VERSITA
DOI: 10.2478/ssa-2013-0022

SOIL SCIENCE ANNUAL
Vol. 64 No. 4/2013: 140–144

JOLANTA DOMAŃSKA*, TADEUSZ FILIPEK, MONIKA KWIECIEŃ

University of Life Sciences in Lublin, Department of Agricultural and Environmental Chemistry, ul. Akademicka 15, 20–950 Lublin

Speciation of Cd and Pb in organic soil treated with municipal sewage

Abstract: The studies were carried out on the basis of field experiment. The purpose of this study was to determine the effect of purified municipal sewage, applied in single (optimal for plant growth) and double doses, on the content of Cd and Pb, and its chemical speciation in organic neutral soil. The sequential extraction procedure was used to separate Cd and Pb from soil into 5 operationally defined fractions: exchangeable F1, "carbonate bound" – specifically bound F2, bound to Fe-Mn oxides F3, bound to organic matter F4, and residual F5. The total content of Pb in reference soil and in soils treated with sewage was lower than permissible values accepted in Poland for natural soils, while the content of Cd exceeded the highest acceptable level for natural organic soils. The Cd association with different geochemical fractions, both in soil fertilized with sewage, and unfertilized (control) soils, followed the order [%]: F3>F2>F4>F1≥F5. Cadmium was associated mainly with F3 (51–60%) and F2 (23–26%) fractions, while 6–8% was stated in exchangeable form (F1). Speciation distribution of Pb was lined up in the order [%]: F3>F4>F2>F5>F1. Lead was retained mainly in F3 (46–56%), F4 (21–30%) and F2 (10–13%) fractions. In soils treated with sewage there were stated the higher amounts of metals bound to organic fraction compared to reference soil.

Key words: cadmium, lead, fractions, organic soil, purified sewage, sequential analysis

INTRODUCTION

Municipal sewage used for fertilization and irrigation of field crops and grasslands is one of the sources of metals (Cd, Pb, etc.) in the environment. This type of recycling of sewage purified to a different degree can largely satisfy plant's demand for water and minerals, and also provides a positive aspect in the protection of surface waters against contamination with biogenic compounds (Olek and Filipek 1996). Some negative result of municipal sewage applying is a soil pollution by toxic substances, especially heavy metals, which when introduced into the soil, may undergo various transformations. A major threat to natural ecosystems appears when concentrations of their active forms increases. Toxicity and mobility of metals in soils depend on many factors, e.g. their total content, speciation, and forms of occurrence, especially pH and organic matter content.

The aim of the study was to determine the content of total and chemical speciation of Cd and Pb in organic soil treated with purified municipal sewage. Determination of Cd and Pb speciation in soil fertilized with sewage, may be helpful in the study of metal mobility, possibility of their mobilization in the soil under the influence of sewage, and uptake by plants.

METHODS

The study was based on the results from a 3-year field experiment carried out in an experimental facility in Hajdów near Lublin (E Poland). The experiment was located in the valley of Bystrzyca river and covered an area of about 8 hectares. The experiment was conducted on Fibric Histosols (Commission V Genesis, Classification and Cartography of Soils PTG 2011). Soil properties before the experiment foundation are summarized in Table 1. The experimental field was divided into seven blocks, and each block into 3 objects – A, B, C. Following plant species were grown in irrigated objects: poplar (*Populus nigra* and *Populus alba*), willow (*Salix americana*) and osier (*Salix viminalis*), maize (*Zea mays*), hemp (*Cannabis sativa*), spring rapeseed (*Brassica napus ssp. oleifera*), as well as two grass mixtures (I – for wet habitats and II – for optimally wet habitats). The species composition of mixture I was following: meadow foxtail (*Alopecurus pratensis* L.), reed canarygrass (*Phalaris arundinacea* L.), tall fescue (*Festuca arundinacea* L.), meadow fescue (*Festuca pratensis* L.), Kentucky bluegrass (*Poa pratensis* L.), creeping bentgrass (*Agrostis alba* L.), fowl bluegrass (*Poa palustris* L.), and perennial ryegrass (*Lolium perenne* L.), while mixture II was composed of: meadow foxtail

*email: jolanta.domanska@up.lublin.pl

TABLE 1. Selected properties and concentration of metals in soil used for the study

pH_{KCl}	Organic matter (%)	Total N (%)	N easily hydrolizing ($mg \cdot kg^{-1}$)	Available forms ($mg \cdot kg^{-1}$)			Total content ($mg \cdot kg^{-1}$)	
				P	K	Mg	Pb	Cd
7.2	33	1.62	668.5	786	183	1662	56.0	5.9

TABLE 2. Doses of sewage in field experiment

Plants	Doses of sewage during vegetation period (mm)		
	A – control	B – best for plant	C – double best
Poplar	0	900	1800
Willow	0	750	1500
Corn	0	750	1500
Hemp	0	600	1200
Rape	0	450	900
Grass mixture	0	600	1200

(*Alopecurus pratensis* L.), meadow fescue (*Festuca pratensis* L.), orchard grass (*Dactylis glomerata* L.), timothy (*Phleum pratense* L.), Kentucky bluegrass (*Poa pratensis* L.), fowl bluegrass (*Poa palustris* L.) and perennial ryegrass (*Lolium perenne* L.). Each plant or grass mixture was grown in three objects: A – control, B – single sewage dose (determined on a base of N and water loads) optimum for a given species, C – double sewage dose (Table 2). Sewage used for treatment was derived from municipal wastewater treatment plant "Hajdów" in Lublin. After harvesting, the unit soil samples, being a basis for preparing the analytical sample, constituted the material for study. The analytical sample was subject to determine the contents of Cd and Pb in particular fractions operationally defined by the method Tessier et al. (1979) (Table 3), and the total contents of these metals in soil according to PN-ISO 11466. Total contents of Cd and Pb were determined by means of soil samples digestion in *aqua regia* (3:1 HCl:HNO_3 acids ratio). Percentage of a given metal fraction in soil was calculated relative to the sum of all its factions. Concentrations of metals in the soil filtrates were determined using flame technique in atomic absorption spectrophotometer. The soil samples used for the experiment were subject to determination of pH – potentiometrically in 1 mol $KCl \cdot dm^{-3}$, organic matter content – by annealing (Bednarek et al. 2004), contents of available phosphorus and potassium – by means of Egner-Riehm method, while content of available magnesium – applying Schachtschabel method.

The degree of soil contamination with Cd and Pb was determined on the basis of the total Cd and Pb contents in soil according to a 6-point scale: 0 – natural content, I – increased content, II – low contamination, III – moderate contamination, IV – heavy contamination, V – very heavy contamination (Kabata-Pendias et al. 1993).

RESULTS AND DISCUSSION

Contents of fundamental nutrients in 1 dm^3 of sewage was as follows: N–NO_3 – 35 mg; N–NH_4 – 4.0 mg; N–Nog – 43.0 mg, P–PO_4 – 4 mg; K – 30 mg; Mg – 10 mg, whereas heavy metals concentrations in 1 dm^3 of sewage were: Pb<0.5 mg, Cd<0.1 mg, Cu<0.5 mg, Zn<2.0 mg.

TABLE 3. Operationally defined fractions of heavy metals

Stage	Fraction	Reagent
1	Exchangeable (F1)	1 mol $MgCl_2 \cdot dm^{-3}$, pH 7
2	"Carbonate-bound" (F2)	1 mol $CH_3COONa \cdot dm^{-3}$, pH 5
3	Fe-Mn oxide bound (F3)	0.04 mol $NH_2OH \cdot HCl \cdot dm^{-3}$ in 25% acetic acid
4	Organic (F4)	0.02 mol $HNO_3 \cdot dm^{-3}$ and 30% H_2O_2
5	Residual (F5)	$HClO_4$ – HF

TABLE 4. Fractions of metals (Cd, Pb) in soil irrigated with purified sewage water

Object	Metal	Fractions ($mg \cdot kg^{-1}$)							Total ($mg \cdot kg^{-1}$)[1]	Recovery %[2]
		F1	F2	F3	F4	F5	F1-F4	F1-F5		
A	Cd	0.3	1.0	2.4	0.4	0.3	4.1	4.4	5.9	73.4
B		0.4	1.4	2.8	0.6	0.3	5.2	5.5	6.3	87.8
C		0.2	1.0	2.6	0.5	0.0	4.3	4.3	5.6	77.1
A	Pb	2.1	4.8	23.2	9.0	2.5	39.1	41.6	57.0	72.9
B		2.1	5.4	19.2	12.2	2.5	38.9	41.4	54.0	76.6
C		2.1	4.5	24.0	9.6	3.5	40.2	43.7	57.0	76.6

[1]analyzed after the digestion of soil samples in the mixture of concentrated acids HCl and HNO_3 in the ratio of 3:1 (*aqua regia*). [2]ratio (%) of metal fraction sum determined by means of Tessier method to its total content determined in *aqua regia.*

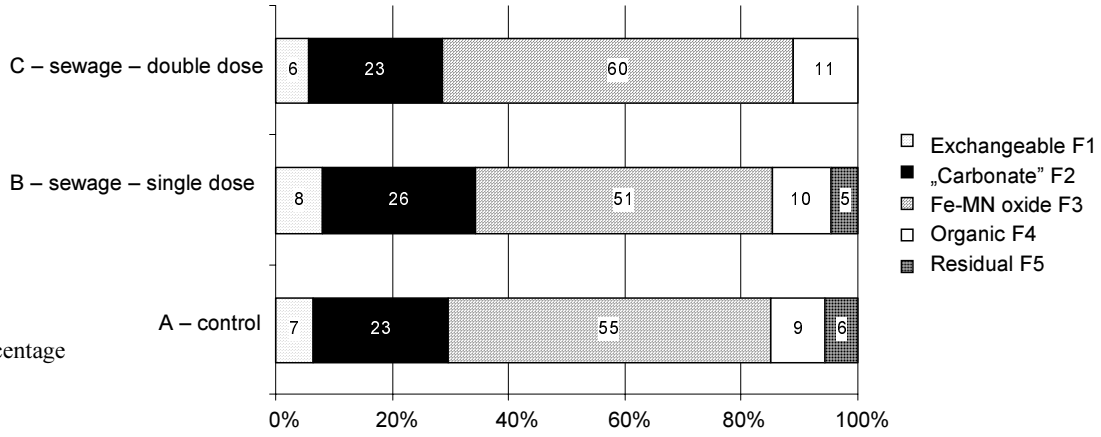

FIGURE 1. Percentage of Cd fractions in soil

The total lead content (Table 4) in the tested organic soil developed from low peat was higher than the average concentration of this metal in Polish organic soils (Kabata-Pendias and Pendias 1999), and it did not exceed 70 mg·kg^{-1}, which is recognized a natural (degree 0) for this type of soil according to the guidelines by Kabata-Pendias et al. (1993). In contrast, the total cadmium content determined in aqua regia exceeded the quantitative standards set for the metal, which according to the assessment proposed by Kabata-Pendias et al. (1993), classified analyzed soils as moderately contaminated (degree III). Total content of Cd and Pb in soils from objects fertilized with purified sewage was similar to their amounts in the soil of the control object (A). Aqua regia proved to be a stronger reagent dissolving the studied soil than reagents used in Tessier method, which allowed to extract approximately 72–88% of the total Cd and Pb.

Based on the results of the sequential extraction according to method by Tessier et al. (1979) (Figure 1), it was found that both in intact soil (object A) and soils fertilized with a single (B) and double (C) doses of purified sewage, the percentage of cadmium in relation to the sum of tested fractions was lined up in the following sequence [%]: F3>F2>F4>F1≥F5. Achieved results show that even 94–100% of cadmium in soil was associated with potentially mobile fractions (F1–F4). The largest amounts of Cd were found in F3 (51–60%) and F2 form (23–26%), whereas exchangeable fraction F1, which was the most bioavailable, accounted for 6–8%. Such high proportion of the metal in potentially mobile forms could encourage its uptake by the test plants, and especially by those species that produced a high yield of biomass per unit area.

The amount of lead bound to fractions F1, F2, F3, F4, and F5 obtained by Tessier method, regardless of the analyzed object (A, B or C), hence doses of treated municipal sewage, formed the following decreasing series (Figure 2): F3>F4>F2>F5>F1. In this range, from 92 to 94% of that amount was made up by lead bound to potentially mobile fractions of the soil (F1–F4). For comparison, in mineral soils contaminated due to the smelting industry, Gworek et al. (2004) reported value of 85% Pb in fractions F1–F4. Lead was mainly present in fraction F3 (46–56%) and F4 (21–30%) of the test peat soil. Proportion of the carbonate form was also high (10–13%), which was favored as in the case of cadmium, by neutral pH of soil abundant in carbonates. The lowest percentage of Pb was composed by F1 fraction (2.1 mg·kg^{-1}). Such an amount of fraction easily available for plants

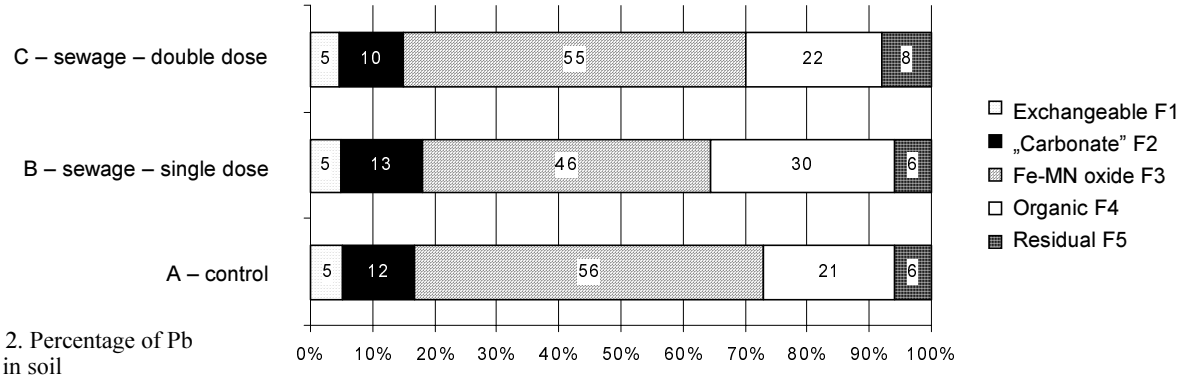

FIGURE 2. Percentage of Pb fractions in soil

can pose a risk of an excessive uptake of the metal by plants. This value is above allowable limit for the mobile fraction, which is set in Sweden for 1.0 mg $Pb \cdot kg^{-1}$ (Lucho-Constantino et al. 2005).

The high abundance of the test soil in organic matter contributed to the accumulation of metals in the organic fraction (F4). The greater amount of lead (21–30%), as compared with cadmium (9–11%) bound to F4 results from a strong affinity of lead to organic matter, which is expressed by the formation of complex connections between this metal and organic compounds in the soil. This is confirmed by numerous results of Pb speciation in soils and sediments (Domańska 2008; Lucho-Constantino et al. 2005; Tarchouna Gharbi et al. 2010; Wysokiński and Kalembasa 2012).

The use of treated municipal sewage resulted in fluctuations in the share of various Cd forms depending on a sewage dose, although the difference in Cd content within a given fraction between the objects fertilized with sewage (B, C) and control (A) was less than 1.0 $mg \cdot kg^{-1}$. Applied sewage could affect the value of determined soil contamination indicators as a source of metals, and on the other hand, as a factor stimulating the plant growth, metal uptake, and thereby reducing their quantities in the soil. After applying the sewage at the optimum dose, contents of carbonate and organic forms of lead increased, while in double-irrigated object, primarily the increase in Pb concentration in the form of residue was observed. Proportion of other lead forms was similar to their contents in the control object. Treated municipal sewage used in the field objects for plant fertilization, in addition to nutrients, also contained heavy metals and were a source of soluble organic compounds, so-called DOC (Dissolved Organic Carbon). In objects fertilized with sewage, it could promote the accumulation of Cd and Pb in organic fraction, which was confirmed by the observed increase of metals quantities in this fraction after sewage application. Tarchouna Gharbi et al. (2010), during studies upon many-year irrigation using purified sewage, found that lead was bound equally in all fractions, copper in organic fraction, whereas chromium was found mainly in reductive fraction after the use of sewage. High affinity of Pb to fulvic acid fraction was also shown (Tarchouna Gharbi et al. 2010), which according to the authors can increase the mobility of organically bound lead. According to Karczewska (1995), in contaminated soils, which are subject to periodic inflow processes, partial release of metals such as Cu, Pb, and Zn can occur, and neutral soil pH probably does not protect against such mobilization. In contrast, Lucho-Constantino et al. (2005) demonstrated a significant correlation between the time of hydration, lead content (total, exchangeable fraction, and fraction bound to organic matter and sulfides), as well as organic carbon.

To conclude, the tested soils showed a significant percentage of metals in potentially bioavailable fractions, which in the case of changes in conditions (acidity, redox processes) may result in the release of metals and increase their mobility and bioavailability.

CONCLUSIONS

1. The total content of lead in soil from experimental field objects corresponded to natural values, while the amount of cadmium exceeded permissible standards set for organic soils according to Kabata-Pendias et al. (1993).
2. The sum of Cd and Pb fractions reported by Tessier was lower than the total contents of each metal determined by means of extraction using *aqua regia*.
3. Results of chemical fractionation of Cd and Pb in soils developed from low peat, both in objects fertilized with purified sewage as well as from control object, provide the following lineup percentage content of particular fractions in descending order: F3>F2>F4>F1≥F5– cadmium, F3>F4>F2>F5>F1 – lead.
4. Treated municipal sewage as a source of easily soluble organic compounds may affect the binding of Cd and Pb in organic fraction, which is confirmed by the increase in the amount of metals in that soil fraction in objects fertilized with sewage.
5. Speciation results indicate that in the test organic neutral soil developed from low peat, proportions of cadmium and lead in the individual fractions were dependent greatly on the soil properties (presence of carbonates, organic matter content) and biogeochemical properties of metals.

ACKNOWLEDGMENTS

The results presented in this paper were obtained as part of the research project PBZ/31–03 funded by Ministry of Science and Higher Education.

REFERENCES

Bednarek R., Dziadowiec H., Pokojska U., Prusinkiewicz Z., 2004. Badania ekologiczno-gleboznawcze. PWN, Warszawa: 103–104.

Domańska J., 2008. Sequential fractionation of Pb in contaminated and non–contaminated soils. Polish Journal of Soil Science 41 (2): 120–126.

Gworek B., Kwapisz J., Jeske K., 2004. Przydatność metody ekstrakcji sekwencyjnej do oceny efektywności fitoremediacji gleb zanieczyszczonych miedzią i ołowiem. Roczniki Gleboznawcze 55 (1): 143–152.

Kabata-Pendias A., Motowicka-Terelak T., Piotrowska M., Terelak H., Witek T., 1993. Ocena stopnia zanieczyszczenia gleb i roślin metalami ciężkimi i siarką. P(53), IUNG Puławy: 1–20.

Kabata-Pendias A., Pendias H., 1999. Biogeochemia pierwiastków śladowych. PWN, Warszawa: 375 s.

Karczewska A., 1995. Przemiany form metali w zanieczyszczonych glebach stref ochrony sanitarnej hut miedzi pod wpływem zawodnienia. Zeszyty Problemowe Postępów Nauk Rolniczych 418: 487–493.

Commission V Genesis, Classification and Cartography of Soils PTG, 2011: Systematyka Gleb Polski, wyd. 5, Roczniki Gleboznawcze – Soil Science Annual 62(3): 1–193.

Lucho-Constantino C.A., Álvarez-Suárez M., Beltrán-Hernández R.I., Prieto-García F., Poggi-Varaldo H.M., 2005. A multivariate analysis of the accumulation and fractionation of major and trace elements in agricultural soils in Hidalgo State, Mexico irrigated with raw wastewater. Environment International 31: 313–323. DOI:10.1016/j.envint.2004.08.002.

Olek J., Filipek T., 1996. Ocena zawartości metali ciężkich w glebach organicznych nawadnianych ściekami miejskimi Lublina. Zeszyty Problemowe Postępów Nauk Rolniczych 437: 299–304.

Tarchouna Gharbi L., Merdy P., Lucas Y., 2010. Effects of long–term irrigation with treated wastewater. Part II: Role of organic carbon on Cu, Pb and Cr behaviour. Applied Geochemistry 25: 1711–1721. DOI:10.1016/j.apgeochem.2010.09.002.

Tessier A., Campbell P.G.C., Bisson M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry 51 (7): 844–851.

Wysokiński A., Kalembasa S., 2012. Fractions of lead and cadmium in sewage sludge composted with addition of calcium oxide and power station ashes. Ecological Chemistry and Engineering. A.; 19 (11): 1321–1330. DOI: 10.2428/ecea.2012.19(11)126.

Received: October 21, 2013
Accepted: January 17, 2014

Specjacja Cd i Pb w glebie organicznej nawożonej ściekami miejskimi

Streszczenie: Badania przeprowadzono w oparciu o wyniki uzyskane z eksperymentu polowego. Celem badań było określenie wpływu oczyszczonych ścieków miejskich, zastosowanych w dawce pojedynczej, optymalnej dla danej rośliny (ustalona w oparciu o ładunek N i wody) i podwójnej dawce ścieków na zawartość i specjację Cd i Pb w glebie organicznej obojętnej. W pobranych z każdego obiektu, uśrednionych próbach glebowych, oznaczono zawartość ogółem Cd i Pb oraz specjację tych metali. Wyodrębniono 5 frakcji Cd i Pb zdefiniowanych operacyjnie: wymienną (F1), węglanową określaną jako „związaną specyficznie" (F2), związaną z tlenkami Fe–Mn (F3), organiczną (F4) i pozostałości (F5). Stwierdzono, że całkowita zawartość ołowiu w badanej glebie odpowiadała wartościom naturalnym, zaś ilość kadmu przekraczała dopuszczalne normy ustalone dla gleb organicznych. Wyniki chemicznego frakcjonowania Cd i Pb w glebie wytworzonej z torfu niskiego, zarówno z obiektów nawożonych oczyszczonymi ściekami, jak i z obiektu kontrolnego przedstawiają następujące uszeregowanie procentowych zawartości poszczególnych frakcji w kolejności malejącej: F3>F2>F4>F1≥F5 – kadm, F3>F4>F2>F5>F1 – ołów. Oczyszczone ścieki miejskie, będące źródłem łatwo rozpuszczalnych związków organicznych, mogą wpływać na wiązanie Cd i Pb we frakcji organicznej, co potwierdza odnotowany w badaniach wzrost ilości metali w tej frakcji w glebie.

Słowa kluczowe: kadm, ołów, frakcje, gleba organiczna, ścieki oczyszczone, sekwencyjna ekstrakcja