CHEMICAL SPECIATION ANALYSIS OF MICROMETALS IN SOILS

Helvi HÖDREJÄRV, Anu VIITAK, and Aini VAARMANN

Tallinna Tehnikaülikool (Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)

Abstract. A sequential chemical extraction was used to speciate Pb, Cu, and Mn in a forest soil, roadside soil, and oil-shale fly ash, a common atmospheric deposit in northeastern Estonia. The concentration of metals in the extracts was determined by atomic absorption analysis in the air–acetylene flame. The solubility of the compounds of lead and manganese is correlated with the humic matter in soil. In roadside soil the solubility of the lead compounds is remarkable at pH 4.8, indicating the presence of oxides, hydroxides, and/or carbonates of lead. Copper remains in a notable concentration insoluble and seems to be a part of the relatively insoluble silicate minerals. The solubility of Pb, Cu, and Mn is low in oil-shale ash as compared to the studied soils.

Key words: speciation analysis, microelements, soil, fly ash.

The heavy metals found in soils are important from the viewpoint of agricultural need for microelements as well as their ecological impact. In both cases, the most important properties of heavy metals are their mobility and bioavailability. The mobility of heavy metals depends on the chemical compounds in which they occur in the soil. Simultaneously, the existing chemical forms of the elements are influenced by the soil characteristics: soil type, pH of the soil solution, the content of organic matter, ion exchange capacity, E_h, ionic strength of the soil solution. The identification of the chemical compounds of the metals in soil is difficult and it is usually carried out by the chemical speciation analysis. The term speciation has been defined as the determination of a specific form (monoatomic or molecular) or configuration in which an element can occur or as a distinct group of atoms consistently present in different matrices [1]. The speciation of metals in soils and sediments has been carried out by chemical extraction procedures and is designed to differentiate between the exchangeable, carbonating, reducible (hydrous Fe/Mn oxides), oxidizable (sulphides and organic phases), and residual

fractions [2]. Speciation, in the functionally defined sense, was widely used in agriculture long before the term speciation was introduced. It was used mainly to predict and assess element deficiency or toxicity in crops or animals eating them by means of analysing soil extracts. At the same time, the most often used extractants in agrochemistry are weak neutral salt solutions such as calcium chloride, ammonium acetate, and/or ammonium acetate mixed with EDTA. The use of such solutes involves analytical difficulties because of the low concentrations of trace elements in the extracts.

The problem of the mobility and bioavailability of heavy metals is particularly important in northeastern Estonia, where the oil-shale ash pollutes the environment with a large spectrum of heavy metals [3]. Information on the further fate of the heavy metals incorporated in soil is almost entirely missing. We made an attempt to study the behaviour of heavy metals in soil using speciation analysis. Extractable amounts of lead, copper, and manganese, as percentage of the total concentration of the elements in the analysed samples, were determined. Analyses were made for a forest soil sample from Kaarma, Lääne-Viru County, for a roadside soil from the city of Tallinn, and for fly ash of oil shale as a typical atmospheric deposit in the oil-shale region.

EXPERIMENTAL PART

1. Description of the experimental objects

(A) Soil samples from Kaarma, Lääne-Viru County. A forest soil profile of 0–50 cm. Samples were collected and prepared by a research group of Tartu Agricultural University.
(B) Soil samples from the city of Tallinn. A soil profile of 0–20 cm, 20 m from the road with a traffic density of 4000–10000 vehicles per day.
(C) Oil-shale fly ash. Collected and prepared by a research group of the Thermal Engineering Department, Tallinn Technical University.

2. Methods

The speciation was carried out by sequential extraction of the samples with five different solutions (Table 1). The concentrations of heavy metals in the extracts were determined by conventional atomic absorption analysis (AAS spectrometer SP9 700 Pye Unicam, air–acetylene flame system, standard solutions of Merck). The total concentration of heavy metals was analysed by AAS, after melting the samples with sodium carbonate, eliminating the silicon with hydrofluoric acid, and dissolving the sample in hydrochloric acid.

Table 1

Solutions used for the sequential extraction of heavy metals

No. of step	Extractant	Operational phase of heavy metals
I	EDTA 0.05 M, pH 10 ($NH_3 \cdot H_2O/HCl$)	Exchangeable and loosely bound elements
II	Ammonium acetate 1 M, pH 4.8 (CH_3COOH)	Adsorbed elements, carbonates
III	Hydroxylamin-chloride 1 M, pH 2.4 (HCl)	Easily reducible elements
IV	Ammonium oxalate 0.2 M, pH 3.0 ($H_2C_2O_4$)	Reducible elements
V	Hydrogen peroxide 15%, pH 1.3 (HNO_3)	Easily oxidizible elements

For the preparation of the extracts 1 g of the sample, finely ground and dried at 40°C, was taken for the sequential extraction with five different extractants; 20 ml of the first extractant (step I, Table 1) was added. The pH value of the suspension was regulated with the reagent shown in parentheses in Table 1. The suspension was left over night, pH was checked again and regulated if needed. The suspension was shaken for six hours in a closed polyethylene vessel. The next morning the solution was separated and the concentration of heavy metals in it was determined by AA-spectroscopy. Then the next extractant was added to the residue in the vessel and the procedure was repeated as described for step I.

3. Results and discussion

The total concentration of lead, copper, and manganese was determined in four horizons (A1–A4) of the forest soil of Kaarma, in the top horizon (B1) of the road-side soil of Tallinn, and in the fraction of fly ash of oil shale (Table 2).

Table 2

Total concentration of main components and Pb, Cu, and Mn in the soils and oil-shale ash (dry weight at 40°C)

Sample No. and soil horizon, cm	pH_{KCl}	Total organic matter, %C	SiO_2, %	CaO, %	Fe_2O_3, %	Pb, mg/kg	Cu, mg/kg	Mn, mg/kg
A1, 0–4	4.9	5.67	83	1.4	2.6	22.4	20.5	320
A2, 10–18	5.4	3.41	80	1.3	2.6	21.1	11.2	403
A3, 25–35	4.9	0.91	80	1.4	2.7	24.3	11.4	332
A4, 45–50	4.9	0.33	80	1.0	2.5	26.2	7.1	262
B1, 0–10	6.8	6.0	71	1.1	0.7	86	24.1	140
C1, oil-shale ash	<12		31	31	1.5	132	70	402

The pH value is nearly constant along the profile of forest soil, but the content of organic matter, mainly humus, is clearly diminishing along the profile. As typical for roadside soil, sample B1 has a nearly neutral reaction and a high organic matter content. Oil-shale ash, rich in basic metals, has a strong alkaline reaction. Obvious differences in the character of the investigated samples as well as the similarity of their mineral parts (SiO_2, CaO, MgO, $(Fe,Al)_2O_3$, $(Na,K)_2O$) make them useful in studying the behaviour of heavy metals by means of sequential analysis. In this investigation Pb, Cu, and Mn, occurring in sufficiently high concentrations, were selected.

The sequential separation of the elements incorporated in the solid samples is based on the different strength of the bonds by which the elements are tied to different structural parts of the solid matter-soil or sediments. Usually the main components of the topmost layer of soil are humus, clay minerals, sand, and carbonates. Humus as well as clay have a colloidal organization: a highly charged anion (micelle) is surrounded by adsorbed cations, mainly calcium and magnesium, and other preferably bivalent cations, among them also trace metals. The adsorption takes usually place by the ionexchange mechanism. Elements occurring in an exchangeable form are released in the sequential separation system in step I and they form stable and soluble complexes with EDTA at pH 10. In step II, the dissolution of hydroxides, oxides, and carbonates, and also of the elements bound to them takes place in the ammonium acetate buffer at pH 4.8. Notable amounts of Pb, Cu, and Mn were released from the soil with a high humus content at step I, but from the roadside soil the same elements were released at step II (Fig. 1). The elements that get free in steps I and II are the most mobile and bioavailable. By these characteristics the investigated matrices can be arranged in the order of descending bioavailability of elements: A>B>C for Pb and Mn; A>C>B for Cu (Table 3).

In step III the elements bound with the minerals whose solubility is growing in the reducing conditions can be released. They are mainly oxides and/or hydrous oxides of Mn(IV) and Fe(III) in an amorphous form. A large quantity of Cu (24%) is released in forest soil (A). The amount of Pb released in ash is also noteworthy (9%).

Fe(III) compounds, but also crystalline Mn(IV) compounds are reduced to more soluble Fe(II) and Mn(II) compounds also in step IV, which has a stronger reducing capability. Copper in the roadside soil is set free mainly in step IV (52%). No Pb was detected in step III and IV in the case of soils. In the reducing conditions 6% of total Pb in ash was dissolved. Summing up the amounts of elements released in steps III and IV, we can draw some conclusions about the elements fixed to the compounds of manganese and iron. In step V, in the oxidizing conditions, the elements fixed as sulphides or incorporated in the stable forms of humus were dissolved. Step VI was obtained as the difference between the total concentration of Pb, Cu, and Mn and their soluble parts (steps I–V). Step VI gives us information about the Pb, Cu, and Mn belonging to the lithogenic insoluble material in the soils and sediments.
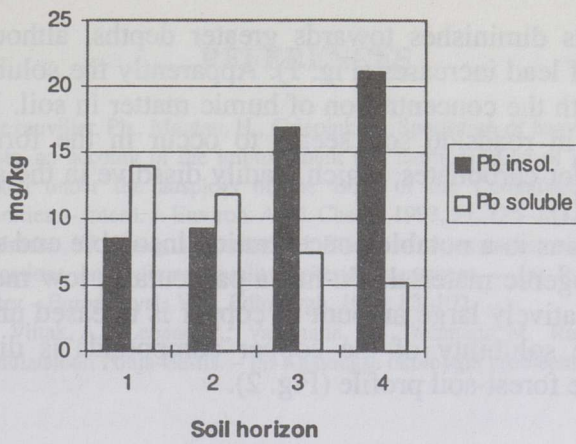
Fig. 1. Changes in the soluble part of lead along the A1–A4 horizons of forest soil.

Table 3

Partitioning of Pb, Cu, and Mn in the soil and sediment components

(A) forest soil of Kaarma, (B) roadside soil of Tallinn, (C) oil-shale fly ash

Step	Sample	Pb, %	Cu, %	Mn, %
I+II		Labile organics and/or carbonates, oxides, hydroxides		
	A	59	16	71
	B	35	2	75
	C	26	10	45
III+IV		Reduction of Mn(IV) and Fe(III) oxides and/or hydroxides		
	A	-	29	13
	B	-	52	20
	C	11	3	21
V		Oxidation of stable humic compounds and sulphides		
	A	3	3	3
	B	1	2	9
	C	4	5	3
VI		Immobile part, closed in silicate lattice		
	A	38	52	13
	B	64	44	14
	C	59	82	31

CONCLUSIONS

Lead is soluble in a relatively high concentration in step I+II. This gives us evidence about the occurrence of exchangeable and adsorbed compounds of lead in soil and ash samples. The Pb compounds in ash are less soluble than those in soil. In the forest-soil profile, the solubility of

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lead compounds diminishes towards greater depths, although the total concentration of lead increases (Fig. 1). Apparently the solubility of lead is correlated with the concentration of humic matter in soil. In contrast to forest soil, Pb in roadside soil seems to occur in the form of oxides, hydroxides and/or carbonates, which readily dissolve in the acetate buffer at pH 4.8 (step II).

Copper remains in a notable concentration insoluble and seems to be a part of the lithogenic material. Cu has a particularly low mobility in oil-shale ash. A relatively large amount of copper is released under reducing conditions. The solubility of the copper compounds is diminishing in depth also in the forest-soil profile (Fig. 2).
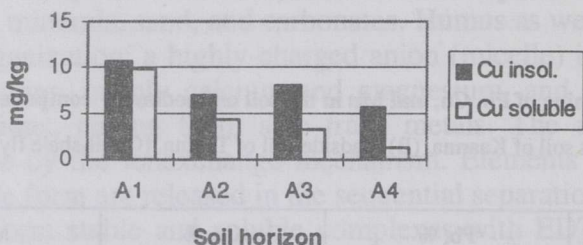

Fig. 2. Changes in the soluble part of copper along the A1–A4 horizons of forest soil.

Manganese occurs in relatively high concentrations in the exchange and adsorbed forms, but also in an easily reducible solid phase. The solubility changes of manganese in the profile of forest soil are similar to those of lead and copper (Fig. 3).

The solubility of Pb, Cu, and Mn is very low in oil-shale ash compared to soil. This is substantial in agricultural use of ash.
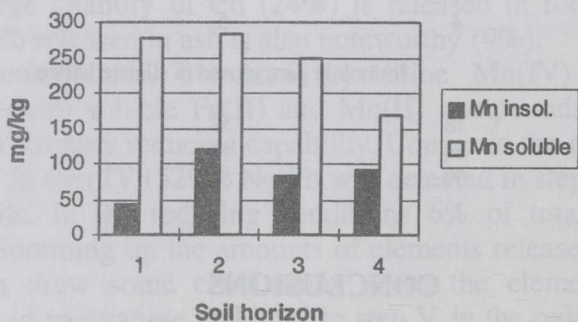

Fig. 3. Changes in the soluble part of manganese along the A1–A4 horizons of forest soil.

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MULLAS LEIDUVATE MIKROMETALLIDE KEEMILISE ÜHENDILIIGITUSE ANALÜÜS

Helvi HÖDREJÄRV, Anu VIITAK, Aini VAARMANN

Raskmetalle kui keskkonnaseisundi iseloomustajaid saab lisaks kontsentratsioonile hinnata nende liikuvuse ja bioomastatavuse põhjal. Viimased sõltuvad raskmetalliühendite lahustuvusvõimest keskkonnatingimustes. Mullaproovi järjestikusel töötlemisel lahustega, mis vabastavad elemendid erinevatest mullastruktuuridest, on võimalik selgitada elementide esinemiskuju (ioonvahetuslik seotus, adsorptsioon või suletus kristallvõresse) huumusainete, karbonaatide, savimineraalide ja muude mullaosade koosseisus. Viieastmelisel ekstraheerimisel töödeldakse mullaproovi järjest EDTA lahusega (pH 10), atsetaatpuhvriga (pH 4,8), hüdroksüülamiinkloriidi lahusega (pH 2,4), oksalaatpuhvriga (pH 3,0) ja vesinikperoksiidi lämmastikhappelise lahusega (pH 1,3). Lahustumatuks jääva osa leidmiseks määratakse elemendi üldsisaldus täielikult lahustatud proovis pärast loistmist soodaga, räni eraldamist ja jäägi lahustamist kloorvesinikhappes. Vaatlusel olid Pb, Cu ja Mn Kaarma metsamulla profiilis, Tallinnast saadud sõiduteeäärses mullas ja lisaks muldadele põlevkivi lendtuhas. Viimane pakkus huvi selle laialdase leviku tõttu atmosfäärse settena pinnasel, aga samuti ka lähtudes põllumajanduses levinud kasutusalast, maade lupjamisest. Huumusrikkas metsamullas on metallid seotud huumusega suhteliselt kergesti lahustuvana ja mobiilsena ioonvahetusliku mehhanismi kaudu. Teeäärses mullas võib aga oletada metallide esinemist kas oksiidide, hüdroksiidide või karbonaatidena, mis on lahustuvad nõrgalt happelises keskkonnas (aste II ekstraktsioonisüsteemis). Pb, Cu ja Mn osutusid põlevkivituhas vähemlahustuvateks kui muldades. Sellel on oluline tähendus põllumajanduslikust ja ökoloogilisest seisukohast.

СПЕЦИФИКАЦИЯ СОЕДИНЕНИЙ МИКРОЭЛЕМЕНТОВ В ПОЧВАХ

Хельви ХЁДРЕЯРВ, Ану ВИИТАК, Айни ВААРМАНН

Возможность влияния тяжелых металлов на окружающую среду зависит прежде всего от их концентрации, а также от подвижности и биоусвояемости. Эти свойства в значительной мере определяются растворимостью соединений тяжелых металлов, входящих в состав почвы и связанных с такими структурами, как гумус, карбонаты и т.д. Широко известным методом спецификации химических соединений металлов в почвах является последовательное их извлечение специальными растворами. Нами использована система из пяти растворов: раствор этилендиаминтетрауксусной кислоты (pH 10), ацетатный буфер (pH 4,8), раствор гидроксиламинхлорида (pH 2,4), оксалатный буфер (pH 3,0), азотнокислый раствор пероксида водорода (pH 1,3). Исследовали растворимость соединений свинца, меди и марганца в лесной почве (Каарма, Вирумаа), в придорожной почве (Таллинн), а также в летучей сланцевой золе. Интерес к последней связан со значительным атмосферным загрязнением Северо-Восточной Эстонии золой, а также с ее использованием для известкования сельскохозяйственных земель.

Установлено, что богатая гумусом лесная почва хорошо связывает металлы, очевидно, по ионообменному механизму, с легкорастворимой частью гумуса. В придорожной почве можно предполагать наличие оксидов, гидроксидов и/или карбонатов металлов, растворимых в слабокислой среде (ацетатный буфер). В сланцевой золе растворимость свинца, меди и марганца ниже, чем в почве.