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Original Research

Distribution, Bioavailability and Fractionation of Metallic Elements in Allotment Garden Soils Using the BCR Sequential Extraction Procedure

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Abstract

Metal associated with urban soils are of environmental concern due to their direct and indirect effects on human health. Metallic elements in contaminated soils are absorbed by plants and undergo biomagnification in the food chain. Allotment gardens are often situated in city centers and in areas with strong anthropogenic pressure – e.g. near industrial plants and roads.

The aim of this study was to identify the bioavailable forms of metals present in urban soils. The sequential extraction procedure was applied to fractionate the following metals in urban soil samples from allotment gardens in Koszalin, Poland: chromium, copper, iron, manganese, nickel, lead, cadmium, and zinc. The mobility of the metals from studied soils decreased in the order: Cd > Mn > Pb > Zn > Ni > Cr > Cu > Fe. The sum of particular metals in the bioavailability fractions BCR I-III was: Cd 77-89%, Mn 72-81%, Pb 64-80%, Zn 54-77%, Ni 31-57%, Cr 32-53%, Cu 20-50%, and Fe 12-17%.

Keywords: bioavailability, sequential extraction procedure, metals, urban soils

Introduction

Soil contamination is a worldwide environmental concern due to the potential risks for human and environmental health. Soils are prone to contamination by trace metals due to anthropogenic activities. Excessive fertilizer and pesticide use, irrigation, atmospheric deposition, and pollution by waste materials or sludge are sources of contamination by metals. Greater soil pollution may be present in heavily industrialized regions and in city agglomerations. The total element content is not the only important factor, as forms and types of metals binding in soils also is relevant. Metal transportation depends on the physiochemical properties of the soil. The comparison of the total element content to forms, mobility, and bioavailability provides more detailed information about metallic elements in the environment [1-5].

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Migration of the elements depends on the forms in which they occur in soils. Metals may be found in one or more of the following forms [5]:

a) dissolved (in soil solution)
b) exchangeable (in organic and inorganic components)
c) as structural components of the lattices of soil minerals
d) as insoluble precipitates with other soil components.

The first two forms are easily available to plants, while the other two are potentially available in the long run. The mechanisms by which a metal element changes from one form to another, and the speed at which it does so, is not completely known. In general, the concentration of an element in the soil solution is believed to depend on the equilibrium between the soil solution and solid phase, with pH playing a decisive role. The mobility of metals decreases with increasing pH [5].

Detailed knowledge of the chemical forms of metals in soils can provide more information about metal behavior.

In order to determine this, a sequential extraction procedure (SEP) has been developed. SEP constitutes a highly utilized tool for understanding the chemistry of metals in the environment. In 1979, Tessier et al. [6] used a five stage extraction procedure to fractionate cadmium, cobalt, copper, iron, lead, manganese, nickel, and zinc in river sediments. Extraction steps corresponded with important changes in environmental conditions that could affect metal binding in sediments: acidification, reduction, and oxidation [6-14]. In the present, a variety of SEP methods are applied for a large number of potentially toxic elements in a wide range of sample types. The most significant advance in sequential extraction studies occurred in 1987, when the European Commission launched a program (in the framework of the BCR, Community Bureau of Reference) aimed at harmonizing extraction procedures. A standardized SEP was proposed and became known as the BCR® SEP (BCR is a registered trademark of the European Commission) [13, 14]. It has the advantage of available certified reference materials (BCR 701) for method validation [15, 16]. Although originally intended for application to sediments, the BCR scheme has been applied successfully in the study of a wide variety of other substrates, including several different types of soils [17-26].

Extraction steps of BCR SEP correspond with, or at least represent extremes of, important changes in environmental conditions that could affect metal binding in soils: acidification, reduction, and oxidation processes.

Fraction of BCR I is acid soluble, and contains the exchangeable and carbonate-bound metals. This fraction represents the amount of metal that would be released into the environment if conditions became more acidic. Fraction of BCR II is reducible, and it contains the metals bound to iron and manganese oxides and hydroxides. BCR II fraction theoretically represents the fraction of metals that would be released in the case of more reductive conditions. Fraction of BCR III is oxidizable, and it identifies the fraction of the metals bound to organic matter and sulfide compounds that would be released if conditions became more oxidizing. The rest metals, in BCR IV residual fraction, are associated with minerals bound to their crystal structure. They are immobilized and in the foreseeable future will not constitute a threat to the ecosystem.

Assuming that the bioavailability of metals is a function of solubility, the mobility of metals in the BCR SEP decrease in the order: exchangeable and carbonate-bound metals > metals bound to iron and manganese oxides and hydroxides > metals bound to organic matter > metals bound to the crystal structure of minerals [7, 9, 13].

Urban soils are less studied than agricultural soils, although they are gaining increased attention. Soils in urban environments are often highly variable in composition, due to the wide variety of human influences, and typically contain higher loadings of contaminants than those from rural settings due to the higher density of anthropogenic activity in urbanized areas. Regions of urban soil also are used for food production, especially for domestic gardens and allotments [27, 28].

This paper describes the application of a harmonized sequential extraction procedure, the BCR protocol [13], to fractionate cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc in soils from allotments in Koszalin, Poland.

On the basis of the total content of metallic elements and the content of bioavailable forms, the bioavailability factor (BF) was calculated. The bioavailability factor is described by the following equation:

$$BF=C_{bio}/C_{total}$$

...where:

C_{bio}– concentrations of bioavailable forms of metals in studied soils

C_{total} – the total concentration of metal in studied soil.

The bioavailable form of a metallic element is considered to be the form contained in the I-III fractions of the sequential extraction of soil, in accordance with the BCR protocol. The bioavailability factor allows the determination of the suitability of soils for their use in agricultural production.

Materials and Methods

Study Area and Sampling

Koszalin is the largest city of middle Pomerania in northwestern Poland. It is located 12 km south of the Baltic

Fig. 1. Sampling map of the study area.

Table 1. Sequential extraction scheme for soil metal fractionation.

Fraction		Extraction solvent	Leaching time and temperature
BCR I	Exchangeable and acid soluble	0.11M CH_3COOH	16 h, 20ºC
BCR II	Reducible	0.5M $NH_2OH{\cdot}HCl$ (pH=1.5)	16 h, 20ºC
BCR III	Organic	a) 30% H_2O_2	a) 1 h, 20ºC
		b) 30% H_2O_2	b) 2 h, 85ºC
		c) 1M CH_3COONH_4 (pH=2)	c) 16 h, 20ºC
BCR IV	Residual	HNO_3+30% H_2O_2	2 h, boiling temp.

Sea coast. The study sites were located at five places around the city (Fig. 1).

Study materials came from five groups of allotment gardens located at different parts (I-V) of Koszalin. The selection of gardens was based on their location relative to urban areas. Garden areas Nos. I-III (soil sample Nos. 1-13) were located in the middle parts of the city while Nos. IV-V (soil sample Nos. 14-24) were in the suburbs areas.

In each studied place, soil samples were collected from 3-6 individual allotments in each group (depending on group size). Each sample was taken from the cultivation surface (0-20 cm). Twenty-four soil samples from the Koszalin area were obtained in total, and were sealed in polyethylene bags on site in September 2008.

Experimental Procedures

The samples were air-dried at room temperature, ground in an agate mortar, and sieved through a 1 mm sieve.

The cation exchange capacity (CEC) in hexaamminecobalt(III) chloride [ISO 23470:2007], the pH value in degassed deionized water, and the organic matter content from incineration at 550ºC were measured for the air-dried soil samples.

The pseudo-total content of metals in the applied soil samples was determined by atomic absorption spectrometry after digestion with 65% nitric acid and 30% hydrogen peroxide.

Sequential extraction according to the BCR procedure [13] was used to investigate the mobility of metals in the allotment soils studied. The scheme of the fractionation process is described in Table 1.

The extract was separated from solid residue by centrifuge after each extraction step. The extracts were stored at 4ºC prior to metal analysis. The concentration of metal (Cu, Zn, Fe, Ni, Mn, Cd, Cr, and Pb) in soils and in fractionation supernatants was determined using atomic absorption spectrometry in an acetylene-air flame (AAnalyst 400, Perkin Elmer). All chemicals used were of analytical reagent grade. All laboratory ware used in the analysis was previously soaked in a nitric acid 4 mol/l solution for at least 24 h and rinsed with deionized water. All analyses were done in triplicate.

For quality control, Certified Reference Materials (CRM) from the Institute for Reference Materials and Measurements (Brussels, UE) also were analyzed in parallel with the studied soils. For pseudototal metal content the BCR-146R "Sewage sludge from industrial origin" reference was used, while for the sequential extraction procedure the BCR-701 "Sediment" standard was used.

Results and Discussion

The physicochemical properties of the studied soils are presented in Table 2.

The pH of the soils was found to range from 5.5 (sample No. 22) to 7.9 (sample No. 15). The neutral and slightly alkaline pH of most samples indicates a relatively low risk for the leaching of metals and thus a low bioavailability in the environment. The average pH was similar in each group, ranging 6.8-7.6. Alkaline reactions can be caused by agrochemical operations, especially liming. Due to the contamination of metals, this situation is positive, because it results in a lesser bioavailability for plants and, moreover, for humans. Only in one individual allotment was the pH of the soil 5.5 (sample No. 22). An acidic pH indicates the possibility for higher mobility of metallic elements, and thus greater bioavailability for living organisms and hence greater potential for toxicity.

The content of organic matter in the soils studied ranged from 3.87% (sample No. 22) to 9.58% (sample No. 17). Organic matter is one of the most important factors in soil fertility. It constitutes the natural protective barrier against metals, as it reduces their mobility. The content of organic matter in the investigated soils was in the range 4.4-6.6% by dry matter, on average.

The cation exchange capacity CEC is used to evaluate soil fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. CEC measurements in the studied soils was in a range from 2.92% (sample No. 22) to 16.3% (sample No. 17), and correlated with the pH value and content of organic matter. The higher the values of the pH and organic matter content, the higher the value of the CEC measured.

The pseudo-total amount (average value ± standard deviation) of each metal in the studied soils is shown in Table 3.

Table 2. Physicochemical properties of investigation soils.

Allotment	Individual allotments		$pH_{(H_2O)}$		Content of organic matter [% d.m.]		CEC [$cmol^+ \cdot kg^{-1}$]	
		No.		average		average		average
Koszalin I	(6)	1	7.0	7.5	5.9	6.6	9.26	12.0
		2	7.3		4.5		8.10	
		3	7.4		6.2		9.31	
		4	7.9		9.1		14.2	
		5	7.8		6.0		15.0	
		6	7.6		7.9		16.1	
Koszalin II	(4)	7	7.3	7.4	5.9	5.2	10.1	8.89
		8	7.6		5.9		9.48	
		9	7.3		5.1		8.70	
		10	7.6		4.1		7.27	
Koszalin III	(3)	11	7.6	7.5	4.2	4.4	8.21	8.55
		12	7.0		4.0		6.34	
		13	7.8		5.0		11.1	
Koszalin IV	(5)	14	7.8	7.6	5.3	6.3	9.86	9.79
		15	7.9		7.2		13.3	
		16	7.2		5.3		7.00	
		17	7.3		9.6		16.3	
		18	7.6		4.1		6.50	
Koszalin V	(6)	19	7.4	6.8	5.6	5.9	9.92	9.62
		20	7.6		6.7		13.0	
		21	7.7		8.6		14.3	
		22	5.5		3.9		2.92	
		23	6.3		4.6		5.62	
		24	6.3		5.9		9.97	

The content of cadmium in the samples ranges from 0.04±0.01 $mg \cdot kg^{-1}$ d.m. in sample no. 12 to 0.53±0.52 $mg \cdot kg^{-1}$ d.m. in sample No. 7. The lead content in the samples ranges from 7.80 $mg \cdot kg^{-1}$ d.m. in sample No. 23 to 57.3 $mg \cdot kg^{-1}$ d.m. in sample No. 7. The copper content in the soil samples ranges from 7.77 $mg \cdot kg^{-1}$ d.m. in soil sample 23 to 33.7 $mg \cdot kg^{-1}$ d.m. in soil sample 15. The chromium content in the analyzed samples ranges from 10.8 $mg \cdot kg^{-1}$ d.m. in soil sample 15 to 31 $mg \cdot kg^{-1}$ d.m. in sample 17. The zinc content in the analyzed samples ranges from 65 $mg \cdot kg^{-1}$ d.m. in sample No. 23 to 262 $mg \cdot kg^{-1}$ d.m. in the soil sample 20. The nickel content in the analyzed soil samples ranges from 15.8 $mg \cdot kg^{-1}$ d.m in sample 15 to 41.2 $mg \cdot kg^{-1}$ d.m. in sample 8. The iron content in the samples of studied soils ranges from 5,620 $mg \cdot kg^{-1}$ d.m. in soil sample 9 to 13,600 $mg \cdot kg^{-1}$ d.m. in sample 6. The content of manganese in the soil samples was within a range from 172 $mg \cdot kg^{-1}$ d.m in sample 7 to 508 $mg \cdot kg^{-1}$ d.m. in sample 13.

The contents of particular metals within the studied allotment complexes in most cases were similar. The several different values of the metal contents noted could have occurred due to the different soil management regimes employed by garden owners.

The contents of Cd, Pb, Cu, Cr, Zn, and Ni in soils did not exceed the limiting values specified in the Polish Ministry of the Environment regulation on standards for soil quality (Table 3). The iron and manganese contents in agricultural soils are not normalized by Polish law.

However, the legal standards were not exceeded, but considering the recommended by the Polish Chemical and Agricultural Stations values the studied soils are not suitable for low metal content consumer crops. Almost every studied soil sample contained an excess concentration of zinc, more than 70 $mg \cdot kg^{-1}$ d.m. (Table 3). The contents of cadmium, lead, and chromium were exceeded once in soil Nos. 7 (Cd and Cu) and soil 17 (Pb). The content of copper

Table 3. Pseudo-total content of metals in individual allotment soils [mg·kg⁻¹ d.m.±S.D.].

Individual allotment	Cd	Pb	Cu	Cr	Zn	Ni	Fe	Mn
1	0.28±0.10	33.9±1.5	17.9±5.9	17.5±7.8	202±68	20.7±3.3	9,260±320	268±79
2	0.17±0.02	24.0±3.8	16.0±3,2	20.3±0.7	220±13	23.0±2.7	12,800±507	292±9
3	0.21±0.01	24.0±0.5	16.8±1.1	22.6±4.5	168±26	20.9±2.5	11,900±143	309±6
4	0.19±0.05	19.3±1.7	17.1±4.4	13.5±6.8	102±25	17.8±3.2	11,300±391	363±17
5	0.19±0.01	35.4±0.2	20.9±1.4	26.4±3.4	133±23	21.5±1.8	13,000±268	375±6
6	0.22±0.04	27.2±3.3	19.0±0.8	31.1±3.6	128±5	21.6±2.2	13,600±345	396±12
7	0.53±0.52	57.3±9.7	18.8±1.5	17.1±0.6	152±3	30.0±8.9	6,110±418	172±6
8	0.34±0.02	22.7±2.1	17.9±5.5	12.9±4.5	113±24	41.2±27.3	7,300±897	337±21
9	0.35±0.07	26.1±0.1	29.1±1.7	17.3±2.5	119±3	19.7±5.8	5,620±623	263±9
10	0.27±0.09	27.3±0.7	16.0±0.6	16.2±1.1	178±7	23.6±1.8	8,650±95	284±31
11	0.08±0.01	22.4±0.7	13.2±0.2	19.0±0.7	146±18	28.4±2.0	10,500±469	352±1
12	0.04±0.01	22.3±0.1	13.5±1.2	19.5±2.6	78±1.3	18.5±2.3	8,510±161	240±6
13	0.14±0.01	30.8±0.8	19.6±3.5	27.1±1.8	129±11	21.8±5.7	12,200±296	508±7
14	0.24±0.03	17.3±1.3	22.5±1.6	16.1±4.1	123±21	23.7±2.5	8,150±954	415±19
15	0.32±0.01	18.1±0.2	33.7±2.7	10.8±0.3	175±17	15.8±2.3	7,190±181	385±6
16	0.20±0.04	16.5±0.1	14.4±0.3	15.1±0.5	78±0.3	17.5±4.3	8,080±393	321±1
17	0.28±0.04	21.5±2.1	21.7±1.4	31.2±0.6	108±7	29.4±2.2	8,550±170	208±9
18	0.19±0.03	11.9±0.1	11.5±1.3	17.0±2.0	88±3.4	19.3±3.5	8,610±434	314±5
19	0.11±0.01	19.0±1.4	14.5±0,5	23.6±1.8	211±30	19.7±2.7	11,300±583	270±7
20	0.20±0.03	39.3±0.2	12.6±0.2	24.0±3.6	262±21	17.8±2.5	11,400±1,080	283±7
21	0.13±0.03	14.8±0.5	13.4±1.6	19.4±6.5	117±10	26.6±6.1	10,350±223	325±11
22	0.11±0.02	12.3±0.8	9.78±2.24	25.3±2.8	78±6.5	24.5±3.6	13,180±260	322±12
23	0.11±0.03	7.80±1.2	7.77±1.26	15.9±1.1	65±15.5	17.2±1.8	8,450±1,810	176±31
24	0.16±0.03	13.1±1.1	12.4±0.3	26.4±2.5	171±12	23.7±3.5	13,000±516	364±39
Limiting value*	4	100	150	150	300	100	n.n.	n.n.
Recommended value**	0.5	40	20	30	70	25	n.n.	n.n.

*Limiting value for agricultural soils according to the Polish Ministry of the Environment regulation on standards for soil quality (J.Law. 2002, 165, 1359),

**Recommended value for uncontaminated soils used for all garden and agricultural crops, according to the Polish Chemical and Agricultural Stations [29],

n.n. – not normalized or recommended

and nickel was exceeded five times in the studied soils. Soils Nos. 5, 9, 14, 15, and 17, and soil Nos. 7, 8, 11, 17, and 21 contained excess concentration of Cu and Ni, accordingly. There were no significant differences in the content of metals in soils from different parts of Koszalin. However, at least exceedances of metals content in the soils was found in the group of allotment gardens number V, located in the suburbs.

The results of the sequential extraction of metals and the relation of each fraction to the total amount (in %) for particular groups of allotments are presented in Fig. 2.

The content of cadmium in the most mobile fractions of the BCR protocol (Ist and IInd) was about 40% of the total content of this metal in the soils. Another 40-50% of cadmium was associated with organic matter (BCR III). The bioavailability factor (BF) was in a range from 0.64 (sample No. 2) to 0.93 (sample No. 8 and 14). This demonstrates the high bioavailability of cadmium and thus potential risk for absorbing large quantities by plants.

Although the smallest amounts of lead occurred in the carbonate fraction (BCR I), a very high content of Pb was noted in the IInd BCR fraction (oxide, approximately 50-

60%), testifying to its high mobility in soil. This is confirmed by its bioavailability factor, being in the range 0.65 to 0.8.

The highest of the copper contents noted was observed in the residual fraction (BCR IV) (50-80%). Approximately 30% of the copper also was associated with the organic matter fraction (BCR III). Most notably, the smallest amounts of this metal, about 5%, were present in fractions I and II. This reflects the low mobility of copper in the studied soils. The bioavailability factor ranged from 0.2 to 0.5 for the particular group of allotments.

The highest chromium content, 50-68%, also was observed in the residual fraction. About 10% of this metal content was noted in the three allotment groups (Koszalin I, II, and IV), they occurred in the most mobile fractions (I and II). In the other two allotment complexes there was only 2-3% total Cr content. The bioavailability factor was in a range from 0.32 to 0.53.

The content of zinc in the most mobile fractions of the BCR protocol (I and II) is about 40-60%, on average. The lowest content of zinc was obtained in the organic fraction BCR III (about 10-20%). The bioavailability factor was in a range from 0.5 to 0.7.

The highest nickel content was determined in residual fraction BCR IV, and was in a range from 43-70%. Much of this element also was associated with the organic matter fraction (BCR III), about 21-51%. The smallest amount of this metal was present in the exchangeable and acid soluble fraction BCR I, up to 3%. The bioavailability factor was in a range from 0.3 to 0.52 for this particular group of allotments.

The obtained results showed that the largest amount of iron was extracted in the residual fraction, BCR IV. The smallest amount of Fe was contained in the carbonate/acid soluble fraction, BCR I. The bioavailability factor (BF) range from 0.12 to 0.17, indicating a stable immobilization of more than 80% of the iron in the studied soil samples.

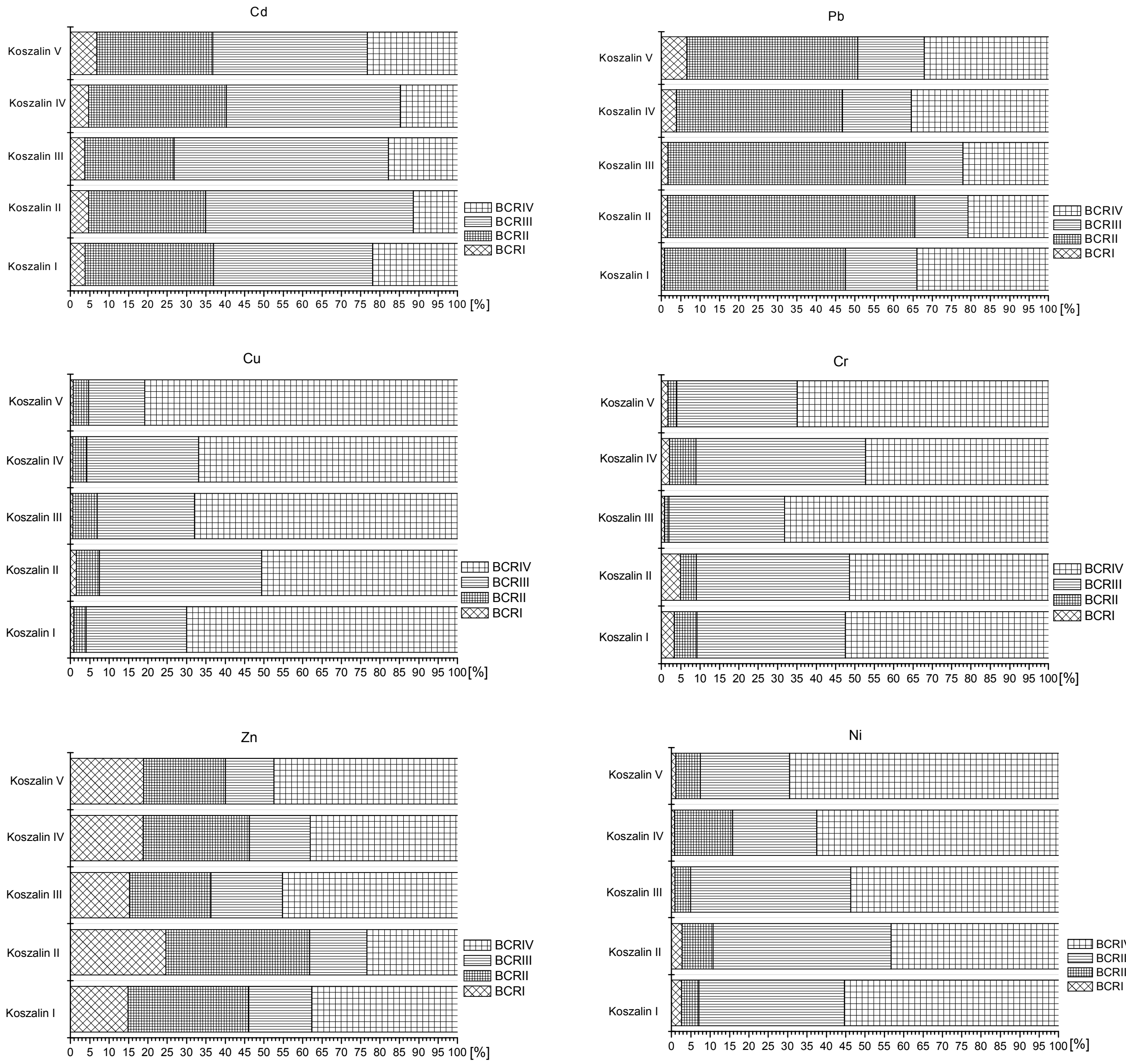

Fig. 2. Sequential extraction of heavy metals.

Table 4. Quality control results obtained for the analysis of BCR-146R: "Sewage sludge from industrial origin," for pseudo-total metals content.

Element	Experimental value [mg·kg^{-1} of dry mass±S.D.]	Certified value [mg·kg^{-1} of dry mass±S.D.]	% Recovery
Cd	18.5±0.56	18.4±0.4	100.5
Cr	170±11	174±7	97.7
Cu	731±3	831±16	88.0
Mn	281±10	298±9	94.3
Ni	68.5±3.7	65.0±3.0	105.0
Pb	515±24	583±17	88.3
Zn	2872±52	3040±60	94.5

The largest amount of manganese was found in the reducible fraction, being approximately 60% of the total Mn content in the studied soils. The smallest amounts of this element were presented in the organic fraction, at a level of about 5%. The exchangeable/acid soluble and residual fractions contained 10 and 20%, respectively. The bioavailability factor was in a range from 0.72 and upwards. This reflects a considerably higher mobility of manganese in the soils.

Generally, most of the BCR I fraction was dominated by zinc and manganese at levels of about 15-25% and 8-17%, respectively. Contents of other measured elements in that fraction totaled less than 5%. The amount of iron in this fraction was less than 0.5%.

Manganese and lead mainly occurred in the reducible fraction (BCR II), ranging between 50-65% and 47-64%, accordingly. The amount of cadmium and zinc was between 22-37%. Chromium and copper had the least percent content – between 2-6%.

The highest percent content of metals in the BCR III fraction (oxidizable) was noticed for cadmium, coming in at about 40-55%. The content of chromium and nickel in this fraction was from 22 to 46%. The iron content was only about 2-4%. In natural conditions the risk of metal wash out for this fraction of soil is much lower than that of the fractions I and II, since the mineralization process of organic matter is rather slow.

The last residual fraction (BCR IV) contains metals that are chemically stable, immobile, and biologically inert. Iron in this fraction was at a level of about 83-88%, copper 51-81%, nickel and chromium at 43-70%, and cadmium at only 11-23%.

In Koszalin soils, the most mobile metals were cadmium and manganese. The sum of cadmium and manganese in the bioavailability fractions BCR I-III was: Cd 77-89% (0.1-0.33 mg·kg^{-1} d.m.), and Mn 72-81% (214-240 mg·kg^{-1} d.m.). The least mobile element was iron. The content of Fe in the bioavailable fractions was only 12-17% (1,440-1,770 mg·kg^{-1} d.m.). The sum of other particular metals in the bioavailability fractions BCR I-III was: Pb 64-80% (11.1-

Table 5. Quality control results obtained in the analysis of BCR-701; "Sediment," for the sequential extraction procedure.

Element	BCR I			BCR II			BCR III			Experimental ∑ I-III [mg·kg^{-1} of dry mass±S.D.]	Certified ∑ I-III [mg·kg^{-1} of dry mass±S.D.]	% Recovery ∑ I-III
	Experimental value [mg·kg^{-1} of dry mass±S.D.]	Certified value [mg·kg^{-1} of dry mass±S.D.]	% Recovery	Experimental value [mg·kg^{-1} of dry mass±S.D.]	Certified value [mg·kg^{-1} of dry mass±S.D.]	% Recovery	Experimental value [mg·kg^{-1} of dry mass±S.D.]	Certified value [mg·kg^{-1} of dry mass±S.D.]	% Recovery			
Cd	7.52±0.5	7.34±0.35	102.4	3.87±0.77	3.77±0.28	102.6	0.28±0.01	0.27±0.06	103.7	11.7±1.28	11.4±0,7	102
Cu	44.9±3.0	49.3±1.7	91.1	125±1	124±3	100.8	49.9±5.6	55.2±4.0	90.4	220±9.6	228±8.7	96.5
Cr	2.04±0.06	2.26±0.16	90.3	41.2±0.8	45.7±2.0	90.2	132±6	143±7	92.3	175±6.86	191±12	91.6
Ni	16.2±0.4	15.4±0.9	105.2	26.6±2.4	26.6±1.3	100.0	16.6±0.6	15.3±0.9	108.5	59.4±3.4	57.3±3.1	103
Pb	3.05±0.08	3.18±0.21	95.9	111±4	126±3	88.1	8.4±0.6	9.3±2.0	90.3	122±4.68	138±5.2	88.4
Zn	206±1.4	205±6	100.5	124±1	114±5	108.8	44.8±0.3	45.7±4.0	98.0	375±2.7	365±15	103

26.7 mg·kg^{-1} d.m.), Zn 54-77% (81.4-108 mg·kg^{-1} d.m.), Ni 31-57% (6.7-16.3 mg·kg^{-1} d.m.), Cr 32-53% (7.0-9.6 mg·kg^{-1} d.m.), and Cu 20-50% (2.35-10.2 mg·kg^{-1} d.m.).

The average content of metals in the bioavailable fractions in the soils of different allotment groups did not differ significantly, regardless of the location relative to the urban center. It is therefore difficult to assess the impact of urbanization on both the total metal content in different soils and in fractions of BCR procedure. Metal content in the studied soils, therefore, may be due to the natural composition of the soils and allotment garden management by the owners, including fertilization, liming, and irrigation.

Tables 4 and 5 summarize the analyzed concentration of metals in the Certified Reference Materials: BCR-146R and BCR-701, accordingly.

Analysis of the two certified reference materials confirmed the good quality of the research. The recovery percentages of individual elements ranged from 88 to 103%.

Conclusions

In this study, eight metal contents for the surface soils from five various allotment groups from Koszalin were evaluated. Our investigation showed that the neutral and slightly alkaline pH (6.8-7.6) of the soils caused less washout of most metals. In the first step of the sequential extraction, only zinc (15-25%) and manganese (8-17%) occurred in significant amounts, while other elements were present at less than 5% of the total.

The overrunning of limiting value for metal content, according to the Polish regulation on standards for soil quality, in studied soils was not found, but considering the recommendations by the Polish Chemical and Agricultural Stations values, the studied soils are not suitable for low metal content consumer crops, especially for infants and children.

Taking into account the results obtained, the mobility of the analyzed metals from Koszalin allotment soils decreased in the order: Cd>Mn>Pb>Zn>Ni>Cr>Cu>Fe. The more mobile metals are more available to plants and can be included in biogeochemical circulation.

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