decrease of Pb^{2+} free ions thermodynamic activity, i.e., the ions not bound into associates with other ions. In the soil solution of alkaline calcareous solonetzic soil the molar fraction of the active concentration (activity) of Pb^{2+} ion does not exceed 0.13%, in the water extract activity of Pb^{2+} is up to 0.24%. Phosphogypsum contains more than 60 chemical elements, thus it is one of the leading pollutants of biosphere. The common practice of its utilization causes the delayed effect of local pollution. This is hazardous in terms of the further ingress of pollutants into the landscape soils and waters. Phosphogypsum terricones unfavorably affect the vast adjacent areas because of aeolian transfer; they abruptly deteriorate the attraction of the areas for habitation and recreation.

In the Russian Federation, phosphogypsum is mainly produced from the Kovdor apatite deposit. Phosphogypsum is a source of additional HM input into the soil. Potential accumulation of Hms in the soil after application of phosphogypsum was noted by some authors [1]. Environmentally safe application rates of phosphogypsum to solonetzic soils were experimentally determined, theoretically substantiated and recommended for wide use [2, 3]. At the same time, the practice of phosphogypsum application to chernozems for solving the problem of its utilization still has no wide use, in particular, because of the possible contamination of agricultural products with potentially hazardous elements. The increased application rates of phosphogypsum to the soil are not theoretically substantiated.

Corresponding Author: A.P. Endovitskii, Institute of Soil Fertility of South Russia, Ul. Krivoshlykova 2, Persianovka,
Oktyabr'skii Raion, Rostov oblast, 346493 Russia. E-mail: msaglara@mail.ru.

The aims of this work were to quantitatively characterize the thermodynamic state of Pb^{2+} in soil solutions of ordinary chernozem before and after the application of standard and high rates of the phosphogypsum.

MATERIALS AND METHODS

The thermodynamic state of the main salt composition of a soil system before and after the addition of phosphogypsum neutralized to pH 5.0–5.3 was studied in a model experiment. Chernozem samples were taken from the 0 to 20 and 0 to 40 cm layers in the region of the village of Kanevskaya, Krasnodar krai. The experiments were performed in triplicate. Phosphogypsum was applied to the soil @ 10, 20 and 40 t/ha. Phosphogypsum is a byproduct in the production of sulfuric acid from the Kovdor apatite raw material at the Belorechensk chemical plant in accordance with Russian state standards. The total content of Pb^{2+} in phosphogypsum is 55.98 mg/kg. The contents of their water-soluble forms are 10.48 mg/kg.

The known sulfuric-acid technology is used at the Belorechensk chemical plant for the production of phosphate fertilizers from apatite. This technology involves the use of a chain of several reactors. In technological terms, this cycle does not differ from the earlier technical solutions. Phosphogypsum is a byproduct.

The concentrations of the main ions in water extracts from soils (1:5) were determined by accepted analytical methods. The studies were performed using methods of soil science, hydrochemistry and physical chemistry [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. The applied classification of waters was developed and used in the hydrochemistry, which studies natural waters on the basis of relationships between the macroconcentrations of the main ions present in the soil solution, which is expressed in meq/L (or cmol(+/−)/kg). The calculation of ion equilibriums in salt solutions was based on the concepts of physical chemistry using ion concentrations. The relationship between the equilibriums and ion concentrations was calculated by the method presented below.

The total concentrations of ions CO_3^{2-} and HCO_3^- were found by calculation from the total alkalinity Alk_Σ, pH and the second-step dissociation constant of carbonic acid $K^0(HCO_3)$:

$$(CO_3^{2-})_A = 0,94 Alk_б 10^{-3}/(2 + aH^+ + y''(K^0(HCO_3)y')^{-1}), \quad (1)$$

$$(HCO_3^-)_A = 0,94 Alk_б 10^{-3} - 2(CO_3^{2-})_A, \quad (2)$$

where, 0.94 is the coefficient accounting for the contribution of carbonate alkalinity to the total alkalinity; 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.

The contents of the total and water-soluble Pb^{2+} forms in the original soil are published in our former reports [11, 15, 16] with consideration for the geographical location of soils and the ionic composition of soil solution. After the addition of phosphogypsum, the contents of both metals were determined in the soil samples. For this purpose, the contents of the corresponding metal forms in the original soil and the added phosphogypsum were summarized [17].

The equilibrium compositions of the main ionic forms in solutions at 25°C were calculated using ION-2 program [15, 18]. The algorithm was realized on the basis of the mass balance equation system for ions and the concentration stability constants for the associates $CaCO_3^0$, $CaHCO_3^+$, $CaSO_4^0$, $MgCO_3^0$, $MgHCO_3^+$, $MgSO_4^0$, $NaCO_3^-$ and $NaSO_4^-$.

The thermodynamic equilibrium constants were taken according to Bjerrum *et al*. [11]: $pK0(CaCO_3) = 3,2$; $pK0(CaHCO_3) = 1,26$; $pK0(CaSO_4) = 2,31$; $pK0(MgCO_3) = 3,4$; $pK0(MgHCO_3) = 1,16$; $pK0(MgSO_4) = 2,36$; $pK0(NaCO_3) = 1,27$; $pK0(NaSO_4) = 0,72$.

The thermodynamic equilibrium constants were converted to the corresponding concentration constants using the activity coefficients (y) of free ions and associates. The activity coefficients were determined from the Davis equation (1962):

$$-\lg y = A z^2 \left(\frac{\sqrt{\mu^*}}{1 + \sqrt[4]{\mu^*}} - 0,2\mu^* \right) \quad (3)$$

where, the coefficient A in Eq. (3) depends on temperature; at 25°C, $A = 0.5085$; z is the charge of the particle (ion or associate); μ^* is the effective ionic strength of the solution.

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 Pb^{2+} and Cd^{2+} forms in water extracts from the mass balance equations [19]:

$$Pb^{2+} = [Pb^{2+}]\{1 + [CO_3^{2-}](K(PbCO_3))^{-1} + [CO_3^{2-}]^2(K(Pb(CO_3)_2))^{-1} + [HCO_3^-](K(PbHCO_3))^{-1} + [SO_4^{2-}](K(PbSO_4))^{-1} + [Cl^-](K(PbCl))^{-1} + [OH^-](K(PbOH))^{-1} + [OH^-]^2(K(Pb(OH)_2))^{-1}\} \quad (4)$$

The thermodynamic stability constants of the associates $PbCO_3^0$, $PbCO_3^0$, $Pb(CO_3)_2^{2-}$, $PbHCO_3^+$, $CdCO_3^0$ and $CdHCO_3^+$ were determined according to Sposito [10]: $pK^0(PbCO_3)=6,49$; $pK^0(Pb(CO_3)_2)=9,30$; $pK^0(PbHCO_3)=3,22$.

The other constants were taken according to Lur'e [4]: $pK^0(PbSO_4)=2,62$; $pK^0(PbCl)=1,62$; $pK^0(PbOH)=7,52$; $pK^0(Pb(OH)_2)=10,54$.

The transformation of Eqs. (4) gave relationships for the calculation of the mobile fractions of free and associated Pb^{2+} forms in the studied water extracts from individual soils. The performed transformations allow increasing the approach of the model of HM behavior in the soil to the local pedogenesis conditions.

The set of associates in this work was selected with consideration for only the inorganic part of soil solution composition determined from the data on the water soil extracts. The stability constants of chemical compounds were reported [4, 10, 11]. The unstable associates were not considered. In the soil solution, the organic matter of soil forms the protonic complexes with salt cations [5].

Water extract before the application of phosphogypsum:

$$8,648 \cdot 10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/4,7292+10^{10}[CO_3^{2-}]^2/7,3247+10^4[HCO_3^-]/7,2848 +10^3[SO_4^{2-}]/3,5060+ 10^2[Cl^-]/2,9001+10^8[OH^-]/3,6509+10^{11}[OH^-]^2/3,8332), \quad (5)$$

After the application of 10 t/ha phosphogypsum:

$$9,034 \cdot 10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/6,7929+10^{10}[CO_3^{2-}]^2/10,5211+ 10^4[HCO_3^-]/8,7308 +10^3[SO_4^{2-}]/5,0359+10^2[Cl^-]/3,4758+10^8[OH^-]/4,3755+10^{11}[OH^-]^2/5,0293), \quad (6)$$

After the application of 20 t/ha phosphogypsum:

$$9,420 \cdot 10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/7,5404+10^{10}[CO_3^{2-}]^2/11,678+ 10^4[HCO_3^-]/9,1986 +10^3[SO_4^{2-}]/5,5900+10^2[Cl^-]/3,6620+10^8[OH^-]/4,6100+10^{11}[OH^-]^2/5,4387), \quad (7)$$

After the application of 40 t/ha phosphogypsum:

$$10,192 \cdot 10^{-5}=[Pb^{2+}](1+10^7[CO_3^{2-}]/8,7857+10^{10}[CO_3^{2-}]^2/13,6074 +10^4[HCO_3^-]/9,9291+10^3[SO_4^{2-}]/6,5132+10^2[Cl^-]//3,9529+10^8[OH^-]/4,9761+10^{11}[OH^-]^2/6,1003), \quad (8)$$

A potentially hazardous HM in the soil can be considered as a microelement and its thermodynamic state in the soil solution and water extract can be characterized using the association coefficient of microelement $k_{as(ME)}$ [18, 19], which indicates the degree of binding of the potentially hazardous HM into associates and complexes with the main ions of the soil solution.

Given the $k_{as(ME)}$ the final version of the HM model, Eqs. (4) and (5) can be written as

$$C_{(ME)} = (1 + k_{as(ME)}) [C_{(ME)}], \quad (9)$$

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

The association coefficients of Pb^{2+} were calculated from the equation:

$$k_{as(Pb)}=[CO_3^{2-}](K(PbCO_3))^{-1}+[CO_3^{2-}]^2(K(Pb(CO_3)_2))^{-1}+ [HCO_3^-](K(PbHCO_3))^{-1}+ +[SO_4^{2-}](K(PbSO_4))^{-1}+ [Cl^-](K(PbCl))^{-1}+[OH^-](K(PbOH))^{-1}+[OH^-]^2(K(Pb(OH)_2))^{-1}, \quad (10)$$

The sense of the term "coefficient of association k_{as}" was considered in detail in our earlier work [19], in the development of current concepts of the thermodynamics of electrolytes and surface waters [20] on the basis of objective data of in vitro [17] and in situ experiments.

Using the coefficients of associated ions, the molar fractions of free and bound microelement (HM) ions can be calculated

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

RESULTS AND DISCUSSION

At the application of neutralized phosphogypsum to the soil, the pH of water extracts decreases by 0.23-0.26 units, when the application rate increases and the soil solution passes to the sulfate class. The chernozem calcareous ordinary of the northern Krasnodar krai, have the ion composition $Ca^{2+} > Mg^{2+} > Na^+$ (calcium water group) both before and after the phosphogypsum application. The original soils have a calcium chloride composition of soil solutions. After the addition of phosphogypsum, the soil solutions become calcium sulfate.

The thermodynamic properties of soil solutions depend on the association of their main ions. The result of ion association is a significant decrease of the concentration of ion free forms and ionic strength of solution (μ). The activity coefficients of singly-charged

Table 1: Equilibrium concentrations, cmol(+/–)/kg (above) and molar fractions, %, (below), of free forms of the main ions in solutions.

Variants	Effective ionic strength, μ*	The activity coefficient of the ions y'/y"	[Ca²⁺]	[Mg²⁺]	[Na⁺]	[SO₄²⁻]	[Cl⁻]	[CO₃²⁻]A, ·10⁻⁴	[HCO₃⁻]ₐ,10⁻²	[OH⁻],·10⁻⁵
					•10⁻¹					
Control	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	
After the application of 10 t/ha 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	
After the application of 20 t/ha 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	
After the application of 40 t/ha 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	

Table 2: Contents of total and water-soluble Pb²⁺ and Cd²⁺ forms in soils, mg/kg

Variants	The total content of Pb²⁺	The content of water-soluble forms of Pb²⁺	The weight fraction of water-soluble Pb²⁺, % of total content Pb²⁺	The total content Cd²⁺	The content of water-soluble forms of Cd²⁺	The weight fraction of water-soluble Cd²⁺, % of total content Cd²⁺
Control	20,0	0,8960	5,60	0,240	0,0348	14,500
After the application of 10 t/ha phosphogypsum	20,2127	0,9356	4,63	0,2505	0,03605	14,392
After the application of 20 t/ha phosphogypsum	20,4254	0,9752	4,77	0,2610	0,0373	14,296
After the application of 40 t/ha phosphogypsum	20,8509	1,0544	5,06	0,2819	0,0398	14,123

(*y'*) and double-charged (*y"*) ions increase. As a result, the stability constants of associates and complexes in the soil solution also change.

The calculation for the forms of the main ions in solutions (Table 1) shows that the cations in the carbonate-free slightly alkaline chernozems are to a significantly lower degree bound into associates than those in the solonetzic soils studied earlier [2]. In the considered soils, the molar fractions of calcium and magnesium associates are similar: 2.0-6.1% (Ca²⁺) and 1.4-6.6% (Mg²⁺) against 13.1-19.2 and 15.7-23.5%, respectively, in the calcareous solonetzes.

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 ions is 27.7-57.7% (in solonetzes, 31.0-38.6%) and that of associated sulfate ions is 6.3-12.9% (in solonetzes, 5.6-7.9%). Thus, chernozems and chestnut solonetzes are similar in terms of carbonate and sulfate associates.

For calcium and magnesium, the molar fractions of associates in the soil solution of chernozem increase to 21.8-20.6% (Ca²⁺) and 18.5-22.4% (Mg²⁺) with increasing phosphogypsum dose. The fractions of carbonate associates increase to 64.7–78.2% and those of sulfate associates increase to 22.5-29.2%.

Along with the main ions, the soils contain different microelements, including HMs, which are potentially hazardous for human health. Among them are lead and cadmium [1, 22, 23]. The total background contents of Pb²⁺ are 20 mg/kg soil. The content of total Pb²⁺ in the soil under agricultural use varies from 0.1 to 20 mg/kg [3]. According the available data, in the calculation of the Pb²⁺ forms, the content of total Pb²⁺ is taken equal to 18–20 mg/kg is taken as 0.22–0.44 mg/kg soil (Table 2). Pb²⁺ readily reacts with the main ions of soil solutions (CO₃²⁻, SO₄²⁻, OH⁻). Hardy soluble carbonates, sulfates and hydroxides are formed.

The contents of total Pb²⁺ and their water-soluble forms in the original soils were taken using the similarity method for the properties of the studied chernozems from the reported data [19]. The contents of water-soluble Pb²⁺ forms were taken as upper limit of variation ranges. On this basis, the environmentally significant calculation of the phosphogypsum application rate was performed.

An even insignificant pH decrease abruptly increases the solubility of lead carbonates and hydroxides. At pH 6.5, the solubility of Pb²⁺ hydroxides in pure water solutions is about 100 μg Pb²⁺/L [20]. At the application of phosphogypsum to the soil, the contents of total and water-soluble Pb²⁺ forms increase with the application

dose. The maximum values are observed at a dose of 40 t/ha. The average increases were 4.9 and 4.2% for Pb^{2+}.

The association coefficient of Pb^{2+} ions is 25.193 for the chernozem. The major part of the bound to associates ions Pb^{2+} ions occurs in the $PbOH^+$ and $Pb(OH)_2^0$ hydroxo complexes. The carbonate associates $PbCO_3^0 + Pb(CO_3)_2^{2-}$ and the hydrocarbonate associates $PbHCO_3^+$ are less in quantity; their content is lower than that of hydroxo complexes by 9.8-15.2 times.

The activity of Pb^{2+} ion in the initial solutions is lower than its equilibrium concentration by 17.7%. At the phosphogypsum dose of 40 t/ha, the association coefficient of Pb^{2+} ion decreases by 2.2 times and the activity of its free ions increases by 60.39% for the chernozem. The molar fractions of hydroxo complexes and carbonate associates decrease by 3.7-4.1 and 3.6-5.7%, respectively; those of sulfate associates increase by 3.9-4.8%. The activity of free ions increases to 95.6% of their total concentration.

It was found that Pb^{2+} added to the soil together with phosphogypsum during both the reclamation and the utilization is of no hazard for soil and ecosystem. The recycling of phosphogypsum calcareous ordinary chernozems in the southern Russia allows utilizing the pollutant, improving the soil fertility, ensuring the ecological stability of the landscape and reaching a recreational effect in the improvement of population life [16, 24, 25, 26].

CONCLUSIONS

• Equivalent concentrations of calcium, magnesium and sodium cations show that the calcareous ordinary chernozem of Krasnodar krai is characterized by the ion composition $Ca^{2+} > Mg^{2+} > Na^+$ (calcium water group) both before and after the application of phosphogypsum. Soil solutions of the original soils have a calcium chloride composition. After adding the phosphogypsum, the soil solutions become calcium sulfate.

• 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 ions and 6.3–12.9% for sulfate ions. The presence of phosphogypsum in the soil increases the proportions of associates of both cations and anions in the soil solution. For calcium and magnesium, the molar fractions of associates in the soil solution of chernozem increase to 21.8–20.6%

(Ca^{2+}) and 18.5–22.4% (Mg^{2+}) with increasing phosphogypsum rate. The fractions of carbonate associates increase to 64.7–78.2% and those of sulfate associates increase to 22.5–29.2%.

• At the application of phosphogypsum to chernozem, the contents of the total and water-soluble forms of Pb^{2+} in the soil increase with the phosphogypsum rate; the highest increases are observed at the maximum phosphogypsum dose of 40 t/ha: 4.9 and 4.2% for Pb^{2+}.

• The calculation of the equilibrium concentrations and molar fractions of Pb^{2+} ions in soil solutions of the original soils showed a high degree of Pb^{2+} binding into associates and hydroxo complexes. Because of the ion association under the effect of the solution ionic strength, the activity of Pb^{2+} ions in the initial solutions is lower than its equilibrium concentration by 17.7% for the chernozem.

• At the phosphogypsum dose of 40 t/ha, the association coefficient of Pb^{2+} ions decreases by 2.2 times and the activity of its free ions increases by 60.39% for the chernozem. The molar fractions of hydroxo complexes and carbonate associates decrease by 3.7–4.1 and 3.6–5.7%, respectively; those of sulfate associates increase by 3.9–4.8%, respectively. The activity of free ions increases and becomes equal to 95.6% of their total concentration.

ACKNOWLEDGEMENTS

REFERENCES

1. Alloway, B., 1990. Y. Heavy metals in Soils. New York: Wiley and Sons, pp: 332.

2. Endovitskii, A., V. Kalinichenko, V. Il'in and A. Ivanenko, 2008. Thermodynamic conditions of cadmium and lead in chestnut soil. Agrokhimiya, 9: 59-65, (in Russian).

3. Lyubimova, I., 2006. Recommendations on the Use of Phosphogypsum for the Reclamation of Solonetzes. Pochv. Inst. im. Dokuchaeva, Moscow, pp: 46, (in Russian).

4. Yu., 1979. Reference Book on Analytical Chemistry. Khimiya, Moscow, pp: 480, (in Russian).

5. Minkin, M., A. Endovitskii and V. Levchenko, 1977. Ion association in soil solutions. Pochvovedenie, 2: 49-58, (in Russian).

6. Minkina, T.M., D.L. Pinskiy, T.V. Bauer, S.S. Mandzhieva, O.N. Belyaeva, V.P. Kalinichenko and A.P. Endovitsky, 2014. Effect of attendant anions on zinc adsorption and transformation in chernozem. Journal of Geochemical Exploration, 144: 226-229.

7. Minkina, T.M., D.L. Pinsky, S.S. Mandzhieva, T.V. Bauer, S.N. Sushkova and A.V. Kushnareva, 2014. Effect of an Attendant Anion on the Balance of Cations in the Soil-Solution System with an Ordinary Chernozem as an Example. Eurasian Soil Science, 47(8): 772-780.

8. Pinskii, D.L., T.M. Minkina and Y.I. Gaponova, 2010. Comparative analysis of mono-and polyelement adsorption of copper, lead and zinc by an ordinary chernozem from nitrate and acetate solutions. Eurasian Soil Science, 43: 748-756.

9. Pinskii, D.L., T.M. Minkina, S.S. Mandzhieva, U.A. Fedorov, T.V. Bauer and D.G. Nevidomskaya, 2014. Adsorption features of Cu(II), Pb(II) and Zn(II) by an Ordinary Chernozem from Nitrate, Chloride, Acetate and Sulfate Solutions. Eurasian Soil Science, 47(1): 10-17.

10. Sposito, G., 1981. The Thermodynamics of Soil Solution. Clarendon Press, Oxford, pp: 250.

11. Bjerrum, J., G. Schwarzenbach and L. Sillen, 1958. Stability constants of metal-ion complexes with solubility products of inorganic substances. Part II. Inorganic ligands. London: The Chemical Society, pp: 131.

12. Han, F.X. and A. Singer, 2007. Biogeochemistry of trace elements in Arid environments. Environmental pollution, 13, Netherlands: Springer, pp: 366.

13. Gray, C., R. McLaren, A. Roberts and L. Condron, 2000. Fractionation of soil cadmium from some New Zealand soils. Communications in Soil Science and Plant Analysis, 31: 1261-1273.

14. Manceau, A., M. Marcus and N. Tamura, 2002. Quantative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. Applications of Synchrotron Radiation in Low-Temperature Geochemistry and E1nvironmental Science. Reviews in Mineralogy and Geochemistry. Washington, DC, 49: 341-349.

15. Bakoev, S., A. Endovitskii, V. Kalinichenko and A. Ivanenko, 2009. ION-2 software for calculating the associate-ion equilibrium in the soil solution. Plodorodie, 6: 22-23, (in Russian).

16. Bakoev, S., N. Mishchenko, A. Endovitskii and V. Kalinichenko, 2010. Thermodynamic substantiation of phosphogypsum recycling in chernozem. Plodorodie, 1: 11-13, (in Russian).

17. Lerner, L., I. Lyubimova, Z. Kakhnovich and A. Grachev, 1984. Atomic absorption determination of Sr in phosphogypsums and soils in model experiments for assessing the potential contamination of soils. Pochvovedenie, 2: 142-148, (in Russian).

18. Endovitskii, A., V. Kalinichenko, V. Il'in and A. Ivanenko, 2009. Coefficients of association and activity of cadmium and lead ions in soil solutions. Eurasian Soil Science, 2: 201-208.

19. Endovitskii, A., V. Kalinichenko, S. Bakoev, A. Ivanenko, V. Sukovatov and E. Radevich, 2009. ION-2 software. State registration certificate. Federal Service for Intellectual Property, Patents and Trademarks, (in Russian).

20. Linnik, P. and B. Nabivanets, 1986. Metal Migration Forms in Surface Fresh Waters. Gidrometizdat, Leningrad, pp: 269, (in Russian).

21. Biogeochemistry of Trace Elements, 1962. Sweden, pp: 116-117.

22. Adriano, D., 2001. Trace elements in terrestrial environments. New York, Berlin, Heidelberg: Springer-Verlag, pp: 868.

23. Sparks, D., 2003. Environmental soil chemistry. Second Edition. Academic press, USA, pp: 352.

24. Kalinichenko, V., 2010. RU patent 2387115 C2. Device for the embedding of substance at the rotary soil loosening. Bulleten' Izobretenii, pp: 12, (in Russian).

25. Minkina, T.M., D.L. Pinskii, S.S. Mandzhieva, E.M. Antonenko and S.N. Sushkova, 2011. Effect of the particle size distribution on the adsorption of copper, lead and zinc by chernozemic soils of Rostov oblast. Eurasian Soil Science, 44(11): 1193-1200.

26. Stanton, S., 2000. Direct and indirect effects of îrganic matter on metal immobilization in soil. In the Proceedings of the Third International Symposium of the Working Group MO Soil-Mineral Organic Matter-Microorganism Interaction and Ecosystem Health, pp: 41.