Soil & Sediment Contamination, 14:143–154, 2005
Copyright © ASP
ISSN: 1532-0383 print / 1549-7887 online
DOI: 10.1080/15320380590911797

Taylor & Francis
Taylor & Francis Group

Removal of Heavy Metals from Sewage Sludge Used as Soil Fertilizer

MARIAN TUREK, TEOFIL KOROLEWICZ, AND JERZY CIBA

Silesian University of Technology, Faculty of Chemistry, Gliwice, Poland

This work has examined sewage sludge of the following heavy metal concentrations (mg/kg): Cd-3.43; Co-5.25; Cu-131; Fe-51300; Mn-177; Ni-37.5; Pb-104; Zn-3300. Metals speciation by sequential extraction according to Tessier et al. (1979), and Rudd et al. (1988), and a procedure recommended by European Community Bureau of Reference (BCR) (Ure et al., 1993; Quevauiller et al., 1996; Davidson et al., 1999), as well as analysis of chemical forms of metals, have been carried out. It has been found that only Zn concentration is higher than the value permissible for agricultural sewage sludge application (2500 mg/kg). The results obtained by Tessier et al. (1979), and BCR procedures (Ure et al., 1993; Quevauiller et al., 1996; Davidson et al., 1999) appeared to be consistent. A comparison of the sequential analysis and the analysis of chemical forms of metals indicates that the sum of metal concentrations for the exchangeable, carbonate and bound to Fe/Mn oxyhydroxides forms (found by Tessier et al., 1979, and BCR analyses (Ure et al., 1993; Quevauiller et al., 1996; Davidson, et al., 1999)) corresponds to the sum of sulfate, oxide, metallic and siliceous forms. The concentrations of the forms bound to organic matter or sulfides correspond to the sulfide form while the residue corresponds to the ferrate form. Preparative extraction of metals from the sewage sludge using sodium salt of ethylenediaminetetraacetic acid (EDTA-Na), sodium pyrophosphate (V) and ammonia water has also been investigated. As far as the examined leaching agents are concerned, EDTA-Na appeared to be the best. Single leaching with this agent results in the following metal concentrations remaining in the sludge (mg/kg): Cd-1.1; Co-2.1; Cu-105; Fe-17700; Mn-28.3; Ni-12.8; Pb-44; Zn-1200. They meet the requirements of Polish regulations concerning the use of sewage sludge as a soil fertilizer.

Keywords Sewage sludge, heavy metal, speciation, extraction.

1. Introduction

The management of raw and post-fermentation sewage sludge from municipal treatment plants is a difficult task due to epidemiological hazards and the occurrence of heavy metals. The main sources of heavy metals in sewage sludge are industrial wastewater and surface flows containing large quantities of zinc, which originate from phosphate fertilizers and plant protection chemicals. The statistical yearbook (Statistical Yearbook, 1997) shows that the sewage sludge accumulated in Poland amounted to 4,703,000 tons. In 1997 a total of 753,000 tons were produced from which 180,000 tons were utilized economically, 56,000 tons were rendered harmless and approximately 517,000 tons were disposed of in landfills. The prospects for sewage sludge to be used in agriculture have been discussed in

---

Address correspondence to Marian Turek, Silesian University of Technology, Faculty of Chemistry, ul. B. Krzywoustego 6, 44-100 Gliwice, Poland. E-mail: turek@polsl.gliwice.pl

numerous publications (Veeken *et al.*, 1999; Lake *et al.*, 1984; Attenborough *et al.*, 1995; Kabata-Pendias *et al.*, 1999). The main hindrance in this respect is the steadily increasing concentration of heavy metals, resulting in their accumulation in soil and plants (McBride, 2003).

Anaerobic sludge digestion produces substances of acidic nature: acetic and formic acids, hydrogen sulfide. The acidification of sludge facilitates the migration of heavy metals into wastewater and consequently into deep and ground waters, causing their transfer into the food chain.

World literature on the topic shows that the contamination of sewage sludge with heavy metals is a very common problem. Several methods dealing with their removal are currently under investigation:

- the addition of substances that bind metals to form sparingly soluble compounds which are not leached by rain (Adamski, 1993,) including sorption methods (Bailey *et al.*, 1999; Chen *et al.*, 1997),
- biological removal via plants and bacteria (Tyagi *et al.*, 1993; Kleiman *et al.*, 1998; Rahmani *et al.*, 1999; Chang *et al.*, 1997),
- metal removal by means of electromigration (Alshawabke at al., 1999; Lehecho *et al.*, 1998; Reddy *et al.*, 1999; Zagury *et al.*, 1999),
- chemical leaching (Veeken *et al.*, 1999; Ciba *et al.*, 1999; Korolewicz *et al.*, 2000; Korolewicz *et al.*, 2001; Das *et al.*, 1995; Thoming *et al.*, 1995; Bordas *et al.*, 2001).

In sewage sludge, metals occur in inorganic forms or organic complexes. In order to assess their mobility (especially the extremely toxic ones such as lead, cadmium and zinc) and the hazards they pose, it is necessary to distinguish their forms and assay their quantities. This may be achieved through speciation analysis (Hulanicki, 1997). The most popular are chemical sequential extractions, which consist of treating a sample with chemical solutions of various leaching strength. Kersten *et al.* (1995) present a large number of examples. Most of them are modifications of the classical techniques developed by Tessier and Rudd (Tessier *et al.*, 1979; Rudd *et al.*, 1988). Because there was a need for the standardization of the methodology concerning extraction leaching in sludges, soils and composts in the EU countries, the Community Bureau of Reference (BCR) recommended a simple, three-stage sequential extraction procedure (Ure *et al.*, 1993; Quevauiller *et al.*, 1996; Davidson *et al.*, 1999). The entrance of Poland into the European Union necessitates certain adjustments to comply with the standards and regulations on environmental protection imposed on EU members; this also applies to standard analytical methods.

A comparison of the results of leached metal fractions obtained applying the above sequential procedures is necessary for both scientific and practical reasons. It enables a determination of correlations between particular metal fractions and assayed chemical forms of elements. The sequential extraction by Rudd *et al.* (1988) determines (depending on a number of fractions assayed) the suitability of individual extractants for preparative extraction.

The objectives of our work were (1) to compare different extraction procedures applied to sludge, and (2) to devise a method, based on the extraction results, of reducing elevated metal contents in sludge to allow safe land application of the sludge.

This work deals with the sewage sludge from municipal treatment plants in Zabrze (sludge I—after fermentation, sludge II—raw) and Siemianowice Śląkie. The tests included the determination of total metal concentration, the process of metal speciation applying the sequential extractions by Tessier *et al.* (1979), Rudd *et al.* (1988), and BCR (Ure *et al.*, 1993; Quevauiller *et al.*, 1996; Davidson *et al.*, 1999), and the analysis of chemical forms of metals. Preparative leaching of zinc and other metals with sodium pyrophosphate (V), sodium salt of ethylenediaminotetraacetic acid and ammonia water was also carried out.

2. Experimental

2.1. Apparatus and Reagents

All metals were assayed by flame atomic absorption spectrometry (FAAS) using a Perkin-Elmer Spectrometer Model 3300 and manufacturer's standard conditions. All reagents were analytically pure and solutions were prepared using deionized water (Elix, Millipore). Stock solutions of analytes (1 g/dm^3) were prepared by dissolving pure metal or the appropriate salts and making up to volume with deionized water. Calibration standards were prepared by appropriate dilution of the stock solution with nitric acid (concentration of 0.1 mol/dm^3) prior to use. A multiposition shaker WU-4 with continuously variable rotation control was used in the investigations of extraction, and laboratory centrifuge WL 5000 rpm was used for separation of the solid phase from the extractant liquid.

2.2. Determination of Heavy Metals

A comparison and assessment of the concentrations of trace elements in sewage sludge can be made only by determining their total concentration, which in this work was conducted applying the following modified procedure (Korolewicz *et al.*, 2000; Alloway, 1990). A sewage sludge sample was dried at 25°C untill stable weight was achieved and then it was ground and homogenized. In order to assay the total concentration of zinc as well as cadmium, cobalt, copper, manganese, nickel and lead, 10 cm^3 of concentrated nitric (V) acid and 5 cm^3 of concentrated chloric (VII) acid was added to each of four sewage sludge samples (1.0000 g each). Then the mixture was heated on a hotplate at 90–100°C for one hour and evaporated to dryness. Nitric (V) acid (7.5 cm^3; concentration of 3.3 mol/dm^3) was added to the dry residue, then it was heated at 90–100°C for one hour and subsequently transferred quantitatively into 25 cm^3 volumetric flasks and filled to volume with redistilled water. The metals were assayed in the solutions obtained by means of FAAS. The allowable levels of heavy metals in sewage sludge used for non-industrial purposes are shown in Table 1 while the concentrations of metals in the sewage sludge are presented in Table 2.

2.3. Sequential Analysis

The comparison of the data in Tables 1 and 2 reveals that the concentrations of all metals in the sewage sludge from Siemianowice Śląkie are very low, which means that it can be used for agricultural purposes and composting. Their concentrations in the sludge from Zabrze are also low, except for zinc, whose value fell within a range of 3300–3500 mg/kg. For this reason, sludge I after fermentation was used in the sequential tests.

Extraction by Tessier et al. (1979). In this method, the extractants used were magnesium chloride, sodium acetate, a mixture of hydroxylamine hydrochloride and acetic acid, a mixture of nitric acid (V) hydrogen peroxide, and a mixture of ammonium acetate and nitric acid (V), aqua regia.

Table 1
The allowable levels of heavy metals in sewage sludge used for non-industrial purposes (MOŚZNiL, 1999)

	Allowable metals concentrations, mg/kg, dry wt.		
Metals	Agricultural[1]	Non-agricultural[2]	Ground maintenance
Pb	500	1000	1500
Cd	10	25	50
Cu	500	1200	2000
Ni	100	200	500
Zn	2500	3500	5000

[1] Reclaim land for farming and composting.
[2] Reclaim land for non-agricultural purposes.

The following procedure was applied: a homogenized sample of sewage sludge was treated with an extractant and shaken. The samples were centrifuged, after washing, the solid phase was treated with another extractant and the concentrations of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn were assayed in the extracts obtained applying FAAS. The extraction conditions are shown in Table 3. The amounts of particular metal forms in the sewage sludge from the four samples are presented in Figure 1.

Extraction by Rudd et al. (1988). The extractants applied were: water, potassium nitrate, potassium fluoride, sodium pyrophosphate (V), sodium salt of ethylenediaminetetraacetic acid, nitric (V) acid and aqua regia. The following procedure was used: a homogenized sample of the sewage sludge was treated with an extractant (solid phase : fluid phase = 1 : 10) and then shaken periodically (15 minutes every hour) for 72 hours. The samples were centrifuged, the solid phase was treated with another extractant after having been washed with water, and lead concentration was determined by FAAS in the extracts obtained. The extraction conditions are shown in Table 4. The amounts of particular metal forms in the sewage sludge from the four samples are presented in Figure 2.

BCR extraction (Ure et al., 1993; Quevauiller et al., 1996; Davidson et al., 1999). The extractants used were: acetic acid, hydroxylamine hydrochloride, hydrogen peroxide, ammonium acetate and aqua regia. The extraction conditions are shown in Table 5. The amounts of particular metal forms in the sewage sludge from the four samples are presented in Figure 3.

Table 2
Total concentrations of metals in sewage sludge

	Concentration of metals, mg/kg*							
Sewage sludge	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Sewage I, after fermentation	3.43	5.25	131	51300	177	37.5	104	3300
Sewage II, raw	4.20	9.50	169	23300	340	31.5	128	3550
Raw sewage, Siemianowice Śl	6.62	2.50	101	42800	241	33.0	238	2100

*Initial sample of sewage sludge.

Table 3

Condition of the sequential extraction by Tessier *et al.*, 1979

No	Form	Extractant	pH	Time, h	Temp., °C	Stirring
I	Exchangeable	$MgCl_2$ 1 mol/dm^3	7	1	25	Continuous
II	Bound to carbonates	CH_3COONa 1 mol/dm^3 + CH_3COOH	5	5	25	Continuous
III	Bound to Fe/Mn oxyhydroxides	$NH_2OH{\cdot}HCl$ 0.04 mol/dm^3 + 25% (v/v) CH_3COOH		6	96	Periodical
IV	Bound to organic matter	H_2O_2 30% + HNO_3 0.02 mol/dm^3		2	85	Periodical
IV		H_2O_2 30% + HNO_3	2	3	85	Periodical
IV		CH_3COONH_4 3.2 mol/dm^3 + (v/v) HNO_3 20%		0.5	25	Continuous
V	Residual	HNO_3 4 mol/dm^3 + HCl 36%		0.5	96	Periodical

2.4. Determination of Chemical Forms of Metals

The chemical forms of zinc were determined applying speciation. On the basis of the literature data collated by Filippova (1964) and Steger (1976) and tabulated in paper (Suwińska *et al.*, 1998), the following procedure was applied:

25 cm^3 of an extractant (in the case of water it was 50 cm^3) was added to 1.0000 g samples of the sewage sludge, which were then subjected to extraction under the conditions shown in Table 6. The bed was centrifuged, washed with 10 cm^3 of H_2O, centrifuged again and subjected to another extraction. The chemical forms of metals were determined in the mixed solutions of the extractant and water after suitable preparation of the samples. The amounts of particular metal forms in the sewage sludge from the four samples are presented in Figure 4.

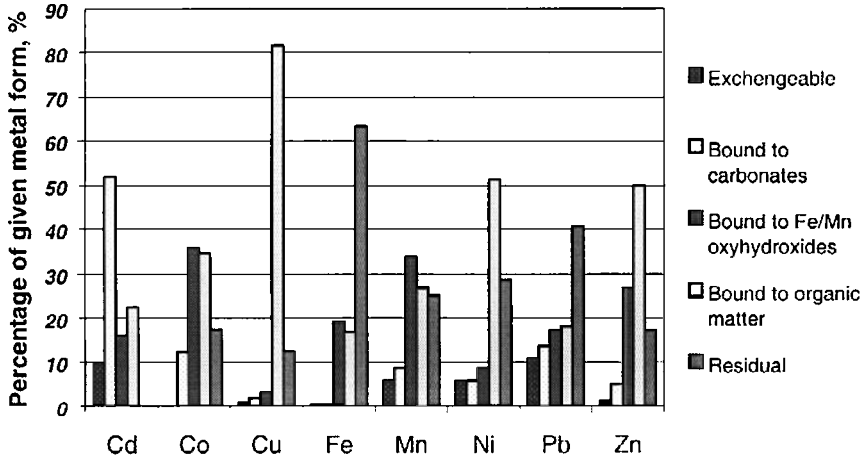

Figure 1. Concentrations of metal forms using the sequential extraction by Tessier *et al.*, 1979.

Table 4

Conditions of the sequential extraction by Rudd *et al.*, 1988

No	Form	Extractant	Concentrat. mol/dm^3
I	Soluble	H_2O	—
II	Exchangeable	KNO_3	1.0
III	Adsorbed	KF	0.5
IV	Organically bound	$Na_4P_2O_7$	0.1
V	Carbonate	EDTA	0.1
VI	Sulfide	HNO_3	6.0
VII	Insoluble	HCl	12.0
		HNO_3	4.0

Table 5

Conditions of the sequential extraction by BCR procedure (Ure *et al.*, 1993; Quevauiller *et al.*, 1996; Davidson *et al.*, 1999)

No	Form	Extractant	Concentrat. mol/dm^3
I	Exchangeable and carbonate	CH_3COOH	0.11
II	Bound to Fe/Mn oxyhydroxides	$NH_2OH{\cdot}HCl$	0.1
III	Bound to organic matter or sulfides	H_2O_2	7.94
		CH_3COONH_4	1.0
IV	Residual	HNO_3	4
		HCl	12

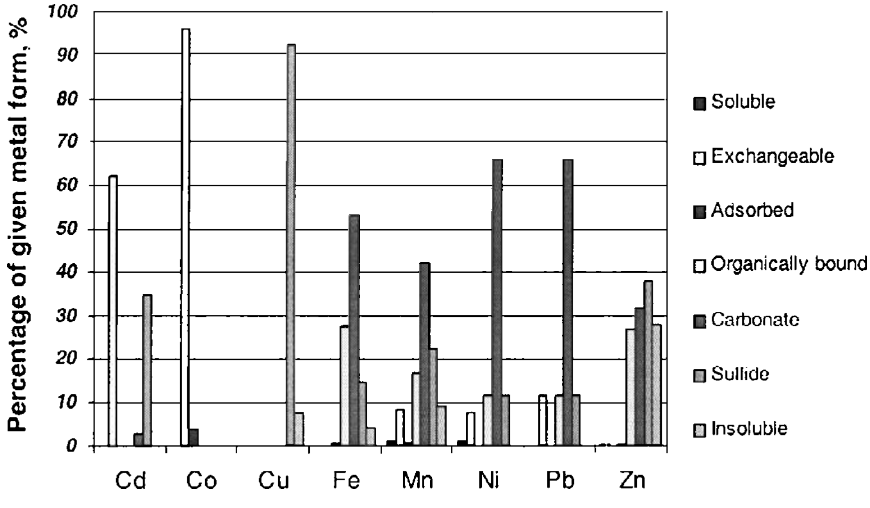

Figure 2. Concentrations of metal forms using the sequential extraction by Rudd *et al.*, 1988.

Table 6
Extraction conditions of chemical forms of metals

No	Form	Extractant	Time, h	Temperature, °C
I	Sulfate	H_2O	1	70
II	Oxide	NaOH 2 mol/dm^3	0.5	50
III	Metallic	CH_3COOH 2 mol/dm^3	0.5	50
IV	Siliceous	CH_3COOH 2 mol/dm^3 + $(CH_3)_2CO$, v/v = 1:1	1	25
V	Sulfide	CH_3COOH 2 mol/dm^3 + 25% H_2O_2, v/v = 1:1	1	
VI	Ferrate	68% HNO_3 + 36% HCl v/v =1:3	1	70

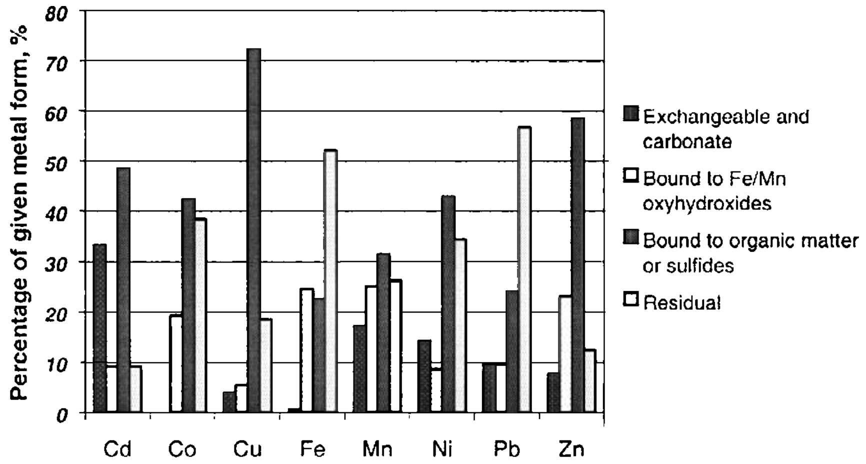

Figure 3. Concentrations of metal forms using the sequential extraction by BCR procedure (Ure *et al.*, 1993; Quevauiller *et al.*, 1996; Davidson *et al.*, 1999).

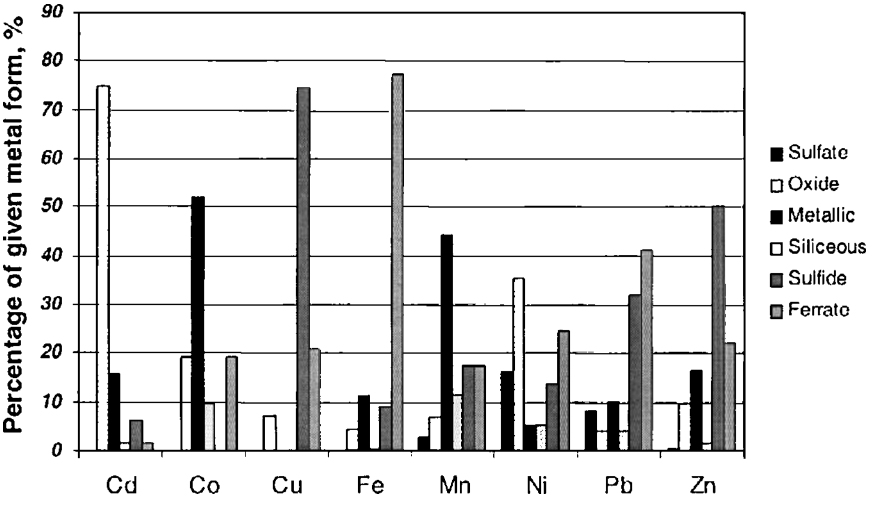

Figure 4. Chemical forms of metals in sewage sludge.

Table 7

Concentrations of metals in sewage sludge from Zabrze after single leaching: sludge I after fermentation, sludge II

			Metal concentrations, mg/kg*							
Sewage sludge	Sludge: solution	Extractant	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Sludge I	1:100	$Na_4P_2O_7$ 0.1M	2.5	4.1	104	23100	88.0	21.5	99.0	1640
”	1:100	$NH_3 \cdot H_2O$ 2M	2.4	4.0	91.5	39100	169	21.0	101	2360
”	1:100	EDTA 0.1M	1.1	2.1	105	17700	28.3	12.8	44.0	1200
	Initial concentration		3.43	5.25	131	51300	177	37.5	104	3300
Sludge II	1:100	$Na_4P_2O_7$ 0.1M	3.1	7.1	140	13400	151	20.1	117	1810
”	1:100	$NH_3 \cdot H_2O$ 2M	2.8	6.7	102	19900	319	16.7	109	1940
”	1:100	EDTA 0.1M	1.4	3.9	129	7600	70.4	10.6	59.0	1380
	Initial concentration		4.20	9.50	169	23300	340	31.5	128	3550

*Initial sample of the sludge.

3. Preparative Extraction of Zinc and Other Heavy Metals

Table 1 shows data concerning permissible concentrations of heavy metals in sewage sludge used for non-industrial purposes in Poland (MOŚZNiL, 1999). The analysis of the sewage sludge presented in Table 2 indicates that the sludge from Siemianowice Śląkie meets the strictest requirements (Table 1). In the sludge from Zabrze, however, the amount of zinc reaches 3500 mg/kg, and in some cases even exceeds this value which is confirmed by the routine tests carried out. This reduces the number of sewage applications. Therefore, it is advisable to develop a method that would decrease zinc concentration in the sludge below the level of 3500 mg/kg. Further reduction below 2500 mg/kg would offer new possibilities for sludge management.

The literature data (Alloway, 1990; Clayton *et al.*, 1971; Sauerbeck *et al.*, 1985) and our own investigations (Reddy *et al.*, 1999; Zagury *et al.*, 1999; Ciba *et al.*, 1999) suggest that sodium pyrophosphate (V) and sodium salt of ethylenediaminetetraacetic acid (EDTA) can be used to leach heavy metals (including zinc) from sludge and compost. Heavy metals form stable and readily water-soluble complexes with the above extractants (Sillen *et al.*, 1964; Lake, 1987).

As for the sewage sludge with abundant iron, ammonium solution seems to be a favorable extractant due to the ability to form soluble amino complexes of zinc, nickel, cadmium, cobalt and copper (Sillen *et al.*, 1964). Under such conditions, iron remains in the sludge.

Preparative leaching of zinc and other metals from sewage sludge I (after fermentation) and sludge II (raw) with the above extractants was carried out.

The extraction was conducted as follows: the sludge was treated with $Na_4P_2O_7$—concn. 0.1 mol/dm^3, EDTA—concn. 0.1 mol/dm^3 and $NH_3{\cdot}H_2O$—concn. 2.0 mol/dm^3 (ratio m:V = 1:1000). The samples were leached periodically for 15 min. every hour during 24 hours. The sludge was centrifuged, washed with 10 cm^3 of water and dried at 105°C. The determination of metals in the leached sewage sludge was carried out by means of the modified method (Biul. FAO, 1989) in which most cations present in carbonates, phosphates, oxides and sulfides are leached and the organic matter easily decomposed, although the aluminosilicates present in the samples are not completely dissolved.

Samples weighing 1.0000g were taken from dry homogenized sludge and treated with a mixture of 10 cm^3 nitric acid (V)—concn. 4 mol/dm^3 and 30 cm^3 hydrochloric acid—concn. 12 mol/dm^3. The solutions were evaporated to dryness. The dry residue was leached with nitric (V)—concn. 0.1 mol/dm^3 at boiling point for 60 min and transferred to 25-cm^3 flasks. The samples obtained were used to determine the concentrations of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn applying FAAS. The results are given in Table 7.

4. Results and Conclusions

The quantity of metals in the sewage sludge of interest (Table 2) and their comparison with permissible levels (Table 1) reveals that in the sludge from Zabrze, only zinc occurs in the quantities, which limit the number of sludge applications.

The analysis of the metal forms (Figures 1–3) shows that the fraction of potentially bioavailable forms (i.e. up to the organically bound form) constitutes the biggest part of the content of all the metals (except for iron, which is regarded as a non-toxic element), the contents of the most mobile exchangeable form and moderately mobile carbonate form being low. The analysis of the metal forms using the BCR method (Ure *et al.*, 1993; Quevauiller *et al.*, 1996; Davidson *et al.*, 1999) determines fewer forms than the methods by Tessier *et al.* (1979) or Rudd *et al.* (1988) (it assays total concentrations for the exchangeable and carbonate forms) and requires slightly different leaching conditions. Nevertheless, the use of those methods yielded very similar concentrations of particular fractions. Some differences are probably due to the transfer (inaccurate separation) of certain amounts of one form into another. This is, however, typical of the sequential analysis.

The individual sequential analysis (Figure 4) enables the differentiation and determination of a larger number of forms than was the case of the methods of sequential analysis discussed above. It distinguishes additionally the soluble sulfate, metallic and sulfide forms, the last being determined in combination with the organically bound form in the method by Tessier *et al.* (1979).

The method of individual sequential analysis determined a negligible fraction of the sulfate form, which is obvious since sewage sludge is produced through filtering water suspensions. The comparison of the data in Figure 1, 3 and 4 reveals that the total of the exchangeable and carbonate forms as well as the forms bound with hydrated manganese and iron oxides (method by Tessier *et al.*, 1979, and Rudd *et al.*, 1988) corresponds to the total of the sulfate, oxide, metallic and silicate forms, while the forms bound with sulfates and organic matter correspond to the sulfide form, and the residue to the ferrate form.

The comparison of the data in Tables 2 and 7 indicates that the preparative leaching of sewage sludge with sodium pyrophosphate (V), sodium salt of ethylenediaminotetraacetic acid and ammonia water results in a significant decrease in the concentrations of all the metals tested. The best results are obtained employing EDTA of 0.1 mol/dm^{3}concentration, which leaches cobalt, iron, manganese, lead and zinc to the highest extent; zinc, the most significant metal in respect of sewage sludge usability, being leached to a level of 12000–1380 mg/kg. The fact that the leaching degrees for lead, nickel and manganese were relatively high is irrelevant due to their negligible occurrence, much lower than the permissible levels (Table 1). The leaching of substantial quantities of iron is unfavorable since it does not affect the quality of the sludge but necessitates the excessive use of extractants. Although the use of ammonia produced the expected effect of iron leaching (23.8%), in the case of zinc it reached its lowest value of a mere 28.5% for sludge I, while for sludge II, at a lower leaching degree of iron (14.6%), the degree for zinc was much higher and reached 45.3%. In the case of $Na_4P_2O_7$ and EDTA, the leaching degrees for zinc were 50.3%, 63.6% and 49.0%, 61.1%, respectively. A substantial reduction in zinc concentrations is not feasible under these conditions due to the occurrence of Zn, mainly in the soluble sulfide and organically bound forms (Figures 1–4).

In conclusion, the use of sodium salt of ethylenediaminotetraacetic acid during a single leaching session results in a deep removal of zinc from sewage sludge. Zinc may be removed to a level of 2500 mg/kg, which allows sludge to be used in the reclamation of land for both non-agricultural and agricultural purposes and might offer better prospects for sewage applications.

References

Adamski, W. 1993. Modern technologies of contaminated soil reclamation. *Ochrona Środ.* 1–2, 7–17 (in Polish).

Alloway, B.J.1990. *Heavy Metals in Soils*, Blackie and Son Ltd., Glasgow.

Alshawabke, A.N., Yeung, A.T., Bricka, M.R. 1999. Practical aspects of in-situ electrokinetic extraction. *J. Environ. Eng-Asce.* **125**(1), 27–35.

Attenborough, G.M., Smith, S.R., Minski, M.J. 1995. The fate and environmental activity of heavy metals in sevage sludge applied to soil. In: International Conference "Heavy Metals in the Environment," September-Hamburg, 2, 459. (Wilken, R., Forstner, U., Knochel, A., Eds).

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D. 1999. A review of potentially low-cost sorbents for heavy metals. *Water Res.* **33**, 2469–2479.

Biul. FAO Res. 1989. Network Trace Elements, Gandawa.

Bordas, F., Bourg, A. 2001. Effect of solid/liquid ratio on the remobilization of Cu, Pb, Cd and Zn from polluted river sediment. *Water, Air, Soil Pollut.* **128**, 391–400.

Chang, L.W., Meier, J.R., Smith, M.K. 1997. Application of plant and earthworm bioassays to evaluate remediation of a lead-contaminated soil. *Arch. Environ. Contam. Toxicol.* **32**, 166–171.

Chen, X.B., Wright, J.V., Conca, J.L., Peurrung, L.M. 1997. Effects of pH on heavy metal sorption on mineral apatite. *Environ. Sci. Technol*. **31**, 624–631.

Ciba, J., Korolewicz, T., Turek, M. 1999. The occurrence of metals in composted municipal wastes and their removal.*Water, Air, Soil Pollut*. **111**, 159–17.

Clayton, P. M., Tiller, K. G. 1971. *CSIRO Div. of Soils. Tech. Papers*. **41**, 1–17.

Das, A.K., Chakraborty, R., Cervera, M.L., Guardia, M. 1995. Metal speciation in solid matrices.*Talanta*. **42**, 1007–1030.

Davidson, Ch., Ferreira, P.C.S., Ure, A.M. 1999. Some sources of variability in application of the three-stage sequential extraction procedure recommended by BCR to industrially-contaminated soil. *Fresenius J. Anal. Chem*. **363**, 446–451.

Filippova, N.A. 1964. Phase analysis of ores and ores processing products. *Metalurgizdat*, Moskva (in Russian).

Hulanicki, A. 1997. Speciation analysis of biological samples.*Wiadomoúci Chemiczne*. **51**(3–4), 187–203 (in Polish).

Kabata-Pendias, A., Pendias, H. 1999. Biogeochemistry of trace elements. *PWN. Warszawa* (in Polish).

Kersten, M., Forstner, U., In: Ure, A.M., Davidson, C.M. 1995. *Chemical Speciation in the Environment*. (Blackie Academic and Professional), Glasgow.

Kleiman, I.D., Cogliatti, D.H. 1998. Chromium removal from aqueous-solutions by different plant-species. *Environ. Technol*. **19**(11), 1127–1132.

Korolewicz, T., Turek, M., Ciba, J. 2000. Extraction removal of lead from soil. *Arch. Environ. Protec* (26), 83–91.

Korolewicz, T., Turek, M., Ciba, J. 2001. Speciation and removal of zinc from composted municipal solid wastes. *Environ. Sci. Technol*. **35**, 810–814.

Lake, D. L. 1987. Chemical speciation of heavy metals in sewage sludge and related matrices, 126–148. In: *Heavy Metals in Wastewater and Sludge Treatment Processes* (Lester, J. N. Ed.). Boca Raton, Florida.

Lake, D.L., Kirk, P.E.W., Lester, J.N. 1984. Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soils. *Review. J. Environ. Qual*. **13**, 175–183.

Lehecho, I., Tellier, S., Astruc, M. 1998. Industrial site soils contaminated with arsenic or chromium-evaluation of the electrokinetic method. *Environ. Technol*. **19**(11), 1095–1102.

McBride, M.B. 2003. Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks? *Adv. Environ. Res*. **8**(1), 5–19.

MOŚZNiL. Regulation dated 11 August 1999 on the standards for the utilization of sewage sludge for non-industrial purposes. *Journal of Laws* No. 72. Item 813 (in Polish).

Quevauviller, P., van der Sloot, H.A., Ure, A.M., Mantau, H., Gomez, A., Rauret, G. 1996. Conclusions of the workshop: harmonization of leaching/extraction tests for envirinmental risk assessment. *Sci. Total Environ*. **178**, 133–139.

Rahmani, G.N.H., Sternberg, S.K. 1999. Bioremoval of lead from water using Lemna-Minor. *Bioresource Technol* **70**(3), 225–230.

Reddy, K.R., Donahue, M., Saichek, R.E., Sasaoka, R. 1999. Preliminary assessment of electrokinetic remediation of soil ands sludge contaminated with mixed waste. *J. Air Waste Manage*. **49**(7), 823–830.

Rudd, T., Lake, D.J., Mehrota, J., Sterritt, R.M., Kirk, P.W.W., Campbell, J.A., Lester, J. 1988. Characterization of metal forms in sewage sludge by chemical extraction and progressive acidification. *Sci. Total Environ*. **74**, 149–175.

Sauerbeck, D.R., Styperck, P. 1985. *Chemical Methods for Assessing Biovailable Metals in Sludges and Soils*. 49. R. Leschber, R.D. Davis, P. L'Hermite, Eds. Elsevier, Amsterdam.

Sillen, L.G., Martell, A.E. 1964. *Stability Constants of Metal-Jon Complexes*. The Chemical Society, Burlington House, London.

Statistical Yearbook. 1997. *Environmental Protection*, Warszawa. (in Polish)

Steger, H.F. 1976. Chemical phase-analysis of ores and rocks. *Talanta*. **23**, 81–97.

Suwińska, T., Ciba, J. 1998. The speciation analysis of zinc and lead in metallurgical dust. *Zesz. Nauk. Pol. Śl., Chemia*, **136**, 197–205 (in Polish).

Tessier, A., Campbell, P.C., Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844–851.

Thoming, J., Calmano, W. 1995. Remediation of heavy metal contaminated soils by acid leaching and electrolytic metal separation. 895–902. In: *Contaminated Soil'95* (Van den Brink, J., Bosman, R., Arendt, F., Eds.). Kluwer Academic.

Tyagi, R.D., Blais, J.F., Auclair, J.C., Meunier, N. 1993. Bacterial leaching of toxic metals from municipal sludge: influence of sludge characteristics. *Water Environ. Res*. **65**, 196–204.

Ure, A.M., Quevauviller, P., Mantau, H., Griepink, B. 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertakten under the auspices of the BCR of the Commision of the European Communities. *Int. J. Environ. Anal. Chem*. **51**, 135–151.

Veeken, A.H.M., Hamelers, H.V.M. 1999. Removal of heavy-metals from sewage-sludge by extraction with organic acids. *Water Sci. Technol*. **40**, 129–136.

Zagury, G.J., Dartiguenave, Y., Setier, J.C. 1999. Ex-situ electroreclamation of heavy-metals contaminated sludge—Pilot-Scale Study. *J. Environ. Eng-Asce*. **125**(10), 972–978.