FRACTIONATION OF HEAVY METALS IN SEWAGE SLUDGE AND THEIR REMOVAL USING LOW-MOLECULAR-WEIGHT ORGANIC ACIDS

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Abstract. The total concentration and the concentrations of individual chemical species of selected heavy metals were estimated in primary and anaerobically digested sewage sludge. The concentration of Zn (1503 mg/kg) was highest and was followed by Cu (201 mg/kg), Cr (196 mg/kg), Pb (56 mg/kg), Ni (44 mg/kg) and Cd (3.6 mg/kg). The metal was divided into 5 fractions (exchangeable (F1), adsorbed (F2), organically bound (F3), bound to carbonates (F4), and residual (F5)) via sequential extraction. The sludge treatment procedure had no significant effect on the fractionation results. In both the primary and anaerobically digested sewage sludge, the heavy metals were ranked according to their mobilities (fractions F1 and F2) in the following order: $Ni > Zn > Cu > Cd > Pb > > Cr$. Metal stability in the environment was evaluated by the sulphide and residual fraction F5, and the following ranking order was identified: $Cr > > Pb \approx Ni > Cd > Zn \approx Cu$. A leaching experiment with low-molecular-weight organic acids (oxalic, acetic and citric acid) revealed that the metal-removal efficiency varied depending on the number of carboxyl groups in the extracting agent, the chemical speciation of the metal (Ni, Zn or Cu) in the sludge and the concentration and pH change of the extracting solution. Acid solutions with a 0.5 M concentration, ranked according to their Zn-removal efficiency, are ranked as follows: citric acid (100%) > acetic acid (78%) > oxalic acid (71%). In all of the cases, citric acid showed the best capacity for the removal of metal from the sludge, with an extraction efficiency ranging from 30–100%, while the Ni and Cu removal efficiencies with the acetic and oxalic acid were less than 40%.

Keywords: sewage sludge, heavy metals, sequential extraction, heavy metal removal, organic acids.

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Introduction

The safe disposal of municipal sewage sludge (SS) remains a major environmental problem both in Lithuania and worldwide. Lithuanian and EU environmental requirements encourage the development of modern and effective wastewater treatment technologies; therefore, the quantities of sludge are steadily increasing. The current sludge-processing methods pose a threat to the environment and contradict both long-term public interests and the principles of sustainable development. The safe disposal of sewage sludge is encouraged by the chief principles of the EU waste-management policy: avoidance of waste, volume and toxicity reduction and waste recycling.

Environmentally sound sewage sludge disposal in Lithuania is still an open question, and the amount of unutilised wastewater sewage sludge grows constantly at a rate of more than 500,000 t per year. Every year, approximately 20 thousand tonnes of sewage sludge are composted and applied to arable lands in Lithuania (Podgaiskytė, Vaitiekūnas 2009). Over 90% of the sewage sludge generated in Lithuania is stored in special deposits that are not always properly equipped. This type of sludge utilisation requires tens of hectares of land annually, which could be used for other public needs. In addition, such sludge landfilling poses a substantial threat to groundwater and surface-water quality.

Of the various methods for sewage sludge disposal, low-cost and highly effective on-land techniques have been widely applied (Bode, Imhoff 1996; Bowen *et al.* 1992; Mossakowska *et al.* 1998; Paulsrud, Nedland 1997). In most EU countries, at least half of the sludge that is produced in wastewater treatment plants is applied to agricultural land. The application of sewage

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sludge to agricultural soils has many advantages, which include providing a full array of nutrients for plant growth (e.g. phosphorus and nitrogen) and organic matter, thereby increasing the number of beneficial soil organisms, reducing the need for fertilisers and pesticides, and improving the physical and biological properties of the soil (Kvasauskas, Baltrėnas 2009; Su, Wong 2003). However, a wide variety of undesirable elements, such as heavy metals (HMs), can be found in sewage sludge and have adverse effects on the environment (Alloway 1995; Jaskelevičius, Lynikienė 2009; Idzelis *et al.* 2010). Many countries have imposed legal restrictions concerning HM content when sludge is used for on-land applications (e.g. agricultural use as an organic fertiliser or soil amendment) because high concentrations in the sludge may result in heavy metal accumulation in cultivated soils. In the European Union, the maximum acceptable total HM concentrations are fixed by Directive 86/278/EEC of the European Commission (CEC 1986); however, most EU countries enforce more stringent local legislation. In Lithuania, the HM limits in sewage sludge are fixed in LAND 20:2005 ("Requirements for Sewage Sludge Usage for Fertilisation and Remediation"). Furthermore, several studies have shown that the available fraction of heavy metals mainly influences the mobility, bioavailability or phytotoxicity of heavy metals in soils (Filgueiras *et al.* 2004; Rauret 1998). Therefore, the quantification of the various chemical fractions of heavy metals in sludge is necessary for a more detailed assessment of metal mobility, metal bioavailability and phytotoxicity.

The behaviours of heavy metals in soils and their plant uptake are strongly dependent on the nature of the metal, the physico-chemical properties of the sludge/soil and the plant species (McBride 2003). The mobilities of trace metals, their bioavailability and their related toxicity to plants strongly depend on their specific chemical forms or the way that they are bound. Consequently, these factors, rather than the total elemental content, are the parameters that must be determined to assess toxic effects and study geochemical pathways (Legret 1993; Pueyo *et al.* 2001). Sludge-derived metals are generally organically bound and less available for plant uptake than the more mobile metal salt impurities found in commercial fertilisers. In recent decades, a large number of extraction schemes have been developed for fractionation purposes and, although a number of methods have been widely used (Emmerich *et al.* 1982; Förstner, Salomons 1980; Tessier *et al.* 1979), none has been unreservedly accepted by the scientific community. In the study described in this paper, a five-step sequential extraction method was applied to Cd, Cr, Cu, Fe, Ni, Pb and Zn fractionation in accordance with the scheme proposed by Emmerich *et al.* (1982).

Heavy metals in sludge cannot be removed by common sludge treatment methods, such as aerobic or anaerobic digestion (Chipasa 2003). Some recently studied advanced sludge treatment processes aimed to reduce the potential environmental risks of sludge. According to the literature (Jankaitė, Vasarevicius 2005; Jankaitė 2009; Mench *et al.* 1994; Paulauskas *et al.* 2006), the remediation methods for soil and sewage sludge contaminated with heavy metals include solidification/stabilisation, vitrification, electrokinetic remediation, chemical extraction, phytoextraction, phytostabilisation, and chemical stabilisation. Each of these techniques has advantages and disadvantages, depending on the cleaned object, its quantity, the pollution levels and other factors. Most of these technologies are still in the research stage. There is a need for more detailed studies to understand better remediation processes in polluted media.

One of the principal technologies used for the removal of heavy metals from contaminated sewage sludge and soils is chemical extraction. The process of heavy metal acidic leaching uses the principle that metal solubilisation occurs as a result of exchanging the protons supplied by the addition of an acidic solution. The most effective chemical extraction technique is washing sewage sludge with strong acids. However, the aggressive agents used during these chemical methods may destroy the soil structure and result in secondary pollution (Cline, Reed 1995).

The use of compounds that are common in nature, such as easily biodegradable, low-molecular-weight (LMW) organic acids, is more publicly acceptable than synthetic chelate or strong mineral acid extraction technologies. Dacera and Babel (2008) investigated the potential of using raw liquids from pineapple waste fermented by *A. niger* as a source of citric acid to extract chromium, copper, lead, nickel and zinc from anaerobically digested sewage sludge. These researchers studied the effects of pH and leaching time on the extraction efficiency (EE), and it was found that the liquid seemed to remove all of the Cr after 11 days at pH 3.73 and 3.98; Ni and Zn were removed at 94% and 100% EE, respectively, at the same leaching time but only at pH 3.73. The study did not compare the extraction efficiency of citric acid to that of other LMW organic acids. Veeken and Hamelers (1999) concluded that citric and oxalic acid have increased heavy metal extraction capacities (70% and 60%, respectively, for Cu; 90% and 70%, respectively, for Zn) at a mildly acidic pH of 3–4, as compared to HNO_3 (38% and 65% for Cu and Zn, respectively, at a pH of 1.5–2). However, these researchers paid little attention to the metal chemical species.

The objectives of this study were as follows: to chemically fractionate heavy metals in primary and anaerobically digested sewage sludge; to compare the copper, zinc and nickel extraction efficiencies from sewage sludge using three different low-molecular-weight organic acids, including citric acid (CA), oxalic

acid (OA) and acetic acid (AA); to evaluate the influences of factors as concentration, pH and the metal chemical species on the removal efficiency.

1. Materials and Methods

1.1. Sludge sampling and sample pre-treatment

Primary and anaerobically digested sewage sludge were collected at a wastewater treatment plant (WTP) in Kaunas, Lithuania. The sewage sludge samples were air-dried, ground to pass through a 2-mm sieve and stored in dry conditions at room temperature without access to light (in the dark glass bottles). The SS samples were dried to a constant mass at 105 °C to determine their water content. The results of all of the measurements were expressed on a dry mass (DM) basis.

1.2. Equipment

An Agilent 7500i inductively coupled plasma spectrometer with a mass detector (ICP-MS) was used to determine the total contents of 26 different elements, including HM, in the sewage sludge samples. A Perkin Elmer AAnalyst 100 atomic absorption spectrometer (AAS) with deuterium background correction was used to determine the content of Cd, Cr, Cu, Ni, Pb and Zn during the fractionation and removal experiments. A fuel-lean air-acetylene flame was used for all of the metals, except Cr, which requires the stoichiometric conditions of flame gases. When the sensitivity of flame atomic absorption spectrometry was insufficient for determining the HM in the extracts, AAS with electrothermal atomisation (Perkin Elmer HGA 800) was applied. $NH_4H_2PO_4$ (1000 mg/l) was used as a matrix modifier to determine the presence of Cd.

1.3. Reagents

All of the reagents were of analytical grade. Suprapur acids (Merck) and deionised water obtained from a Millipore MilliQ system were used to prepare the samples, extraction solutions and standard solutions. A stock standard solution of HM (1000 ± 2 mg/dm^3 in 5% HNO_3) was obtained from Merck.

The potassium nitrate, sodium hydroxide and nitric acid used in the sequential extraction procedure were obtained from Merck, and disodium ethylenediamine tetraacetate was obtained from Fluka.

All of the standards, reagent solutions and samples were stored in glass containers that were previously cleaned with 4 M HNO_3, rinsed with deionised water and dried.

Sartorius cellulose nitrate membrane filters (pore size, 0.45 μm) were used during the filtration procedure.

1.4. The total concentration of the heavy metals

For the total HM values, the sludge solids were digested with concentrated HNO_3 according to the slightly modified ISO procedure described below. A 0.2000-g quantity of the air-dried sample was accurately added to a 50-ml polytetrafluorethylene (PTFE) crucible and digested with 5-ml of concentrated nitric acid in a closed PTFE vessel on a heat plate at 170 °C. Heating was stopped after 6 h, and the crucible was maintained overnight and allowed to digest while slowly cooling to a constant (room) temperature. Next, the residue was centrifuged and diluted to a volume of 50 ml. The solution was subsequently analysed via ICP-MS using the Agilent 7500i. The obtained data are presented as mg/kg of dry matter (DM) in Table 2.

1.5. The sequential extraction procedure

Sequential extraction was performed using a five-step fractionation procedure recommended by Emmerich *et al.* (1982) in which the metals are divided into five fractions: exchangeable (F1), adsorbed (F2), bound to organic matter (F3), bound to carbonates (F4) and residual (F5) (Table 1).

The extraction procedure was performed with 1.0000 g of air-dried sewage sludge. After each successive extraction, the mixture was centrifuged at 3000 rpm for 30 min, the supernatant was decanted into polyethylene bottles, and the metal concentration in the filtered solution was determined via AAS using a flame or graphite furnace atomiser. The amount of the extracted heavy metal in each fraction was calculated as a percentage ratio of the total metal content. This analysis was performed on three parallel sewage-sludge samples.

Table 1. Sequential extraction procedure according to Emmerich *et al.* (1982)

Fraction	Chemical form of heavy metal	Extraction conditions	
		Reagent	Time and temperature
F1	Exchangeable	25 ml 0.5M KNO_3	16 h at 20 °C
F2	Adsorbed	25 ml deionized H_2O	2 h at 20 °C
F3	Bound to organic matter	25 ml 0.5M NaOH	16 h at 20 °C
F4	Bound to carbonates	25 ml 0.05M Na_2EDTA	6 h at 20 °C
F5	Residual	30 ml 4M HNO_3	16 h at 80 °C

1.6. Heavy-metal extraction using low-molecular-weight organic acids

Heavy-metal extraction with LMW organic acids (acetic, oxalic and citric) was performed using solutions of various concentrations (0.01, 0.05, 0.1, 0.5 and 1.0 M) at a liquid (ml) /solid (g) ratio of 50/1. Extraction was performed using a Heidolph® Reax overhead shaker (60 rpm) at a temperature of 20 °C for 24 h. The pH of all of the solutions was measured before and after extraction. At the end of extraction, the samples were centrifuged and filtered, and the concentration of HM in the solution was determined by applying the flame or graphite furnace AAS procedure.

The results of all of the experiments were collected as an average value derived from three established values of the measured parameter. Any values that differed from the other two values by more than 30% were excluded. The results were statistically evaluated using MS Excel and STATENG.

2. Investigation results

2.1. The total amount of heavy metals in the sewage sludge

ICP-MS analysis of 26 elements in the sludge, including Cd, Cr, Pb, Cu, Ni and Zn (Table 2), identified a wide variation in the total concentration of heavy metals in the investigated samples. In general, the Kaunas WTP sludge samples had low concentrations of Cr, Ni, Pb and Cd but relatively high concentrations of Cu and Zn compared to the limit values fixed in LAND 20:2005. However, the total concentration of heavy metals in the sludges reported by Ščančr *et al.* (2000), Wang *et al.* (2005), Alonso Álvarez *et al.* (2002)

Table 2. Elemental composition of anaerobically digested sewage sludge (ICP-MS data)

Element	Unit mg/kg DM	Element	Unit mg/kg DM
Cr	**196.00 ± 6.8**	Ba	811.87 ± 16.2
Cd	**3.63 ± 1.1**	Li	14.30 ± 2.8
Ni	**44.06 ± 3.5**	B	196.60 ± 5.9
Pb	**56.00 ± 5.8**	Na	1021.47 ± 28.9
Cu	**201.73 ± 6.1**	K	2656.99 ± 89.5
Zn	**1503.07 ± 22.4**	V	16.00 ± 2.8
Mg	3320.91 ± 98.2	Ga	25.73 ± 3.0
Ca	41410.82 ± 316.4	As	2.81 ± 0.8
Fe	26789.72 ± 186.1	Rb	12.66 ± 1.8
Mn	326.19 ± 11.6	Mo	4.02 ± 1.0
Co	10.71 ± 0.16	Ag	14.61 ± 2.2
Sr	105.31 ± 6.8	Pt	0.01 ± 0.002
Al	27339.18 ± 156.8	Tl	3.57 ± 0.7

In bold – heavy metals investigated in fractionation experiment

and others were much higher than the results of this investigation.

Nevertheless, the agricultural application of such sludge, with its elevated concentrations of heavy metals, is restricted. The limit values for HMs in SS applied to agricultural land (Class-I SS) according to the Lithuanian normative document LAND 20:2005 are as follows: Cr < 140 (–) mg/kg, Cd < 1,5 (20–40) mg/kg, Ni < 50 (300–400) mg/kg, Pb < 140 (750–1200) mg/kg, Cu < 75 (1000–1750) mg/kg, Zn < 300 (2500–4000) mg/kg. (The limit values for HMs in sludge that are fixed by Directive 86/278/EEC of the European Commission are in brackets.) Therefore, in an effort to increase the on-land recycling of SS and extend other sludge utilisation alternatives, research should focus on efficient methods for HM removal from sludge. Furthermore, the ICP analysis (Table 2) revealed high contents of divalent metals in the sludge, such as Ca, Mg, Fe, and Ba, which may serve as competing ions for the divalent ions of heavy metals during chemical extraction procedures.

2.2. The distribution of the sewage sludge heavy metals among the chemical fractions

A sequential extraction procedure was used to characterise the retention of the metals in the sewage sludge, depending on the sludge treatment (primary or anaerobic). The concentrations of the metals in fractions F1–F5 were summed and compared to the total metal concentrations. Metal partitioning among the various chemical fractions in the primary sewage sludge and the anaerobically treated SS is reported in Fig. 1.

The fractionation experiment showed that the distribution of HMs in the fractions depended on the solid matrix composition and its properties, but it mainly depended on the nature of the metal itself. The distribution of the metal fractions varied widely for various metals.

The exchangeable fraction of almost all of the metals only represented a small portion (less than 10%) of the total amount of metal found in the sewage sludge. This fraction shows the concentrations of the metal cations, which are non-specifically adsorbed and can be easily replaced by competition with divalent metal ions. The concentration of Ni (12%) in this fraction alone is higher than that of any other metal. The proportion of other metals in this fraction was below 8% and ranged from 2% for Cr to 8% for Zn.

The Cr and Cd contents of the F2 fraction of the primary and anaerobically digested SS were below the detection limit; therefore, these metals were not taken into consideration during the statistical analysis and are not shown in Fig. 1. It is evident from the fractionation analysis data that Cr predominantly accumulated in the F5 fraction in both samples. This
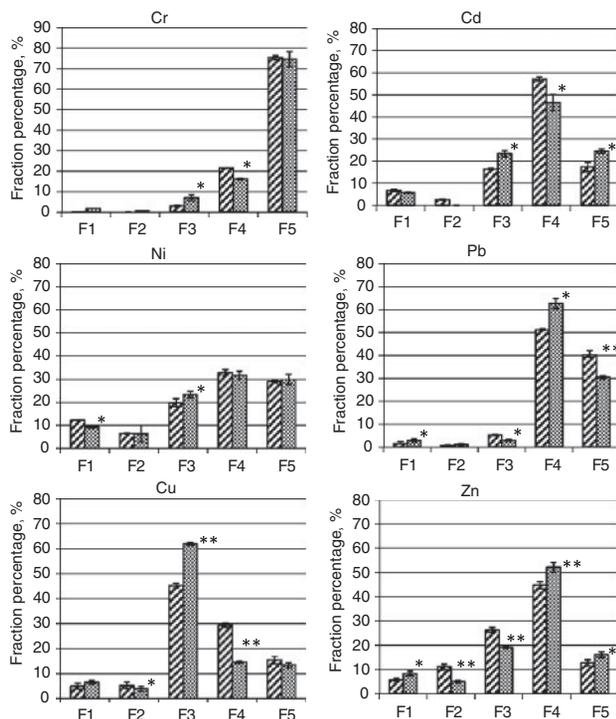
Fig. 1. The chemical fractions (F1–F5) of the heavy metals in the sewage sludge: ▨ – before anaerobical treatment; ▩ – after anaerobical treatment
Note: * – $p \leq 0.05$; ** – $p \leq 0.01$, significant differences indicated before and after treatment

metal binds exceptionally strongly to mineral SS components and does not pose an environmental risk due to its mobility.

Approximately 50% of the total Cu content is associated with the organically bound fraction. The remainder of this element is predominantly distributed between the F4 and F5 phases (22% and 14%, respectively). The preference of Cu for organic matter is supported by the high stability of Cu complexes with organic components (Pardo *et al.* 1990). The sequential extraction procedure also clearly showed that the predominant fractions of Cd and Zn (and Pb in SS after anaerobic processing) are found in fraction F4 (bound to carbonates).

The fractionation data showed that the anaerobic treatment of the sludge had no significant influence on heavy-metal mobility, except in the case of Pb (Fig. 1). The F3 fraction of Pb significantly decreased in the sludge after anaerobic treatment, and Pb was predominantly distributed in the carbonate-bound (F4) and residual (F5) fractions. In general, there were no other significant differences in the heavy-metal distribution between the fractions in the primary and anaerobically processed sludge samples.

The HM mass percentage presented in the first two fractions (F1 and F2, the exchangeable and adsorbed fractions, respectively) was less than 20% in all of the cases (Fig. 1). Because these two fractions can

be characterised as highly mobile and easily bioavailable, the investigated heavy metals can be ranked in the following order according to their availability to living organisms in the environment:

$$Ni > Zn > Cu > Cd > Pb >> Cr.$$

The mobility and bioavailability of both Ni and Zn in the sludge were higher than those of the other investigated heavy metals. These results support the findings of Ščančr *et al.* (2000). Furthermore, fractions F3 and F4 (organic and carbonate–bound matter, respectively) can be described as potentially mobile, and long-term changes related to the soil acidity or intensive organic matter mineralisation can lead to increased heavy metal mobility.

Finally, fraction F5 (the sulphide and residual fraction) can be characterised as absolutely immobile. This fraction contains the portion of the HM ion mass that is bound to insoluble, stable, and poorly degradable compounds. The greater the mass percentage of the HMs that are found in this fraction, the lower the HM mobility in the environment. This observation leads to reduced HM leaching and migration potential. Therefore, in terms of their long-term stability in the environment, the investigated HMs can be ranked as follows:

$$Cr >> Pb \approx Ni > Cd > Zn \approx Cu.$$

These metal partitioning results are equally important for HM removal as stabilisation. It can be anticipated that Cr and Pb are the metals that will be the most difficult to remove from SS, while Cu, Zn and Ni will demonstrate rather high leacheability.

Given the mobility, potential bioavailability, and total concentrations of the heavy metals, it can be concluded that HM-containing sewage sludge cannot be used in agriculture because of the potentially hazardous effects of Ni, Cu and Zn on the environment. Furthermore, these elements should be easily leachable from the sludge and are expected to be characterised by high extraction efficiencies. Nevertheless, such results can be controversial because the removal process is also strongly influenced by many other factors, such as the matrix composition, the chemical properties of the extractant, the concentration and pH of the extracting solution and the temperature.

2.3. The removal of heavy metals using low-molecular-weight organic acids

For the removal of Ni, Cu and Zn from anaerobically processed sewage sludge, LMW organic acids with strong chelating properties were chosen. As shown in the literature (Yuan *et al.* 2007), the soil heavy metal removal capacity of a low-molecular-weight organic acid is affected by the number of carboxylic groups in

that particular acid. Therefore, organic acids with different numbers of carboxyl groups (-COOH) were selected for this experiment:

- monocarboxylic acid – acetic acid (AA) with 1 carboxyl group;
- dicarboxylic acid – oxalic acid (OA) with 2 carboxyl groups;
- tricarboxylic acid – citric acid (CA) with 3 carboxyl groups.

The HM extraction efficiency can be strongly influenced by the acidity of the liquid medium; therefore, the pH values of the organic acid solutions were measured before and after extraction (Table 3). The data show that an increase in the organic acid concentration resulted in smaller changes in the solution pH during extraction because of the limited SS buffering capacity.

Obviously, a lower organic acid solution pH results in the increased dissolution of other competitive divalent cations, such as Ca and Fe, which can also be combined with the anions in the washing solution. Therefore, the large differences among the pH changes in the various organic acid solutions (Table 3) can explain the high variation of their extraction efficiencies. The number of carboxyl groups was also very important for the removal process; a monocarboxylic acid (acetic acid) had the lowest extraction capacity, while a tricarboxylic acid (citric acid) exhibited the strongest extraction capacity. No results were obtained using 1.0 M oxalic acid because the resulting supersaturated solution precipitated.

Additional HM removal experiments showed that the extracted metal content depends on both the nature of the organic acid and its concentration (Figs 2–4). Higher extractant concentrations resulted in more heavy metal extraction. The experimental data showed that the zinc extraction efficiency strongly depended on the organic acid concentration (Fig. 2). At the lowest concentrations of the various acid solutions (0.01 mol/L), the zinc EE was very low (0.5%, 0.9% and 1.4%, for acetic, oxalic and citric acid respectively). The pH values of all of the studied acid solutions after extraction were higher than their values before metal removal (Table 3). The data also showed that the pH values approached neutrality after extraction. This neutralisation could be one of the chief reasons for such a low heavy-metal EE. Polettini *et al.* (2007) reported that during metal extraction from sediments at a low citric acid concentration (0.02 mol/L), more than 72% of the acid combined with competing elements (Ca and Mg). It was also determined that the extraction efficiency decreased with an increasing pH.

The zinc extraction efficiency increased as the acid concentration increased. The 0.05-M LMW organic acid solutions can be ranked by their ability to remove zinc from the SS in the following order: oxalic acid (51%) > >citric acid (13%) $\approx$ acetic acid (12%).

Such a high oxalic acid extraction efficiency may be associated with its low initial pH of 1.6 compared to 2.3 and 3.1 for citric and acetic acid, respectively. The highest pH values were observed for acetic acid before and after extraction. Thus, AA was only able to remove a small amount of the zinc from the sludge. The solutions of 0.05 M AA and CA were able to extract all of the zinc in the highly mobile fraction (below the dotted line). However, 0.05 M oxalic acid exhibited over four times more extraction capacity than 0.05 M AA and CA. However, for all of the studied acids, this solution concentration enabled the removal of the zinc ions associated with the more or less mobile metal fractions (below the dashed line).

Citric and oxalic acid extracted nearly equal amounts of zinc at a solution concentration of 0.1 mol/L, extracting 74% and 72%, respectively, while the acetic acid extraction efficiency was only 29% (Fig. 2). Di Palma and Mecozzi (2007) found that citric acid (0.1 mol/L at a solution-to-sediment ratio of 12.5) was able to extract up to 82% of the total Zn content from the sediment. It is likely that with an increasing concentration of oxalic acid, the concentrations of competing dissolved metal ions (such as Ca^{2+} and Fe^{2+}) that can form stable complexes with this acid also increase.

The difference in the extraction efficiencies of the 0.5-mol/L acid solutions correlates well with the various pH values of the extracting media. The organic

Table 3. The pH values of solutions of LMW organic acids before and after the extraction procedure

Acid solution		pH value at concentration, mol/L				
		0.01	0.05	0.10	0.50	1.00
Acetic acid	Before extraction	3.32 ± 0.01	3.09 ± 0.01	2.99 ± 0.01	2.58 ± 0.01	2.26 ± 0.01
	After extraction	6.89 ± 0.02	4.71 ± 0.01	4.58 ± 0.02	3.82 ± 0.02	3.35 ± 0.01
Oxalic acid	Before extraction	1.90 ± 0.01	1.65 ± 0.02	1.49 ± 0.01	1.07 ± 0.01	n
	After extraction	7.45 ± 0.03	7.15 ± 0.02	1.94 ± 0.01	1.10 ± 0.01	n
Citric acid	Before extraction	2.80 ± 0.01	2.30 ± 0.01	2.26 ± 0.01	1.98 ± 0.01	1.78 ± 0.01
	After extraction	6.93 ± 0.02	3.69 ± 0.01	3.19 ± 0.01	2.83 ± 0.01	2.66 ± 0.01

Mean ± standard deviation; n, no results obtained using 1.0 M oxalic acid because the resulting supersaturated solution precipitated
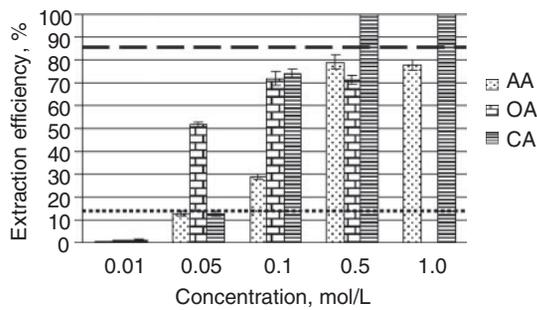
Fig. 2. The zinc-extraction efficiency (%) using various concentrations of organic acids: AA, acetic acid; OA, oxalic acid; CA, citric acid. Below the dotted line, the HM percentage in the mobile fractions (F1 + F2); between the dotted and dashed lines, the HM percentage in the potentially mobile fractions (F3 + F4); above the dashed line, the HM percentage in the immobile fraction (F5)

acids selected for this study are nonspecific acids, and thus may also react with other metal ions, rather than with Zn ions exclusively. The competition between zinc and other metal ions depends on the concentrations of the metal cations and the acid anions in the solution, the pH, and the stability constants of the corresponding metal complexes. Higher concentrations of oxalic acid produced lower pH values after the extraction procedure, which indicates that the competition of Zn with the other dissolved cations was stronger. These results (Fig. 2) show that at a 0.5-mol/L concentration, the investigated acids can be ranked according to their Zn EEs, as follows: citric acid (100%) > acetic acid (79%) > oxalic acid (71%).

Other investigations have shown that organic acids (1 mol/L), including citric acid, acetic acid, and four other investigated acids (except oxalic acid), are able to remove Zn from the soil completely. The total zinc content in the soil was 84.4 mg/kg (Khodadoust *et al.* 2005). Our results showed that 1 mol/L acetic and citric acid removes of the majority of the zinc accumulated in SS (78% and 100% respectively). The lower EE of acetic acid compared to that which has been reported in the literature may be associated with the much higher total zinc concentration in Kaunas sewage sludge and also with lower ratio of carboxyls to zinc.

Fig. 3 shows the dependence of the nickel EE (%) on the organic acid concentration; the superior extraction efficiency was determined by the higher acid concentration. The most nickel (53%) was removed by citric acid (1 mol/L), and the least nickel was removed by acetic acid. Contradictory results were found in the literature. Khodadoust *et al.* (2004) determined that organic acids (1 mol/L) effectively removed nickel, and they were ranked as follows: acetic acid > citric acid > oxalic acid. Their extraction efficiencies were 80%, 60% and 30%, respectively. It should be noted that the pH values of the studied solutions were below 3.5. Furthermore, various extraction conditions and solid matrix compositions are important factors that could lead to various extraction efficiencies. The distribution of Ni in various chemical forms (depending on the results of the sequential extraction) could also substantially influence the metal-extraction efficiency.

Fig. 4 shows the dependence of the copper extraction efficiency (%) on the organic acid concentration. Copper forms specific stable compounds with the OH groups that occur at higher pH values. The solubility constant of $Cu(OH)_2$ is 19.66 (Wuhan University 2004). The formation of this compound may result in a lower Cu extraction efficiency when the solution pH is neutral or alkaline. The fractionation results (Fig. 1) showed that Cu predominantly accumulated in the F3 fraction (bound to organic matter). These results confirm other findings that reported that copper tends to form relatively stable organic-metal complexes that can further reduce copper's leachability from sewage sludge after treatment with LMW organic acids.

The experimental data show that low-concentration organic acid solutions only removed a small amount of the copper and produced a post-extraction solution pH close to neutrality. The results of the sequential extraction confirmed the earlier findings (Fig. 1) that in the investigated sludge samples, most of the copper ions were bound to the sludge organic matter. Furthermore, the majority of the Zn was in the carbonate fraction (Fig. 1), which is easily destroyed in an acidic environment. This difference results in a lower copper extraction efficiency compared to that of zinc.

The investigated LMW organic acids may be ranked according to their Cu extraction efficiencies, as follows: citric acid > oxalic acid > acetic acid. Citric acid (0.1 mol/L) has demonstrated 2 and 10 times more copper EE than oxalic and acetic acid, respectively, with its extraction efficiency approaching 50%.
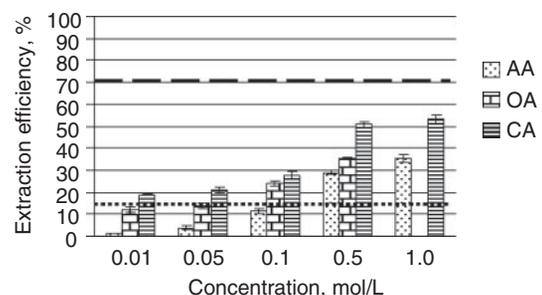

Fig. 3. The nickel extraction efficiency (%) using various concentrations of organic acids: AA, acetic acid; OA, oxalic acid; CA, citric acid. Below the dotted line; the HM percentage in the mobile fractions (F1 + F2); between the dotted and dashed lines, the HM percentage in the potentially mobile fractions (F3 + F4); above the dashed line, the HM percentage in the immobile fraction (F5)
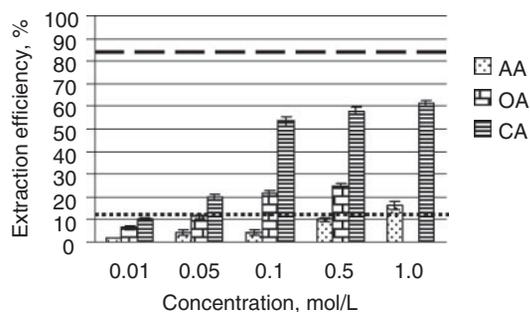
Fig. 4. The copper extraction efficiency (%) using various concentrations of organic acids: AA, acetic acid; OA, oxalic acid; CA, citric acid. Below the dotted line, the HM percentage in the mobile fractions (F1 + F2); between the dotted and dashed lines, the HM percentage in the potentially mobile fractions (F3 + F4); above the dashed line, the HM percentage in the immobile fraction (F5)

This study revealed that a tricarboxylic acid (citric acid) is a stronger extraction agent than oxalic acid (a dicarboxylic acid). In addition, oxalic acid is a strong reducing agent, and, therefore, it can be oxidised by sewage sludge organic matter, leading to fewer oxalate anions in the extraction solution.

The results of the extraction experiment show that all three investigated acids are able to remove the Cu, Zn and Ni found in the mobile metal fractions (F1 and F2). The potentially mobile metal fractions (F3 and F4) of zinc can be effectively removed, and those of nickel and copper can be removed to a lesser extent. Only a tricarboxylic acid (citric acid) was able to remove all of the zinc accumulated in the SS, including the most immobile fraction, F5. None of the investigated acids was able to remove the Ni and Cu associated with the immobile fraction (F5).

Conclusions

1. The results of sequential extraction showed that the heavy metal chemical species in sewage sludge depend less on the solid matrix composition and properties and more on the nature of the metal itself. Anaerobic digestion of the sludge did not change the mobility order of the heavy metals (Ni > Zn > Cu > Cd > Pb > >Cr). When evaluating the metal stability in the environment according to the sulphide and residual fraction (F5), the ranking order was as follows: Cr > >Pb ≈ Ni > Cd > Zn ≈ Cu.

2. The heavy-metal-extraction efficiency using low-molecular-weight organic acids depended on their solution concentration and number of carboxyl groups; a tricarboxylic acid (citric acid) had much more extraction capacity than a dicarboxylic acid (oxalic acid) or a monocarboxylic acid (acetic acid). It was determined that the optimal concentration of citric acid was 0.1 mol/L, which exhibited a metal-extraction efficiency as high as 75% for Zn.

3. The heavy-metal extraction efficiency increased with an increasing solution concentration. No results were obtained for 1.0 M oxalic acid because the supersaturated solution precipitated in this case. The 0.5-M solutions may be ranked according to the percentage of extracted zinc, as follows: citric acid (100%) > acetic acid (78%) > oxalic acid (71%). Furthermore, the extraction efficiency of copper was much less than that of zinc. The ranking order of the organic acids was also different, as follows: citric acid (58%) > oxalic acid (25%) > acetic acid (10%). In the case of nickel, the order was as follows: citric acid (51%) > oxalic acid (35%) > acetic acid (29%). In all of the cases, compared to oxalic and acetic acid, citric acid had a much greater capacity for HM extraction from sewage sludge.

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