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Lead(II) retention by Alfisol and clinoptilolite: cation balance and pH effect

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Abstract

Lead (Pb^{2+}) sorption by Alfisol and zeolite was studied at pH 3, 4, and 5 to find the relationship between the amounts of Pb retained and ions displaced from the soil into the solution. In Alfisol Pb sorption was accompanied by the increase in contents of both Ca^{2+} and H^+ constituting about 2/3 and 1/3 of the total amount of displaced cations, respectively. Increase in pH enhanced sorption of Pb. Hystersis of lead adsorption was observed in Alfisol. Clinoptilolite zeolite sorbed 20–30 times more Pb than the soil. Lead sorption by zeolite was not influenced by pH and was accompanied by the increase of Ca^{2+}, Na^+, and K^+ contents in solution, whereas amounts of displaced H^+ were negligible. The research indicates that Pb retention both by Alfisol and zeolite can be viewed as the result of ion exchange reaction with strong (soil) or very strong (zeolite) specific binding of Pb. Application of zeolite in some instances may appear the most efficient treatment for reclamation of lead-contaminated soils due to its high ability to retain Pb in a wide range of pH.

Keywords: Lead in soil; Zeolite; Ion exchange in soils; Sorption of trace elements in soils; Soil remediation

1. Introduction

Reducing the availability of trace metals to plants is critical for optimizing agricultural production at the lands contaminated due to military, urban, or industrial

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use. Decreasing plant uptake of trace metals from soil may enable permissible contaminant levels in crops. Phytoavailability of trace metals correlates best with their concentrations in soil solution rather with their total content in soil (Kabata-Pendias and Brümmer, 1992; Kabata-Pendias and Pendias, 1992). So, it may be reduced if the metals are sorbed or precipitated from the soil solution.

Lead (Pb^{2+}) is a widespread soil contaminant that represents a major challenge for soil remediation. One of the most important methods to decrease lead availability to plants is liming which increases soil pH and enhances Pb retention in the solid phase (Tsadilas, 2000). Liming has its limitations. It is not efficient in strongly acid soils and large amounts of lime are not available in many regions. Continued influx of acidic water, even slightly acidic rain water, can eventually neutralize the lime and cause Pb remobilization. Another method to immobilize lead is application of organic fertilizers or phosphates. In particular, solution lead concentration in Pb-enriched soil can be substantially reduced by adding hydroxyapatite [$Ca_5(PO_4)_3(OH)$] (Ma et al., 1992; Ma, 1996), monocalcium phosphate [$Ca(H_2PO_4)_2 \cdot 2H_2O$] (Kalbasi et al., 1995), or Na_2HPO_4 (Rabinovitz, 1993). This response is attributed to the precipitation of hydroxypyromorphite [$Pb_{10}(PO_4)_6\ (OH)_2$].

An alternative way to Pb immobilization may be the application of zeolites (Tsitsishvili et al., 1985; Leppert, 1990). Some zeolites, e.g. clinoptilolite, are stable in acid conditions up to pH 2 (Ming and Mumpton, 1989). High affinity of zeolites to trace metals has been demonstrated (Barrer, 1978; Tarasevich et al., 1997; Tsadilas et al., 1997). Application of zeolites could potentially be an efficient method to immobilize Pb in soil, and thus decrease lead concentration in the soil solution. However, no quantitative estimates of this effect are available in the literature.

Lead retention in soils is commonly attributed to the ion exchange or specific sorption on silicates, metal oxide-hydroxides, and organic matter (Kabata-Pendias and Pendias, 1992; Tills and Alloway, 1983; Sauvé et al., 2000), penetration of Pb ions in the interlayer space of clay minerals (Zyrin et al., 1986), as well as precipitation of Pb minerals. Processes causing lead retention may be distinguished by comparing amount of retained Pb and amount of ions displaced from the soil surface into soil solution (Ponizovsky and Mironenko, 2001a). A process may be called cation exchange when some cations are displaced into solution in the amount equal to the amount of Pb^{2+} retained in solid phases. If Pb^{2+} is removed from solution into solid phase without displacement of any cations into solution or removal of equal amount of anions, the process should be referred as adsorption. Adsorption of ions should cause changes in the surface charge of soil particles (Bolt et al., 1978). Precipitation of sparingly soluble salts or lead hydroxide is accompanied by the simultaneous removal of some anions from the solution and no sorbed cations are displaced. Thus, a comparison between amount of retained lead and amounts of cations appearing in solution can provide information about the mechanism of immobilization of this trace metal in soil.

The objective of this study was to use the cation balance to infer a mechanism of Pb retention in Alfisol soil and in zeolite mineral.

2. Materials and methods

2.1. Soil and zeolite properties

The study was carried out on a sandy loam Alfisol (Typic Rhodoxeralf, A_p horizon) from Magnesia (Central Greece), and clinoptilolite zeolite from 'Beli Plast' mine (Bulgaria). Selected properties of the soil and zeolite are presented in Table 1. The soil was slightly acid with low contents of organic matter and phosphorus. The zeolite contained 70.1% SiO_2, 11.4% Al_2O_3, 0.78% Fe_2O_3, 0.13% TiO_2, 2.95% CaO, 0.37% MgO, 0.70% Na_2O, and 3.30% K_2O, while loss on ignition was 10.2%. A description of the methods used to estimate zeolite composition along with some additional data on the chemical properties of the zeolite from the same mine can be found elsewhere (Tarasevich et al., 1997).

2.2. Equilibrium of Pb retention by soil and zeolite

In order to determine the time necessary to obtain Pb sorption equilibrium, 4-g samples were suspended in 75 ml of 3 mM $Ca(NO_3)_2$ solution. One milliliter of 0.05 M $Pb(NO_3)_2$ solution was added and the pH adjusted to 3, 4, and 5 by adding 0.1 M HNO_3 or 0.01 M KOH as necessary. The suspensions were shaken at 25 ± 1 °C using an end-to-end shaker. After 1, 3, 5, 10, 24, 72, and 120 h the suspensions were allowed to settle for 1 h and solutions were sampled. The samples were filtered through a 0.2-μm membrane filter and lead concentration was measured with atomic absorption spectroscopy. The solution pH was monitored in the same intervals and adjusted to the initial values by titration with 0.1 M HNO_3 or 0.05 M KOH. Sorbed Pb amount was calculated as the difference between the amount of Pb added and the amount recovered in the supernatant solutions. The period necessary to obtain constant Pb concentration in the solution was used as the time required to obtain sorption equilibrium in subsequent experiments.

2.3. Lead retention isotherms

The batch sorption isotherm study was conducted according to the procedure similar to that described by Ponizovsky et al. (2001). Four-gram soil samples were suspended in 50 ml of 3 mM $Ca(NO_3)_2$ background solution in 100 ml conic flasks. From 0.5 to 10 ml of 25 mM $Pb(NO_3)_2$ were then added. An additional suspension, without $Pb(NO_3)_2$, was taken as a control. The pH was adjusted to 3, 4, or 5 by adding 0.05 M HNO_3 or 0.04 M KOH, and the samples were shaken at 25 ± 1 °C for 2 days. The pH was re-adjusted in 2 h and 1 day by titration with HNO_3 or KOH. The suspensions were centrifuged and supernatant solutions were sampled. Samples were filtered through 0.2-μm membrane filter.

Pb, Ca, and Mg were determined in supernatant solutions with atomic absorption spectroscopy. Concentrations of K and Na were measured by flame photometry. The amount of Pb retained was estimated as the difference between the Pb added and that remaining in solution at equilibrium basing on measured concentrations and actual volumes of the solutions. The amounts of Ca, K, and Na displaced by Pb were calculated

Table 1
Selected properties of soil and zeolite

Sample	pH (H_2O)	Organic matter (%)	P[a] (mg kg^{-1})	Clay (%)	Silt (%)	Sand (%)	CEC (cmol(+) kg^{-1})	Exchangeable cations[b]			
								K^+ (cmol(+) kg^{-1})	Na^+ (cmol(+) kg^{-1})	Ca^{2+} (cmol(+) kg^{-1})	Mg^{2+} (cmol(+) kg^{-1})
Soil	5.67	0.84	5.15	18	30	52	7.39[c]	0.32	0.08	3.57	0.29
Zeolite	7.65	–	–	–	–	–	118[b]	33.4	16.9	64.8	2.69

[a] Extraction with 0.5 M $NaHCO_3$, pH 8.5, according to Olsen et al. (1954) method.

[b] NH_4OAc, pH 7.0.

[c] NaOAc, pH 8.2.

as the differences between the amounts found in the supernatant solution of the suspension with added $Pb(NO_3)_2$ and in the control with the same pH without $Pb(NO_3)_2$. The amount of H^+ displaced from the soil due to Pb^{2+} sorption was calculated from the amounts of HNO_3 or KOH used to adjust pH.

To determine Pb desorption from the treated samples, the residues obtained after centrifugation were transferred from the centrifuge flasks with 50 ml of 3 mM $Ca(NO_3)_2$ solution to 100 ml conic flasks. Then pH was adjusted and suspensions were mixed as mentioned above. After 2 days, the suspensions were centrifuged, and the samples of supernatant solutions were filtered and analyzed.

Isotherms of Pb sorption by zeolite were obtained with the same procedure differed only in using 2-g samples suspended in the background solution, and adding of more concentrated 200 mM $Pb(NO_3)_2$ in the amounts of 0, 0.5, 1, 2, 3, and 5 ml. More concentrated $Pb(NO_3)_2$ was applied since zeolite strongly sorbed Pb decreasing solution concentration up to the levels close to detection limit of atomic absorption spectroscopy. The above amounts of $Pb(NO_3)_2$ added enabled to obtain Pb concentrations in the equilibrium solution close to those observed in soil suspensions with additions of 25 mM $Pb(NO_3)_2$.

Chemical equilibrium calculations were performed using RAME software (Mironenko et al., 1996) with constants compiled by Sauvé et al. (1998).

3. Results

Only a minor increase in Pb retention was observed in soil suspensions shaken at constant pH after 48 h for the subsequent period up to 120 h. The sorption rate was highest at pH 5 (approximately 95% of the maximal Pb retention was observed in 2 h) and lowest at pH 3. In zeolite suspensions constant Pb level in the solutions was attained in 2 h. So, the period of 48 h was taken as sufficient to obtain quasi-equilibrium in all experiments.

Isotherms of Pb sorption and desorption by soil at pH 3, 4, and 5 are presented in Fig. 1a–c. The data are approximated by the Freundlich equation:

$$S_{Pb} = K(m_{Pb})^{\alpha}$$

where S_{Pb} and m_{Pb} are amount of lead(II) sorbed (mmol kg^{-1}) and Pb concentration (mmol l^{-1}) in the equilibrium solution, respectively; K and α are constants.

Higher pH enhanced sorption of Pb. Lead retention by soil was accompanied by the displacement of both Ca^{2+} and H^+ cations while the amounts of K^+, Na^+, and Mg^{2+} displaced were negligible (Fig. 1d–f). Linear regression was fitted to the data on the relationships between the amounts of displaced cations and sorbed Pb. Correlation coefficients of the regressions were 0.84–0.95. The slope of each regression equation is an estimate of the mean quantity of the ion displaced by 1 mol of lead. The obtained values together with their standard deviations for all the displaced ions are presented in Table 2. Such estimation of the amounts of H^+, Ca^{2+}, K^+, Na^+, and Mg^{2+} displaced from the soil by Pb is unaffected by acid–base buffer ability of soil and minerals dissolution since the starting point of linear regression is the value obtained in the blank without any addition of Pb but with the identical pH value (Ponizovsky et al., 2001).

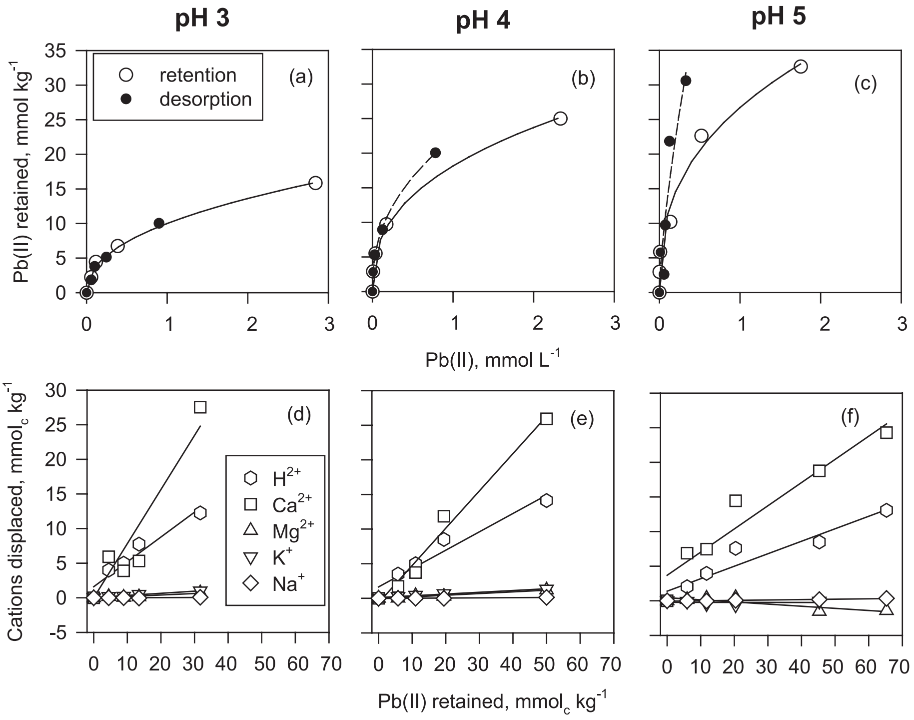

Fig. 1. Isotherms 25 °C of lead(II) retention by soil at pH 3 (a), 4 (b), and 5 (c) (lines—calculated with Freundlich equation), and dependences of the amounts of replaced cations on the amount of Pb(II) retained at the same pH values (d, e, and f, respectively).

As can be seen from Table 2, for each pH the sum of mean amounts of all the displaced cations per mol(+) of Pb retained was close to 1. The observed differences from 1 were statistically insignificant (*t*-test, $P=0.05$) and can be attributed to analytical errors. Thus, the amount of displaced ions was close to the amount retained.

Table 2

Amounts of cations displaced per mol$_c$ of lead(II) retained by soil and zeolite (mean ± S.D.)

Sample	pH	Ions displaced					
		K^+ (mol(+) mol(+)$^{-1}$)	Na^+ (mol(+) mol(+)$^{-1}$)	Mg^{2+} (mol(+) mol(+)$^{-1}$)	Ca^{2+} (mol(+) mol(+)$^{-1}$)	H^+ (mol(+) mol(+)$^{-1}$)	$\Sigma\mathrm{Kt}$[a] (mol(+) mol(+)$^{-1}$)
Soil	3	0.03 ± 0.005	0.002 ± 0.001	0.02 ± 0.005	0.78 ± 0.16	0.36 ± 0.06	1.19 ± 0.16
	4	0.03 ± 0.002	0.003 ± 0.001	0.02 ± 0.003	0.64 ± 0.04	0.27 ± 0.04	0.96 ± 0.06
	5	0.002 ± 0.007	0.01 ± 0.002	0.05 ± 0.018	0.67 ± 0.10	0.36 ± 0.06	0.99 ± 0.15
Zeolite	3	0.08 ± 0.006	0.09 ± 0.009	0.04 ± 0.0001	0.65 ± 0.03	0.04 ± 0.006	0.90 ± 0.02
	4	0.18 ± 0.01	0.15 ± 0.017	0.03 ± 0.002	0.71 ± 0.09	0.02 ± 0.003	1.00 ± 0.07
	5	0.08 ± 0.007	0.21 ± 0.04	0.03 ± 0.003	0.67 ± 0.05	0.03 ± 0.002	1.01 ± 0.05

[a] Sum of displaced cations.

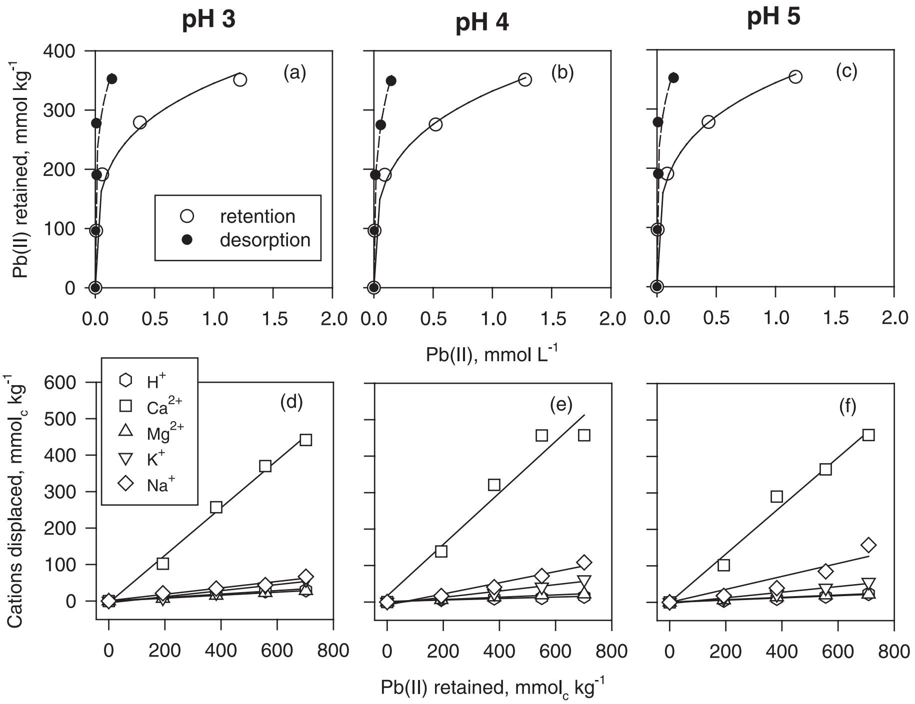

Fig. 2. Isotherms 25 °C of lead(II) retention by zeolite at pH 3 (a), 4 (b), and 5 (c) (lines—calculated with Freundlich equation), and dependences of the amounts of replaced cations on the amount of Pb(II) retained at the same pH values (d, e, and f, respectively).

Clinoptilolite sorbed much more Pb than soil and the sorbed amount was independent of pH (Fig. 2a–c). The retention was accompanied by displacement mainly of Ca^{2+} and small amounts of K^+ and Na^+ cations (Fig. 2d–f). The amounts of displaced H^+ and Mg^{2+} were negligible (Table 2). The sums of the displaced cations were close to the amount of Pb retained. Treatment of Pb-containing zeolite with $Ca(NO_3)_2$ solution did not result in any significant desorption of Pb(II).

Maximal sorption capacity of zeolite calculated based on the data presented in Fig. 2 using Langmuir adsorption equation (Alloway, 1995) appeared to be 360 mmol kg^{-1}.

4. Discussion

Lead retention in our experiments was not caused by precipitation of slightly soluble Pb salts. Lead carbonate $PbCO_3$ and base carbonate $3Pb(CO_3)_2 \cdot 2Pb(OH)_2$ are the least soluble salts of Pb besides sulfide and chloropyromorphite. Both carbonates precipitate only in alkali range of pH (Gmelins Handbook, 1961). Calculations based on the solubility constants of these salts using the RAME software (Mironenko et al., 1996) revealed that solutions used in this study were undersaturated with respect to both of these salts. Surface precipitation of them on the surface of soil particles can be also excluded due to the extremely low concentrations of OH^- and CO_3^{2-} ions at pH 3–5. Total content of phosphate in the soil samples (5.15 ppm or 0.17 mmol kg^{-1}) was much lower than the amount of sorbed Pb, so Pb was not retained due to precipitation of chloropyromorphite.

Based on the balance between sorbed and displaced ions, Pb sorption may be considered as an ion exchange since it is accompanied by the displacement of ions and the amounts of retained Pb and displaced cations are equivalent. So, it is not necessary to speculate about some changes in the surface charge or sorption of charged complexes. The exchange is not binary and involves three cations, namely $(H^+ + Ca^{2+})-Pb^{2+}$ at all the pH values. The ratio between the amounts of H^+ and Ca^{2+} displaced per mol(+) Pb^{2+} retained at all the pH values studied is close to 1/2 (Table 2). Similar results were obtained for lead retention on Chernozem, Dernovo-Podzolic, and Gray Forest soils (Ponizovsky and Mironenko, 2001b). Copper(II) sorption by soils is also accompanied by simultaneous displacement of these two cations (Ponizovsky et al., 2001). Displacement of H^+ ions may be a common phenomenon for the retention of trace metals in the soils.

Some hysteresis between sorption and desorption isotherms is observed in Fig. 1a–c. It increases with the increase in solution pH. This hysteresis may be attributed to the different rates of sorption and desorption processes as it was suggested by Strawn and Sparks (2000), assuming that 2-day period may be not sufficient to attain complete desorption equilibrium. Sorbate may undergo some transformation and being transformed may slower interact with the species in the solution. The composition and properties of forming surface complex may be affected by solution pH.

Clinoptilolite sorbed 10–20 times more Pb than the same mass of soil, and only a small portion of Pb was released while the treated sample was exposed to fresh Pb-free background solution. Lead sorption by zeolite was accompanied by the release of mainly Ca^{2+} and minor amounts of Na^+ and K^+. The process was irreversible or with a very strongly emphasized hysteresis (Fig. 2a–c). Cation exchange capacity of clinoptilolite is about 16 times larger than that of the soil (Table 1). However, not only the quantity of the element sorbed but the sorption mechanism is very different: zeolite strongly binds Pb^{2+} ions within the crystal (Barrer, 1978; Tarasevich et al., 1997).

Sorption is independent on pH for zeolite where we did not observe any displacement of H^+. So, the impact of pH on Pb retention may be attributed to the shift of H^+-Pb^{2+} exchange equilibrium.

Application of zeolite leads to a decrease of Pb concentrations in soil solution retaining the metal in the solid phase, where it should be less available for plants. Calculations basing on the value of maximal sorption capacity of zeolite reveal that 1% added zeolite can retain 3.6 mmol Pb kg^{-1} or 750 mg kg^{-1} soil. Advantage of zeolite for soil amelioration is its high efficiency independent on soil pH in the pH range 3–5.

A practical consequence of the dependence of sorbed Pb on solution pH is the necessity to stabilize this parameter while obtaining sorption isotherms.

5. Conclusions

Lead sorption by Alfisol is accompanied by simultaneous displacement in the solution of both Ca^{2+} and H^+ in the amounts close to the quantities of Pb sorbed. So, the process may be assumed as a three-cation ion exchange. Hysteresis between sorption and desorption isotherms obtained within a 2-day shaking of soil-solution suspensions increased with the increase in pH. Clinoptilolite zeolite sorbed Pb in the amounts about 20–30 times higher than the soil. Lead sorption by zeolite was accompanied by the displacement mainly of Ca^{2+} and minor amounts of Na^+ and K^+. Lead sorbed by zeolite could not be displaced by the applied low concentrations of Ca^{2+} in batch experiments. The results indicate that Pb retention by both Alfisol and zeolite may be assumed as an ion exchange process with strong (soil) or very strong (zeolite) specific binding of Pb.

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References

Alloway, B.J., 1995. Soil processes and the behaviour of metals. In: Alloway, B.J. (Ed.), Heavy Metals in Soils, 2nd ed. Blackie Academic & Professional, Glasgow, pp. 11–37.

Barrer, R.M., 1978. Zeolites and Clay Minerals as Sorbents and Molecular Sieves Academic Press, New York. 497 pp.

Bolt, G.H., Bruggenwert, M.G.M., Kamphorst, A., 1978. Adsorption of cations by soil. In: Bolt, G.H., Bruggenwert, M.G.M. (Eds.), Soil Chemistry. B. Basic Elements. Elsevier, Amsterdam, pp. 54–90.

Gmelins Handbuch der anorganischen Chemie, 1961. 8. Auflage. B.47. Teil C 4. Lieferung 1. S.200, Lieferung 2. S. 704. (Ge).

Kabata-Pendias, A., Brümmer, G.W., 1992. Ecological consequences of As, Cd, Hg, and Pb enrichment in European soils. In: Hutchinson, T.C., Meema, K., Gordon, K. (Eds.), Global Perspectives on Lead, Mercury, and Cadmium Cycling in Environment. Wiley Eastern, New Delhi, pp. 107–114.

Kabata-Pendias, A., Pendias, H., 1992. Trace Elements in Soils and Plants CRC Press, London. 365 pp.

Kalbasi, M., Peryea, F.J., Lindsay, W.L., Drake, S.R., 1995. Measurement of divalent lead activity in lead arsenate contaminated soils. Soil Sci. Soc. Am. J. 59, 1274–1280.

Leppert, D., 1990. Heavy metal sorption with clinoptilolite zeolite: alternatives for treating contaminated soil and water. Min. Eng. 42, 604–608.

Ma, L.Q., 1996. Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite. J. Environ. Qual. 25, 1420–1429.

Ma, Q.Y., Traina, S.J., Logan, T.J., 1992. Effects of ligands on hydroxiapatite-induced immobilization of aqueous Pb. Agronomy Abstracts. ASA, Madison, p. 47.

Ming, D.W., Mumpton, F.A., 1989. Zeolites in soils. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environment, 2nd ed.SSSA Book Series, pp. 874–911. Madison, WI.

Mironenko, E., Ponizovsky, A., Studenikina, T.A., 1996. Chemical equilibrium model in soils containing heavy metals, low-molecular weight organic acids and fulvic acids. Heavy Metals in the Environment, International Symposium, Pushchino, Russia, pp. 153–154. Ru.

Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ., vol. 939. US Gov. Print. Office, Washington, DC.

Ponizovsky, A., Mironenko, E., 2001a. Speciation and sorption of lead(II) in soils. In: Iskandar, I.K., Kirkham, M.B. (Eds.), Trace Elements in Soil: Bioavailability, Flux, and Transfer. CRC Press, pp. 257–275.

Ponizovsky, A., Mironenko, E., 2001b. Lead(II) retention by soils at pH 4 to 6. Pochvovyedeniye, 25–34 (Ru).

Ponizovsky, A.A., Studenikina, T.A., Mironenko, E.V., Kingery, W.L., 2001. Copper(II) retention by Chernozem, Dernovo-Podzolic, and Gray Forest soils: pH effect and cation balance. Soil Sci. 166, 239–249.

Rabinovitz, M.B., 1993. Modifying soil lead bioavailability by phosphate addition. Bull. Environ. Contam. Toxicol. 51, 438–444.

Sauvé, S., McBride, M.B., Hendershot, W.H., 1998. Lead phosphate solubility in water and soil suspensions. Environ. Sci. Technol. 32, 388–393.

Sauvé, S., Martinez, C.E., McBride, M.B., Hendershot, W.H., 2000. Adsorption of free lead (Pb^{2+}) by pedogenic oxides, ferrihydrite, and leaf compost. Soil Sci. Soc. Am. J. 64, 595–599.

Strawn, D.G., Sparks, D.L., 2000. Effect of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. Soil Sci. Soc. Am. J. 64, 144–156.

Tarasevich, Yu.I., Kardashova, M.B., Polyakov, V.E., 1997. Selectivity of ion exchange on clinoptilolite. Kolloid-Z 59 (6), 813–818 (Ru).

Tills, A.R., Alloway, B.J., 1983. The speciation of lead in soil solution of very polluted soils. Environ. Technol. Lett. 4, 529–533.

Tsadilas, C.D., 2000. Effect of soil pH on the distribution of heavy metals among soil fractions. In: Iskandar, I. (Ed.), Environment Restoration of Metals Contaminated Soils. Lewis Publishers, pp. 107–119.

Tsadilas, C.D., Dimoyiannis, D.G., Samaras, V., 1997. Effect of zeolite application and soil pH on cadmium sorption in soils. Commun. Soil Sci. Plant Anal. 28 (17–18), 1591–1602.

Tsitsishvili, G.B., Andronikashvili, T.G., Kirov, G.N., Filizova, L.D., 1985. Natural Zeolites Khimiya Publishers, Moscow. Ru.

Zyrin, N.G., Serdyukova, A.V., Sokolova, T.A., 1986. Lead sorption and speciation of the sorbed element in soils and soil constituents. Pochvovedeniye 39 (3), 47–54 (Ru).