Technical paper

The Influence of Lime and Hydroxyapatite Addition on Metal Partitioning and Stabilisation in Sewage Sludge

Ksenija Cer Kerčmar, Marija Zupančič* and Peter Bukovec

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5,
SI-1000 Ljubljana, Slovenia

** Corresponding author: E-mail: marija.zupancic@fkkt.uni-lj.si*
Phone: +386 1 2419126; Fax: +386 1 2419220

Received: 26-03-2008

Dedicated to the memory of Professor Ljubo Golič

Abstract

The influence of lime addition on metal mobility in sewage sludge was studied. The sequential extraction procedure by Tessier was used to evaluate metal mobility in dehydrated sewage sludge with and without lime addition. Data from the partitioning study indicate that As is the most mobile metal in sewage sludge sample, while Ni and Cd are slightly less mobile. Addition of lime in general decreased the mobility of metals. Exceptions are Ni and Cu. The mobility of Ni slightly increased after lime addition, while a great increase in mobility of Cu was observed.

The phosphate stabilisation agent hydroxyapatite was added to sewage sludge to evaluate its stabilisation efficiency for metals and to determine its influence on metal mobility in lime-treated sewage sludge. Water and acetic acid extractions were used for determination of water soluble and potentially bioavailable metal fractions. Results showed a decrease in the mobility of all metals after hydroxyapatite addition, especially Pb and Zn. Concentrations of water soluble metals in lime-treated sewage sludge also decreased after hydroxyapatite addition, but less than in sewage sludge without added lime. In general, lime had a higher stabilization efficiency than hydroxyapatite, but special attention should be given to sewage sludges containing high concentrations of Cu.

Keywords: Hydroxyapatite, immobilization, lime, metals, sewage sludge

1. Introduction

Sewage sludge is recognised as a valuable source that can be recycled as fertilizer and soil improvement material for land because it consists largely of organic substances and also contains nitrogen and phosphorus, which are the main nutrient elements of plants. However, high contamination of sewage sludge with metals has become an obstacle to sludge reuse.[1]

Chemical speciation of heavy metals in sewage sludge evaluates their bioavailability and sustainability for land application. Partitioning of heavy metals involves the fractionation of the total content into exchangeable, acid extractable (carbonate bound), reducible (Fe–Mn oxides bound), oxidizable (organic bound) and residual forms. The exchangeable and acid extractable fractions are mobile fractions and easily available. The oxidizable and reducible forms are leached out only under extreme conditions, while the residual fraction is almost inert. Different methods have been proposed for metal speciation, but the method developed by Tessier et al. is one widely used for this purpose.[2–4]

One approach to reduce the availability of heavy metals is to decrease the concentrations of available chemical species. Immobilization limits the solubility of metals and locks pollutants within the sewage sludge by processes of precipitation, adsorption or complexation.[5] Lime treatment of sewage sludge has been used for centuries to reduce odour generation and pathogen levels in biological matter. It is a simple and effective method of sludge processing that requires little specialized equipment.[1] Liming by increasing the pH enables formation of sparingly soluble hydroxides that in general decrease the mobility of heavy metals.

Many studies on chemical stabilisation were performed using various phosphorus-containing amendments such as synthetic and natural apatites and hydroxyapatites,[6–7] phosphate rock,[8] phosphate-based salts,[9] phosphoric acid[10–11] and their combination. The apatite mineral hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is known to react with many metals and metalloids, rapidly forming secondary phosphate precipitates, that are stable over a wide range of geochemical conditions.[5] Interaction between apatite and metals in solution is controlled by apatite dissolution and results in the precipitation of various phosphate phases.[12–13] The mechanisms suggested by different workers vary, often depending on the cation considered. Proposed mechanisms include ion exchange by diffusion, adsorption, dissolution/precipitation or a combination of several of these.[13]

To evaluate the stabilization efficiency of amendments, different extraction procedures are used. In Slovenian legislation metal concentrations in water extracts are the stated limiting factors.[14–15] The Toxicity Characteristic Leaching Procedure (TCLP) is a regulatory test used widely to classify solid waste materials as hazardous or non-hazardous, based on the potential to leach certain toxic elements.[16] The TCLP was designed to reflect the availability of contaminants under extreme environmental conditions, such as low pH, that could cause the release of contaminants that would otherwise be stable.

The present study was performed to: (i) evaluate the mobility of metals in sewage sludge samples, (ii) determine the influence of lime addition on metal mobility, (iii) evaluate the stabilization efficiency of hydroxyapatite for untreated sewage sludge and (iv) evaluate the influence of hydroxyapatite addition to lime-treated sewage sludge. The study was focused on the mobility of Cr, Ni, Cu, Zn, As, Cd and Pb.

2. Experimental

2. 1. Sampling

Two samples of dehydrated untreated (raw) sewage sludge (SS) and lime-treated sewage sludge (LTSS) that contained 6% (of dry sewage sludge mass) of lime, were obtained from a wastewater treatment plant in Maribor. Subsamples of homogenised sewage sludge used for analysis were pre-treated according to SIST ISO 11464:1996. Subsamples of sewage sludge used for the metal stabilization study were preserved at 4 °C.

2. 2. Analytical Procedures

pH values of sewage sludge samples and its mixtures with hydroxyapatite were determined according to SIST ISO 10390:1996 in a 0.01 M $CaCl_2$ suspension (liquid to soil ratio 5:1) using a WTW inoLab pH Level 2 laboratory pH meter (Weilheim, Germany), equipped with a SenTix 81 electrode. pH of SS and LTSS was also determined in water suspensions (liquid to soil ratio 5:1).

CNS analysis was performed according to ISO 10694, ISO 13878 and ISO 15178 after combustion of samples in a CNS LECO 2000 at 1350 °C.

The concentration of metals in diluted samples was analysed with an Agilent 4500 series ICP-MS instrument, equipped with a Babington nebuliser with a Peltier-cooled spray chamber (carrier gas Ar with a flow of 1.05 L/min, RF power 1300 W). The standard addition technique (N=10) was used to avoid matrix interferences. The limit of detection (LOD) was calculated as the concentration corresponding to three times the standard deviation (3s, N=6) of the blank determinations. Blanks were subjected to the same digestion procedure as samples.

2. 3. Determination of Total Metal Concentrations

To determine the total metal concentration in sewage sludge samples and their mixtures, samples were first dried at 105 °C, powdered and sieved through 0.250 mm test sieve (RETSCH, Haan, Germany). To determine total metal concentration, approximately 0.5 g of air-dried sewage sample was digested in 10 mL of *aqua regia* (HNO_3: HCl=1:3, both TraceSelect, Fluka, Germany) at 473 K for 4 h, using a PFA digestion vessel (561B, Savillex, Minnesota, USA). The contents were filtered through a 0.45 µm membrane filter and diluted to 30 mL with Milli-Q water. Digestion of samples was performed in duplicate including six blank samples in each digestion series. The certified reference material CRM 145R (Trace elements in sewage sludge) obtained from the Community Bureau of Reference (BCR, Geel, Belgium) was used to check the accuracy of the analytical procedures. The concentration of metals in digested diluted samples was analysed by ICP-MS.

2. 4. Partitioning of Metals in Untreated and Lime-treated Sewage Sludge

Fractionation of metals in sewage sludge was determined according to the Tessier five step sequential extraction procedure.[4] Samples used for metal fractionation determination were first dried at 105 °C, powdered and sieved through a 0.250 mm test sieve (RETSCH, Haan, Germany). The extraction was performed in 30 mL polypropylene centrifugation tubes (Sarstedt, Nümbrecht, Germany). A Vibromix 403 EVT mechanical shaker (Tehtnica Železniki, Slovenia) was used to agitate samples during extraction. Between each successive extraction, separation was effected by centrifuging in a CENTRIC 322 A (Tehtnica, Železniki, Slovenia) centrifuge at 3500 rpm for 20 min. The supernatant was removed with a pipette and filtered through a membrane filter of 0.45 µm pore size. After each extraction step 8 mL of Milli-Q water was added to the residue, centrifuged for 30 min at 3500 rpm and the supernatant discharged. Metal concentrations in extraction solutions were determined with ICP-MS. Water used in preparing stock solutions was obtained from a Millipore Milli-Q Ultrapure Water Purification

System. All reagents used for the sequential extraction procedure were of analytical grade. Extraction of samples was performed in triplicate with six blank samples for each series.

Separate steps of the sequential procedure were performed as follows.

Step 1: Exchangeable fraction

To 1.00000 ± 0.00001 g of sample 8 mL of 1M $MgCl_2$ (pH 7, adjusted with NaOH) solution was added. The suspension was then extracted at room temperature for 1 h with continuous agitation.

Step 2: Bound to carbonates

The residue from Step 1 was leached at room temperature with 8 mL 1 M $NaCH_3COO$ (pH 5, adjusted with CH_3COOH) with 5 h agitation.

Step 3: Reducible fraction

20 mL 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) CH_3COOH was added to the residue from Step 2. The suspension was heated at 96 ± 3 °C for 6 h with periodic agitation of the sample.

Step 4: Oxidizable fraction

The residue from Step 3 was extracted with 3 mL 0.02 M HNO_3 in 5 mL 30% H_2O_2 (pH 7, adjusted with 0.02 M HNO_3) at 85 ± 3 °C for 2 h with periodic agitation. After 2 h 3 mL 30% H_2O_2 was added and the sample further heated for 3 h at 85 ± 3 °C. After cooling 5 mL 3.2 M NH_4CH_3COO in 20% (v/v) HNO_3 was added and the samples were diluted to 20 mL with Milli-Q water.

Step 5: Residual

The residue from Step 4 was digested with aqua regia according to the procedure described above for total metal analysis.

2. 5. Preparation of Sewage Sludge Mixtures With Hydroxyapatite

For stabilization studies of hydroxyapatite five mixtures of LTSS with hydroxyapatite addition (samples A) and five mixtures of SS with hydroxyapatite addition (samples B) were prepared. The amount of hydroxyapatite added was calculated as 0% (samples A1 and B1), 5% (samples A2 and B2), 10% (samples A3 and B3), 15% (samples A4 and B4) and 20% (samples A5 and B5) of dry sewage sludge mass. Mixtures were prepared in duplicate.

2. 6. Water and Acetic Acid Extraction of Sewage Sludge Mixtures

To evaluate the stabilization efficiency of metals in sewage sludge by hydroxyapatite, extractions of samples with water and 0.11 M acetic acid were performed. Maximum permitted concentrations of metals leachable in water (m/V = 1:10) ratio are stated in the Regulations on Soil Pollution Caused by Waste Deposits.[14] Beside the water leachable metal concentration, extraction of sludge samples with acetic acid was performed to evaluate the exchangeable fraction.[16–17] This fraction should describe that part of the metals bound on soil sorption complexes, which are potentially bioavailable to plants. Extraction was performed only with sewage sludge mixtures prepared from sludge without lime addition. Since metal solubility strongly depends on pH, 0.11 M acetic acid (pH is 2.8) is not an appropriate extracting solution for estimation of the easily soluble portions of heavy metals in lime-treated sludge.[18]

Extraction of metals from samples with water and 0.11 M acetic acid was carried out in 30 mL polypropylene centrifugation tubes (Sarstedt, Nümbrecht, Germany). 10.0 mL of Milli-Q water or 20.0 mL of acetic acid, respectively, was added to 1.00000 ± 0.00005 g of air-dried sludge sample. Samples were shaken for 16 h at 150 rpm using a Vibromix 403 EVT mechanical shaker (Tehtnica Železniki, Slovenia), centrifuged in a CENTRIC 322 A (Tehtnica, Železniki, Slovenia) centrifuge at 3500 rpm for 20 min, decanted and filtered through a membrane filter of 0.45 µm pore size. Extraction of samples was accomplished in duplicate with six blank samples for each series.

3. Results and Discussion

Results of dry mass content, pH, CNS analysis and total metal content in SS and LTSS are presented in Table 1. The addition of lime to dehydrated sewage sludge (6%) increased the dry mass content and pH of sewage sludge. It should be emphasised that the pH of LTSS determined in $CaCl_2$ solution (standard pedological data – potential acidity of soil) quite differs from the pH determined in water solution due to the higher ionic strength of $CaCl_2$.

Table 1: Dry mass content, pH, results of CNS analysis and total metal concentrations in SS and LTSS sample.

parameter	SS	LTSS
dry mass [%]	14.0 ± 0.12	21.5 ± 0.30
pH (in H_2O)	6.6	13.0
pH (in CaC_2)	6.71	9.44
C [%]	34.9	24.7
N [%]	6.01	4.01
S [%]	0.69	0.47
Cr [mg/kg]	40.1 ± 0.3	28.4 ± 0.7
Ni [mg/kg]	36.5 ± 0.1	22.3 ± 0.4
Cu [mg/kg]	288 ± 0.6	177 ± 6.6
Zn [mg/kg]	678 ± 6	466 ± 3.7
As [mg/kg]	3.89 ± 0.7	2.67 ± 0.7
Cd [mg/kg]	1.38 ± 0.07	0.78 ± 0.02
Pb [mg/kg]	52.8 ± 0.3	35.1 ± 0.3

3. 1. Partitioning of Metals in Untreated and Lime-treated Sewage Sludge

The partitioning study of metals in SS and LTSS was performed by applying Tessier`s five-step sequential extraction procedure.[4] The results of the partitioning study for Cr, Ni, Cu, Zn, As, Cd and Pb in both sludge samples are presented in Figures 1 and 2.

The main fractions between which Cr was partitioned in SS as in LTSS were the residual (52%, 61% respectively), organic (23%, 25% respectively) and Mn and Fe oxide fractions (13%, 20% respectively). Addition of lime to sewage sludge had a negligible effect on the exchangeable and carbonate-bound fraction. The main shift in redistribution of metals caused by lime addition was observed in the reducible fraction, leading in an increase of residual fraction concentrations.

The highest proportion of Ni in the SS sample was associated with carbonate-bound (32%), exchangeable (25%) and residual (22%) fractions. Lime addition slightly increased the Ni concentration in the easily soluble exchangeable fraction (30%), resulting in a decrease in the carbonate-bound fraction (19%). These changes agree with the changes reported by Staelens et al.[19] A significant increase in Ni concentration (from 1 to 24%) in the exchangeable metal fraction after lime addition to sewage sludge was reported by Ščančar et.[20]

Of the heavy metals which commonly occur in sewage sludge, Cu has a relatively high affinity for organic ligands.[17] The results of sequential extraction showed that in the SS sample Cu is predominantly partitioned between the organic (75%) and residual fractions (14%). Lime treatment caused the Cu contained in sewage sludge to become unstable. Only 26% of Cu in LTSS was associated with the organic fraction, whereas 55% of Cu was found in the exchangeable fraction. This phenomenon was also observed by other authors.[1, 20] The alkaline lime can neutralize organic acids and thus reduce the formation of metal-organic matter complexes.[21] The data of Sims showed an increase in plant uptake of Cu due to increasing liming rate in soils amended with composted sewage sludge.[22] There was no change in the Cu concentrations observed in the carbonate-bound fraction after lime addition.

In both sludge samples Zn was mainly associated with Mn and Fe oxides (30% for SS and 42% for LTSS), residual (29% and 32%, respectively) and organic fractions (12% and 26%, respectively). A smaller share of total Zn was bound to carbonates (9% and 11%, respectively) and to exchangeable fractions (3% and 5% respectively). The addition of lime decreased the exchangeable and organic fraction associated Zn concentrations and increased Zn concentrations in the carbonate-bound, reducible and residual fractions.

A major redistribution of metal due to lime treatment of sewage sludge was observed for As, too. In SS As was mainly associated with carbonates (51%). The exchangeable fraction portion represented 28% of the total As concentration. In LTSS As was redistributed from the carbonate fraction to the most sparingly soluble residual fraction that represented 42% of the total As concentration. The exchangeable fraction still contained 23% of total As, whereas the remaining fraction in LTSS was distributed between the reducible fraction (11%), organic matter (15%) and carbonate-bound fractions (8%).

Cd in the SS sample was mainly associated with carbonates (38%). The remaining fraction was distributed between the residual (21%), Mn and Fe oxides (18%), organic matter and exchangeable (12%) fractions. In LTSS the proportion of total Cd bound to carbonates was redistributed to the Fe and Mn oxide (35%) and residual fractions (40%).

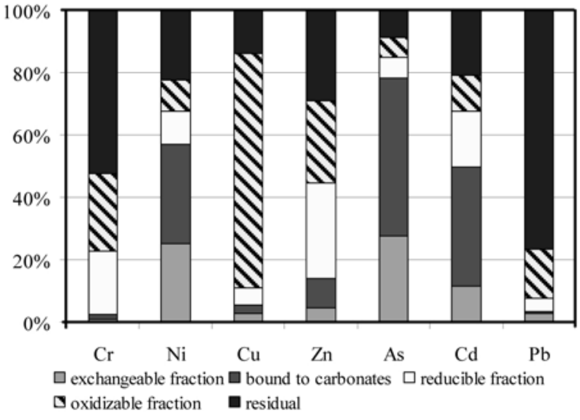

Figure 1: Partitioning of heavy metals in SS.

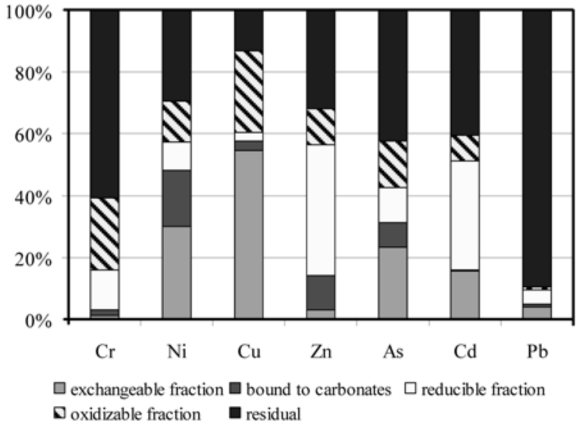

Figure 2: Partitioning of heavy metals in LTSS.

In SS Pb was predominantly partitioned between the residual (up to 76%) and organic fractions (16%). In LTSS the percentage of Pb in the organic matter fraction decreased to less than 1%, with an increase in the residual fraction to 90%, while the proportion in the other fractions remained broadly the same.

Table 2: Comparison of total metal concentrations in SS and LTSS samples with sum the of concentrations determined in separate steps of sequential analysis.

sample		unit	Cr	Ni	Cu	Zn	As	Cd	Pb
untreated	sequential extraction	[mg/kg]	37.7	36.7	280	650	3.98	1.31	51.8
sludge	total metal	[mg/kg]	40.1	36.5	288	678	3.89	1.38	52.8
	recovery	%	94.0	100.4	97.4	95.8	102.3	95.1	98.1
lime-treated	sequential extraction	[mg/kg]	28.2	22.5	180	457	2.61	0.72	34.1
sludge	total metal	[mg/kg]	28.4	22.3	177	466	2.67	0.78	35.1
	recovery	%	99.6	101.2	101.9	97.9	97.7	92.2	97.2

To check the precision of the analytical work, the concentrations of heavy metals in steps 1–5 of the extraction procedure were summed and compared to the total metal concentration. This comparison of results is presented in Table 2. The sum of the concentrations of the separate steps of the sequential extraction procedure ranged from 94 to 102% of the total metal concentration.

3. 2. Water and Acetic Acid Extraction of Sewage Sludge Mixtures

Addition of hydroxyapatite to sludge samples has a negligible influence on the pH of the samples. The pH of sludge mixtures determined in $CaCl_2$ suspension shifted from 6.7 in sample B1 to 6.8 in sample B5, and from 9.4 in sample A1 to 9.2 in sample A5.

Results of water and acetic acid extraction of SS and LTSS and hydroxyapatite mixtures are presented in Figure 3–5. The efficiency of immobilization was proportional to the amount of hydroxyapatite added for all metals.

The mobility of Cr in the environment depends on its oxidation state. Cr stabilization mainly involved Cr reduction from its toxic and mobile hexavalent form Cr(VI) to the rather stable Cr(III) form in natural environments. Water leachable concentrations of Cr in SS represented only 0.7% of total Cr concentrations, confirming that in sewage sludge, due to its high organic matter content, the majority of Cr is in the less mobile Cr(III) oxidation state. Although alkaline materials like lime that increase soil pH above neutral favour the oxidation of Cr(III) to Cr(VI), the leachable concentrations of Cr in LTSS was comparable with the Cr leachable concentrations in untreated sludge. In acetic acid media the solubility of Cr increased to 2% of the total Cr concentration. Results showed that hydroxyapatite did not have a high stabilization efficiency for Cr. The water leachable Cr concentration in sample B5 was reduced by only 30% in comparison with sample B1. The same result was obtained for LTSS mixtures with hydroxyapatite. A comparable stabilization efficiency of HA (27%) was observed for the acetic acid soluble metal fraction of untreated (without lime) sewage sludge samples, too.

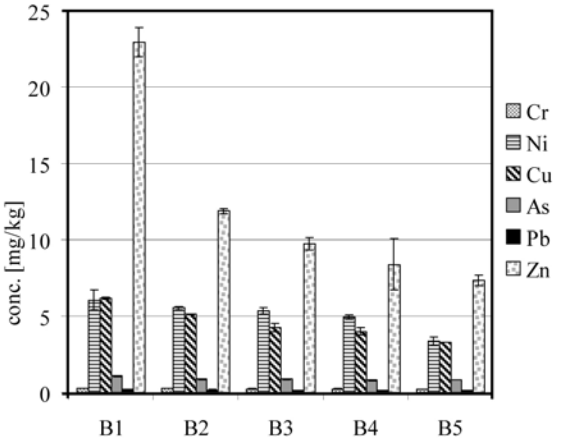

Figure 3: Water leachable metal concentrations in SS mixtures with hydroxyapatite. Results are represented as the average of two duplicates with ± deviations as error bars. Water leachable Cd concentrations are below the LOD for Cd (< 0.01 mg/kg).

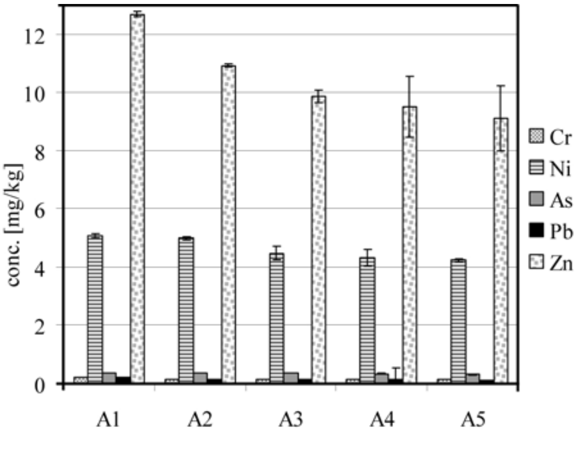

Figure 4: Water leachable metal concentrations in LTSS mixtures with hydroxyapatite. Results are represented as the average of two duplicates with ± deviations as error bars. Water leachable Cd concentrations are below the LOD for Cd (< 0.01 mg/kg). To improve the clarity of the figure, water leachable concentrations of Cu (> 75 mg/kg) are omitted.

17% and 23% of total Ni concentration in SS and LTSS are water leachable. Ščančar et al. also reported an increase in water soluble Ni concentrations after sewage sludge treatment with lime, but to a much higher extent.[18]

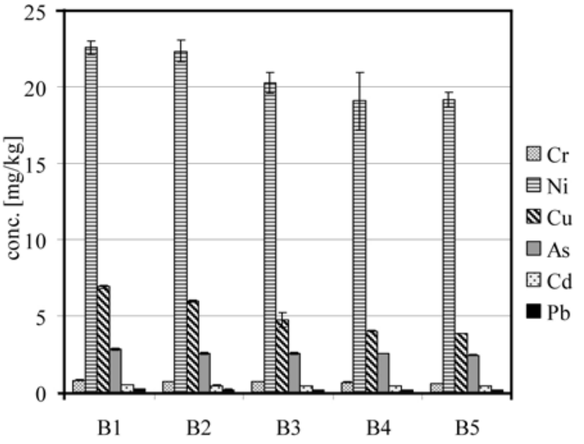

Figure 5: Acetic acid leachable metal concentrations in SS mixtures with hydroxyapatite. Results are represented as the average of two duplicates with ± deviations as error bars. To improve the clarity of the figure, water leachable concentrations of Zn (> 55 mg/kg) are omitted.

The extent of stabilization of hydroxyapatite is 45% (comparing samples B1 and B5) in SS and only 16% in LTSS. The stabilisation efficiency of Ni with hydroxyapatite was even smaller for the acetic acid leachable fraction of Ni (15%), where the leachable Ni concentration in sample A1 represents 62% of the total Ni concentration. There are only a few reports in the literature dealing with Ni stabilization. Misra et al. reported a 40% decrease in Ni bioavailability after application of 1% of hydroxyapatite to soil artificially contaminated with $NiSO_4 \cdot 7H_2O$.[5] A much higher stabilisation rate (up to 60%) of Ni was reported by Zupančič et al., but a quite high addition of hydroxyapatite was used.[23]

As can be already observed in determination of the partitioning of metals by Tessier's extraction procedure, the mobility of Cu in sewage sludge increased to a great extent by addition of lime. The water leachable Cu concentration at sample B1 represented 2.7% of the total Cu concentration, while in lime-treated sludge the proportion increased to 53%. Addition of hydroxyapatite reduced Cu mobility by 47% in untreated sludge (sample B5 in comparison with sample B1). In lime-treated sludge Cu reduction was only 20%. The results for the acetic acid leachable Cu fraction in LTSS were similar. The acetic acid leachable Cu concentration represented 3% of the total Cu concentration, while reduction in the leachable concentration in sample A5 was 45%.

Water leachable Zn concentrations represented 3.4% of the total Zn concentration in SS and 2.7% at LTSS. The stabilisation efficiency of hydroxyapatite for Zn in SS was quite high (68% for sample B5), whereas in LTSS it reached only 28% in sample A5. The acetic acid leachable concentration of Zn represents 7.4% of the total Zn concentration, but the stabilisation efficiency was surprisingly only 24%. A higher stabilisation efficiency of hydroxyapatite for the acetic acid extractable Zn fraction was observed by Zupančič et al., but a higher amount of hydroxyapatite was used.[23]

Water leachable As concentrations in SS represented 28% of the total concentration and 14% in LTSS, while the acetic acid concentration increased to 72%. It was expected that addition of HA to sewage sludge would lead to higher As mobility due to phosphate-arsenate competition for the sorption complex of the solid sewage sludge phase. Results showed that hydroxyapatite reduced As mobility by 25% in sample B5 and 16% in sample A5 in the water leachable fraction and by 13% in sample B5 in the acetic acid leachable fraction.

The water leachable concentrations of Cd in SS and LTSS samples were below the LOD, while the acetic acid leachable fraction represented 30% of the total metal concentration, with a stabilisation efficiency of HA of 20%.

Far the best stabilization efficiency of HA was achieved for Pb. The water leachable concentrations represented only 0.4% of the total Pb concentration in sample B1 and 0.6% in sample A1. The decrease in water leachable concentration was 40% for sample B5 and 45% for sample A5. In the acetic acid fraction leachable concentrations represented 2.1% of the total metal concentration, while the stabilization efficiency of hydroxyapatite was as high as 72%. It is well known that phosphate amendments added to contaminated soil efficiently reduce Pb mobility by ion exchange and precipitation of pyromorphite-type minerals $[Pb_5(PO_4)_3X$; X = F, Cl, B or OH$]$.[24] USEPA even included phosphate application, alone or in conjunction with lime, in the manual on Best Management Practices for lead in outdoor shooting ranges.[25]

4. Conclusions

Data from this partitioning study indicate that As is the most mobile metal in the SS sample since 28% of total As was extracted in the first step and 51% in the second step of Tessier's sequential extraction procedure. Slightly less mobile are Ni and Cd. The major portion of Cu was associated with the organic fraction and the major portion of Zn was partitioned between Fe and Mn oxides, organic and residual fractions. In SS Pb and Cr are less mobile and mainly extracted in the most sparingly soluble residual fraction.

However, despite the beneficial effects of liming, the increase of pH can also cause negative effects such as an increase in the mobility of some metals. The data on metal fractionation of LTSS indicate that special consideration should be given to sewage sludge containing high concentrations of Cu.

According to the metal water leachable fraction in SS samples, hydroxyapatite demonstrated the highest stabilization efficiency for Zn and Pb, followed by Cu, Ni, Cr and As. In the LTSS sample the stabilization efficiency of hydroxyapatite for metals decreases in the order Pb > Cr > Zn > Cu > Ni > As. For the acetic acid fraction in SS samples the highest stabilization efficiency was observed for Pb, followed by Cu, Cr, Zn, Cd, Ni and As. Although the addition of hydroxyapatite to LTSS samples decreased Cu mobility, the water leachable Cu concentrations in LTSS samples with the highest addition of hydroxyapatite (sample A5) are still ten times higher than in the SS sample without hydroxyapatite (sample B1).

The results of our study showed that in general lime had a higher stabilization efficiency than hydroxyapatite. If we compare samples A1 (6% of lime on a dry sewage sludge mass) and sample B5 (20% of hydroxyapatite on a dry sewage sludge mass), there was a better imobilization by hydroxyapatite only for Pb.

5. Acknowledgement

The research work was funded by financial support from the Ministry of Higher Education, Science and Technology (P1-0134) of the Republic of Slovenia.

6. References

1. P. C. Hsiau, S. L. Lo, *Water Res.* **1998**, *32*, 1103–1108.
2. A. Sahuquillo, A. Rigol, G. Rauret, *Trac-Trend. Anal. Chem.* **2003**, *22*, 152–159.
3. P. H. T. Beckett, Advances in soil science, Springer-Verlag, New York, **1989**, 143–176.
4. A. Tessier, P. G. C. Campbell, M. Bisson, *Anal. chem.* **1979**, *51*, 844–851.
5. V. Misra, P. K. Chaturvedi, *Environ. Monit. Asses.* **2007**, *133*, 169–176.
6. T. Suzuki, Y. Hatsushika, Y. Hayakawa, *J. Chem. Soc., Faraday Trans.1* **1981**, *77,* 1059–1062.
7. T. Suzuki, K. Ishigaki, *Chem. Eng. Commun.* **1985**, *34*, 143–151.
8. Q. Y. Ma, T. J. Logan, S. J. Traina, *Environ. Sci. Technol.* **1995**, *29*, 1118–1126.
9. R. X. Cao, L. Q. Ma, M. Chen, S. P. Singh, W. G. Harris, *Environ. Pollut.* **2003**, *122*, 19–28.
10. R. Melameda, X. Caob, M. Chenb, L. Q. Mab, *Sci. total environ.* **2003**, *305*, 117–127.
11. S. Brown, B. Christensen, E. Lombi, M. McLaughlin, S. McGrath, J. Colpaert, J. Vangronsveld, *Environ. Pollut.*, **2005**, *138*, 34–45.
12. Q. Y. Ma, S. J. Traina, T. J. Logan, J. A. Ryan, *Environ. Sci. Technol.* **1993**, *27*, 1803–1810.
13. E. Valsami-Jones, K. V. Ragnarsdottir, A. Putnis, D. Bosbach, A. J. Kemp, G. Cressey, *Chem. geol.* **1998**, *151*, 215–233.
14. Official Gazette of the Republic of Slovenia 3/2003: Regulations on Soil Pollution Caused by Waste Deposits, 3/2003, amendment 44/2003.
15. Official Gazette of the Republic of Slovenia 32/2006: Decree on the Landfill of Waste, 32/2006, amendment 98/2007.
16. U. S. EPA. Toxicity Characteristic Leaching Procedure Analytical Method 1311, In SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Washington: Office of Solid Waste, 1992.
17. G. Rauret, J. F. López-Sánchez, A. Sahuquillo, E. Barahona, M. Lachica, A. M. Ure, C. M. Davidson, A. Gomez, D. Lück, J. Bacon, M. Yli-Halla, H. Mautau, P. Quevauviller, *J. Environ. Monit.* **2000,** *2*, 228–233.
18. J. Ščančar, R. Milačič, O. Burica, M. Stražar, *Ann. Chim.* **2001,** *91*, 375–379.
19. N. Staelens, P. Parkpian, C. Polprasert, *Chem. Spec. Bioavailab.* **2000,** *12*, 97–107.
20. J. Ščančar, R. Milačič, M. Stražar, O. Burica, P. Bukovec, *J. Environ. Monit.* **2001**, *3*, 226–231.
21. D. B. Levy, K. A. Barbarick, E. G. Siemer, L. E. Sommers, *J. Environ. Qual.* **1992**, *21*, 185–195.
22. J. T. Sims, J. S. Kline, *Environ. Qual.* **1991**, *20*, 387–395.
23. M. Zupančič, N. Bukovec, R. Milačič, J. Ščančar, *Water air soil pollut.* **2004**, *156*, 57–69.
24. J. Kumpiene, A. Lagerkvist, C. Maurice C, *Waste Manage.* **2008**, *28*, 215–225.
25. U. S. Environmental Protection Agency, Best management practice for lead at outdoor shooting ranges, EPA-902-B-01-001, Washington, D. C., **2001**.

Povzetek

V prispevku so prikazani rezultati raziskave mobilnosti kovin v dveh vzorcih odpadnega blata – surovo dehidrirano odpadno blato in dehidrirano odpadno blato s 6 % (na suho težo) dodatkom apna. Mobilnost kovin v obeh vzorcih smo ovrednotili s Tessierjevo zaporedno ekstrakcijo. Rezultati so pokazali, da je v odpadnem blatu najbolj mobilen As, sledita mu pa Ni in Cd. Dodatek apna je močno zmanjšal mobilnost kovin, razen Cu, katerega mobilnost je močno porasla, opazili pa smo tudi rahel porast mobilnosti Ni. Proučevali smo tudi spremembo mobilnosti kovin v obeh blatih ob dodatku fosfatnega vezalca hidroksilapatita. Spremembo mobilnosti smo opazovali v frakciji izlužljivi z vodo in frakciji izlužljivi z ocetno kislino. Dodatek hidroksilapatita je močno zmanjšal predvsem mobilnost Pb in Zn. V splošnem kaže apno večjo moč stabilizacije kot hidroksilapatit. Posebno pozornost je potrebno nameniti odpadnemu blatu z višjo vsebnostjo Cu.