# Sorption and Migration of Selected Heavy Metals in Different Soil Matrices

T. Kowalkowski, B. Buszewski

Department of Environmental Chemistry and Ecoanalitics Faculty of Chemistry, Nicolaus Copernicus University ul. Gagarina 7, 87-100 Toruń, Poland

> Received: October 15,2001 Accepted: January 4, 2002

### **Abstract**

Soils and ground waters have been extensively exposed to pollution by heavy metals from various anthropogenic sources. The presence of these metals in soils poses a significant environmental hazard, and one of most difficult contamination problems to solve. Description of some sorption and migration phenomena involving Pb, Zn, Ni and Cu in the surface layer of soil and sewage sludge compost was the primary objective of this work. A wide range of pH (3.0 - 5.5) of simulated acid rains, used to study the elution of metals from these matrices allowed a qualitative description of these metals' behaviour.

Keywords: heavy metals, migration, soil, sewage sludge compost

## Introduction

The transportation mechanisms of heavy metals through the soils and other environmental matrices have long presented great interest to both environmental and soil scientists because of the possibility of groundwater contamination through metal leaching [1-3]. In general, many types of soil contain a wide range of heavy metals at varying concentrations depending on the surrounding geo-chemical condition and anthropogenic and natural activities (occurring at present or in the past). Metal transportation depends not only on the physiochemical properties of soil, but also on the physical and chemical properties of the soil, which collectively determine the binding ability of soil [4]. The complexity of the soil matrix makes it difficult to identify the interactions determining the adsorption of a specific metal. This problem becomes more difficult in the process of formulating effective soil models for the prediction of metal transportation. Therefore, it is necessary to fully understand the

metal binding properties of the soil, develop and validate procedures for metal speciation in soils and carefully choose the appropriate models, to understand the adsorption and migration of heavy metals in the soil matrices [5-9].

In 1998 in Torun a new waste water treatment plant was built. This plant produces a large amount of sewage sludge (90 t/day), formed as a result of mechanical, biological and chemical sewage treatment. The composition of the sewage sludge is very complex; it is rich in microand macroelements useful in agriculture, but can contain toxic compounds, i.e. heavy metals and pathogenic organisms. There is a large variety of methods of neutralisation of the sewage sludge, of which the most preferred is composting [10]. In Torun composting is applied to soil reclamation of the area adhering to this plant, which had been destructed by sulphuric acid rain from a near factory. The main aim of this work is investigation of the sorption and migration phenomena of selected heavy metals (Cu, Zn, Ni, Pb) in sewage sludge compost profiles.

# **Experimental**

# Reagents and Instruments

Soil samples were extracted with 0.5 M HNO<sub>3</sub> (pure for analysis, *Polskie Odczynniki Chemiczne - POCh;* Lublin, Poland) or aqua regia (pure for analysis, *POCh;* Lublin, Poland) by 0.5h mechanical shaking (shaking water bath GFL 1086, Burgelwedel, Germany). The acid rain was prepared as a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (pure for analysis, *POCh;* Lublin, Poland). Total concentration of metals in solution was determined by flame atomic absorption spectrometry (FAAS) or graphite furnace atomic absorption spectrometry (GFAAS) using a PU 9100X Philips spectrometer (Cambridge, Great Britain).

#### Methods

In this work we apply a column leaching experiment to predict behaviour of selected heavy metals (Pb, Zn, Ni and Cu) and check the possibility of ground water pollution with these metals. Two columns (100 cm length and 85 mm diameter) were used. One of them was filled with 40 cm layer of soil and 40 cm layer of the compost, while the second one was filled with 80 cm layer of soil only. Both soil and compost samples were taken from the same place of the area under reclamation. Before filling, the samples were dried for 7 days at room temperature. The elution of the so-prepared profiles was carried out with a HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mixture (3:7 v/v ratio). After elution each profile was split into 10 cm parts. Each sample from these profile pieces was extracted by mechanical shaking or heating for 0.5h. The total concentration of metals in the extracted solution was determined by flame atomic absorption spectrometry (FAAS). In the leaching experiment, the volume of the eluent and the concentration of Pb, Zn, Cu and Ni were also measured.

# **Results and Discussion**

The first step of our experiment was the optimisation of the extraction procedures. This optimisation relied on the use of different extraction solvents: 0.5 M HNO<sub>3</sub> (30 min. shaking 10g sample with 50 ml of solvent) and aqua regia (30 min. heating 5g of sample with 30 ml of solvent). Tables 1 and 2 show the results and their residual standard deviations.

Table 1. A comparison of soil extraction solutions.

	Soil	Extraction	on		
metal		Cu	Zn	Ni	Pb
HNO <sub>3</sub>	average [mg/kg]	4.43	12.26	0.81	6.64
	RSD [%]	11.24	10.57	39.04	0.05
Aqua regia	average [mg/kg]	0.22	6.09	0.12	2.52
	RSD [%]	69.53	8.35	14.43	6.32

Table 2. A comparison of compost extraction solutions.

	Comp	ost Extra	ction		
metal		Cu	Zn	Ni	Pb
HNO <sub>3</sub>	average [mg/kg]	0.15	5.35	3.37	0.50
	RSD [%]	59.71	62.76	8.89	10.25
Aqua regia	average [mg/kg]	95.95	57.07	67.48	37.38
	RSD [%]	0.21	0.91	0.61	2.08

In the case of soil samples with regard to reproducibility of results and recovery of metals, extraction with 0.5M HNO $_3$  rather than an extraction with aqua regia was chosen. The extraction with aqua regia mixture was more effective for compost samples. Because of the presence of large amount of organic matter in compost. Mineralization of compost samples gives much higher recovery of metals than simple extraction.

The second part of the experiment was elution of heavy metals with acid rain. The concentrations of all metals were relatively small. In the case of copper the elution surfaces have similar shape (Figs. 1, 2). The maximum concentration of this metal was at pH 5.3, but for soil profile we observed two maxima: at first millilitres of eluent and at a volume equal to 400 ml; for compost profile the maximum was at 200 ml volume.

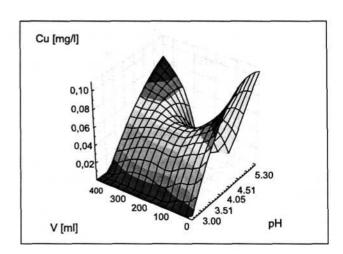


Fig. 1. Soil profile -elution surface for Cu.

Sorption and Migration ...

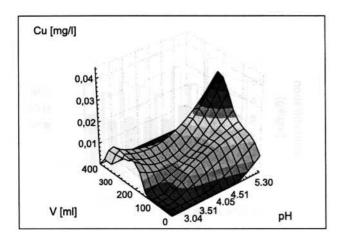


Fig. 2. Compost profile -elution surface for Cu.

The maximum concentration of zinc in the soil profile was observed at lower pH (3.0) in contrast to the compost, where this maximum appears at a higher pH (5.0). The concentration of zinc in the eluent in both cases was 0.

137

The final step of our experiment was extraction of metals in 10 cm parts of profiles. The total concentrations in each profile depth gives us information about the residual amounts of these metals. In the case of soil profile almost constant decreases of metal concentrations were observed (Fig. 9). Its goes to show that the metal ions are strongly bound at the binding sites of the soil. An interesting situation was in the compost profile (Fig. 10). Metals were transported from the compost layer through the soil. This means that a soil layer is a natural barrier for these heavy metals.

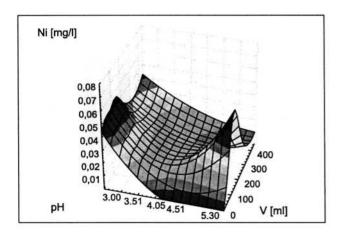


Fig. 3. Soil profile -elution surface for Ni.

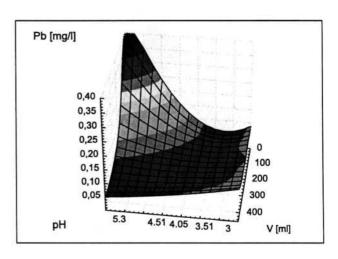


Fig. 5. Soil profile -elution surface for Pb.

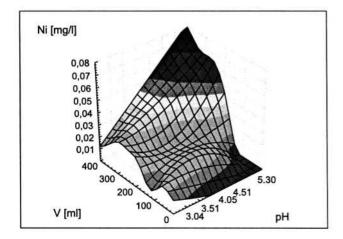


Fig. 4. Compost profile -elution surface for Ni.

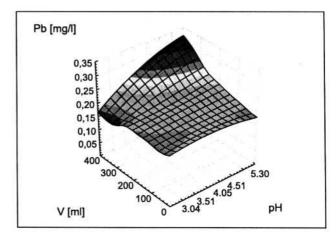


Fig. 6. Compost profile -elution surface for Pb.

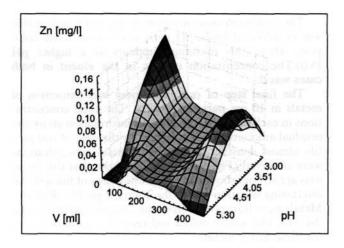


Fig. 7. Soil profile -elution surface for Zn.

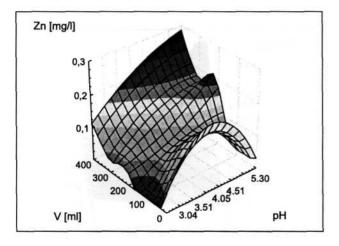


Fig. 8. Compost profile -elution surface for Zn.

Explicit influence of acid rains on the metals leeching from the compost layer was observed. The metals were transported to the soil layer, where there were immobilised. The concentration of the metals in the eluents shows that only their inconsiderable amounts exist in forms capable of being transported across the soil profile.

## **Conclusions**

- 1. Optimisation of extraction has shown that for the soil better recoveries and higher repeatability has been obtained with 0.5 M. HNO<sub>3</sub> extraction, however, the ex traction aqua regia was more effective for compost samples.
- 2. Analysis of the extracts from different depths of profiles allowed us to describe the metal contents at each depth and give a quantitative description of their trans portation across the profile. Only insignificant changes of metals concentrations across the soil profile were ob-

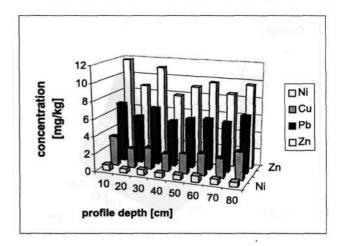


Fig. 9. Soil profile - sorption curves after elution step.

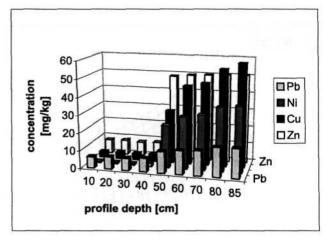


Fig. 10. Compost profile - sorption curves after elution step.

- served, in contrast to the compost, where metal transport from compost to soil layer has been observed.
- 3. Only insignificant concentrations of the metals were transported through the deeper layers of soil. Analysis of metals in eluents has shown also that there are no significant differences between leeching with acid rains at various pH.
- 4. This work focused on the study of only one type of compost sample, but estimation of the influence of compost on the soil environment is difficult on account of different compositions of this material. The composition of the compost changes with the composition of the sew age and depends on the season, time, amount of rain, temperature, etc.

# Acknowledgment

This work was supported by KBN (State Committee for Scientific Research) Grant No. 7 T09D 028 21.

## References

- 1. KUN-HUAN H., DAR-YAUN L. Soil Science, 2,115, 1998.
- SCHEIDEGGER A. M, SPARKS D. L. Soil Issues, 12, 813, 1996.
- TESSIER A., TURNER D. R., Metal speciation and bi oavailability in aquatic systems, John Wiley and Sons, New York, USA, 1995.
- 4. KABATA-PENDIAS A, PENDIAS H. Biogeochemia pierwiastkow sladowych, PWN, Warszawa, 1993.
- DUBE A, ZBYTNIEWSKI R, KOWALKOWSKI T., CUKROWSKA E., BUSZEWSKI B., Pol. J. Environ. Stu dies, 10(1), 1, 2001.
- MOOR C, LYMBEROPOULOU T., DIETRICH V.J., De termination of heavy metals in soils, sediments and geologi cal materials by ICP-AES and ICP-MS, Microchimica Acta, 136, 123, 2001.
- 7. HE M., WANG Z., TANG H., Modeling the ecological im pact of heavy metals on aquatic ecosystems: a framework for development of an ecological model, the Science of Total Environment, **266**, 291, **2001**.
- 8. FACCHINELLI A., SACCHI E., MALLEN L., Multivariate statistical and GIS-based approach to identify heavy metals sources in soils, Environmental Pollution, **114**, 313, **2001**.
- 9. HASSOUNEH O, JAMRAH A, QAISI K., Bioprocess En gineering, 20, 413, 1999.