Buletinul Ştiinţific al Universităţii "Politehnica" din Timisoara, ROMÂNIA
Seria CHIMIE ŞI INGINERIA MEDIULUI
Chem. Bull. "POLITEHNICA" Univ. (Timişoara) *Volume 51(65), 1-2, 2006*

The Use of Sequential Extraction for Characterization of Polluted Soils

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Abstract: Sequential extraction method allows determination of metals from operationally defined fractions: ionic exchangeable fraction, fraction adsorbed onto iron and manganese oxyhydroxide surfaces, fraction linked by organic matter and that linked by mineral networks. The analysis of metals distribution in fractions of a waste mining deposit and in zones covered with soils cultivated with grass plants, showed a change of concentrations in operationally defined fractions. Changes depend on both metal type and grass plant. In case of iron, copper and zinc, accumulation processes were recorded in zones cultivated with grass plants.

1. Introduction

It is appreciated that during the last century about 1.350.000 t of Zn, 783.000 t Pb, and 939.000 t Cu were introduced in environment. These chemical species, which are not degradated by physico - chemical processes, are cause of different illnesses.

Pollution of large soil areas and of ground waters are due to wastes from mining exploitations, chemical industry, municipal wastes, etc. Soil is polluted with heavy metals like Cu, Cd, Pb, Ni, Zn and Cr. The widespreading of mining wastes onto large areas represents risks both for human health and environment. Pollution due to sterile mining is widespread in mining areas from Germany, Czech Republik, Poland, Russia, Finland (Harjavalta and Tornio), neighbourhood of Sevilla city, from Spain.

Copper concentration identified in soil of Harjavalta county were 5800 mg/Kg d.s., from which, 4700 mg/Kg d.s. are in ionic exchangeable fraction. Iron in organic fraction was about 18600 mg/Kg d.s. By use of lichens, pollution due to Ni, Zn, Pb, Cd and Hg were identified up to 9 Km far away from pollution source.

Metals are found in soil as different chemical species. One form is that placed in ionic exchange centers, the others are linked in mineral networks or as precipitated forms, and these are not available to plants and animals. One part of metallic species is linked as organic complexes. Transport processes of metals from one soil fraction to other, e.g., from an unavailable to an available form, depends on physico-chemical factors and time [1, 2, 3, 4].

Metal content from soil shows environment quality, and this is expressed by term "total metal content", which is compared with the term referring to bioavailable metal content from soil: i.e., metals which can be taken by organisms through difussion, adsorption.

Sequential extraction of metals from solid media is an analytical tool used for soil geochemical characterization and searching. Sequential extraction allows that in every stage to be dissolved different components. Thus, the result is the determination of an operational series of fractions [5, 6, 7, 8].

In this paper, the method proposed by European Community Bureau of Reference (BCR) for sequential extraction of metals from soils was used, to analyze metals distribution in a waste mining deposit, resulted by copper ore processing at Moldova Noua enterprise, placed in south – west part of Romania.

2. Materials and methods

Sequential extraction method proposed by European Community Bureau of Reference (BCR), allows determination of metals from operationally defined fractions:

I - exchangeable fraction (extraction with acetic acid);

II - fraction adsorbed onto iron and manganese oxyhydroxide surfaces (extraction with hydroxylamine hydrochloride);

III - fraction linked by organic matter (oxidation with hydrogen peroxide, extraction with ammonium acetate);

IV - fraction linked by mineral networks (treatment with aqua regia).

Experimental extraction procedure is presented in table 1.

TABLE 1. Sequential extraction method of metals from soils, proposed by European Community Bureau of Reference (BCR).

Stage	Extracted fraction	Chemical reagents and working conditions
1.	ionic exchangeable	1g soil sample is mixed with 40 ml solution 0.11 M acetic acid under stirring at room temperature for 16 hours; extract is separated from solid residue by centrifugation, 20 minutes.
2.	adsorbed onto iron and manganese oxyhydroxide surfaces	Solid residue from the first stage is treated with 40 ml 0.1 M $NH_2OH{\cdot}HCl$ at pH = 2 under stirring for 16 hours at room temperature, and then is centrifugated for 20 minutes.
3.	fraction linked by organic matter	Solid residue from the second stage is treated with 10 ml H_2O_2, at pH = 2 - 3 with HNO_3, and is heated for 1 hour at room temperature. Then, 10 ml H_2O_2 are introduced again in sample, heated 1 hour at 85 ˚C. 50 ml of ammonium acetate is introduced and sample is stirred 16 h at room temperature; sample is centrifugated for 20 minutes.
4.	fraction linked by mineral networks	Solid residue from the third stage is decomposed with aqua regia, under heating at 100^0 C.

Some areas of two deposits (A and B) were covered with non-polluted soil layers, thickness of 10 cm from deposits neighbourhood, and were cultivated with grass plants like *Onobrychis viciifolia*, *Trifolium repens*, *Festuca arundinaceea*, *Medicago sativa*, *Lotus corniculatus*, in order to evaluate the efficiency of metals separation.

3. Results and Discussion

Sequential analysis of metal species from first waste mining deposit (A) covered with spontaneous vegetation of *Phragmites*, horizons 0 - 10 cm and 20 - 30, are presented in table 2. Some areas of this deposit were covered with a layer of 10 cm deeep, consisting of non-polluted soil, cultivated with grass plants like *Onobrychis viciifolia* and *Trifolium repens*. In these areas, samples were taken from the horizon 20 - 30 cm.

In areas cultivated with *Onobrychis viciifolia* and *Trifolium repens* there is less ionic exchangeable (mobile) copper, 70.9 mg/Kg d.s. (20.3 %) and 52.6 mg/Kg d.s. (40.8 %) respectively, table 3, than in waste minig area (A), 89 mg/ Kg d.s., used as blank sample.

Decreasing of mobile copper concentrations in zones covered with soil and cultivated, shows a change of distribution process; this is realized by increasing concentrations of fraction II, adsorbed onto iron and manganese oxyhydroxide surfaces, with 10.9 % and respectively 12.3 %, for the two grass plants and in fraction IV, linked by mineral networks, with 9.8 % for Onobrychis viciifolia.

An important decreasing of copper concentrations took place from fraction linked by organic matter, both in zone with *Onobrychis viciifolia*, 12.1 % and in that with *Trifolium repens*, 31.2 %, comparatively with blank sample.

Zinc and manganese presented a similar mobilization process, like copper. In case of iron, mobilization process is more intens; it was found more ionic content of iron in both zones, 115.7 mg/Kg d.s. *Onobrychis viciifolia* (21.5 %) and 136.4 mg/Kg d.s. *Trifolium repens* (33.4 %) than in sterile deposit, 90.8 mg /Kg s.u.

TABLE 2. Sequential analysis of metal species from waste mining deposit A, covered with spontaneous vegetation (Phragmites) samples from the horizons 0 – 10 cm and 20 -30 cm.

Extracted fraction	Horizons, cm	Metals, mg / Kg.d.s.			
		Cu	Zn	Mn	Fe
I	0-10	38.6	57.3	212.7	135.5
	20-30	89.6	165.6	179.1	90.8
II	0-10	107.6	42.9	206.7	593.6
	20-30	126.6	77.6	158.9	444.8
III	0-10	260.9	59.8	122.5	19.6
	20-30	308.3	101.5	83.8	15.4
IV	0-10	224.0	103.4	141.8	15360
	20-30	388.6	197.2	194.8	1199
Total	0-10	631.1	263.4	683.7	16180.7
	20-30	913.1	541.9	616.6	1750

TABLE 3. Sequential analysis of metal species from waste mining deposit A, areas covered with non-polluted soil cultivated with Onobrychis viciifolia and Trifolium repens, samples from the horizon 20 – 30 cm.

Extracted fraction	Grass plants	Metals, mg / Kg.d.s.			
		Cu	Zn	Mn	Fe
I	Onobrychis	70.9	150	179.6	115.7
	Trifolium	52.6	101	212.2	136.4
II	Onobrychis	139.2	84	146	489
	Trifolium	144.4	68	178	495
III	Onobrychis	271	81.2	80,5	81.3
	Trifolium	212	88	67	75.6
IV	Onobrychis	430.8	178	169.5	26605
	Trifolium	364.7	148	164.5	74200
Total	Onobrychis	911.8	493.2	575.6	27291
	Trifolium	773.7	405	621.7	74907

In fraction of iron adsorbed onto oxyhydroxide surfaces, there are small variation of concentrations, but in that linked by organic matter important changes were recorded: from 15.4 mg/Kg d.s. in sterile area to 81.3 mg/ Kg d.s. in *Onobrychis viciifolia* zone, and 75.6 mg /Kg d.s.. in that with *Trifolium repens*.

The greatest increasing of iron concentrations appeared in fraction linked into mineral networks: 26605 mg/Kg d.s. and 74200 mg d.s. respectively, comparatively with 1199 mg/Kg d.s. from waste mining deposit. These results show an accumulation process of iron in soil cultivated with grass plants.

Some areas of the second zone (B) covered with non-polluted soil, were cultivated with three grass plants, *Festuca arundinaceea*, *Medicago sativa* and *Lotus corniculatus*. Fraction of ionic exchange in these three zones increased in the following order: 74.2 mg/Kg d.s. *Festuca arundinaceea*, 134.2 mg/Kg d.s. *Medicago sativa*, 160.5 mg/Kg d.s. *Lotus corniculatus*, comparatively with copper from soil blank sample, 94.0 mg/Kg d.s., tables 4 and 5.

In case of fraction adsorbed onto iron and manganese oxyhydroxides, there is a different situation for the order of concentrations: 92.8 mg/Kg d.s. *Medicago sativa*, 245.6 mg/Kg d.s. *Lotus corniculatus*, 630 mg/Kg d.s. *Festuca arundinaceea*, and soil blank sample had 303.2 mg/Kg d.s.

TABLE 4. Sequential analysis of metal species from waste mining deposit B, covered with spontaneous vegetation (Festuca arundinaceea), samples from the horizon 10 - 20 cm.

Extracted fraction	Grass plants	Metals, mg / Kg.d.s.			
		Cu	Zn	Mn	Fe
I	Festuca	94	56	260.8	193.2
II	Festuca	303.2	52.8	304	528.7
III	Festuca	462	154	131	4200
IV	Festuca	542	146	126	46000
Total	Festuca	1401.2	408.8	821.8	50921

Table 5. Sequential analysis of metal species from waste mining deposit B, areas covered with non-polluted soil cultivated with grass–plants, samples from the horizon 10 - 20 cm.

Extracted fraction	Grass plants	Metals, mg / Kg.d.s.			
		Cu	Zn	Mn	Fe
I	Festuca	74.2	51.6	276.8	82
	Medicago	134.2	200	214.8	199.6
	Lotus	160.5	180	260.9	156.8
II	Festuca	630	54	364	496.1
	Medicago	92.8	80.8	255	569
	Lotus	245.6	1056	231.6	536.4
III	Festuca	466.1	171.8	95.9	3913
	Medicago	518	196	92.7	4165
	Lotus	514.8	350	107.6	3100
IV	Festuca	320.2	102.4	136.8	32150
	Medicago	465.8	184.2	121.1	41480
	Lotus	1029.2	387	179.7	39880
Total	Festuca	1401.2	408.8	821.8	50921

There is a small increasing in the content of organic linked fraction, which takes place in the order, *Medicago sativa ≈ Lotus corniculatus > Festuca arundinaceea*. In case of fraction retained into mineral networks, concentrations decreased in zones with *Festuca arundinaceea* 320.2 mg/Kg d.s., and *Medicago sativa* 465.8 mg/Kg d.s. comparatively with waste minig area (B) blank sample, 542 mg/Kg d.s., but increasing about two times in zone with *Lotus corniculatus*, 1029.2 mg/Kg d.s.

Zinc is concentrated especially in zones with *Medicago sativa*, four times and *Lotus corniculatus*, three times for fraction l, comparatively with blank waste deposit; the process is similar for the other three fractions, but in small extent.

In case of manganese, the concentration from fraction linked by organic matter decreased with 17.8 - 29 %, and that adsorbed onto iron and manganese oxyhydroxide surfaces with 16 - 24 %. Concentrations of iron from zones covered with soil had also small variations, e.g., for fraction linked by organic matter there are 3100 - 4165 mg/Kg d.s., comparatively with that from waste deposit, 4200 mg/kg d.s., the horizon 10 – 20 cm.

4. Conclusions

Sequential extraction method, allows determination of metals from operationally defined fractions:

I - ionic exchangeable fraction,

II - fraction adsorbed onto iron and manganese oxyhydroxide surfaces,

III - fraction linked by organic matter,

IV - fraction linked by mineral networks.

The analysis of metals distribution in fractions of a waste minig deposit and in zones covered with soils cultivated with grass plants, showed a change of concentrations in operationally defined fractions. Changes depend on both metal type and grass plant. E.g., decreasing of mobile copper with 20.3 - 40.8 %, and copper linked by organic matter 12.1 - 31.2 %, but increasing both of concentrations adsorbed onto iron and manganese oxyhydroxide surfaces with 10.9 - 12.3 %, and that linked by mineral networks with 9.8 % in zone A, took place. Zinc and manganese presented similar mobilization processes. In case of iron an accumulation process in soil cultivated with grass plants especially in mineral networks, from 1199 mg/ Kg d.s up to 27291 - 74907 mg/ Kg d.s. was recorded. Similar concentrations processes took place in zone B, for copper and zinc.

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