

The risk scale estimation of the agricultural environment pollution by heavy metals using the sequential extraction method

¹Janusz Rosada, ¹Joanna Grzesiak, ²Grzegorz Schroeder

¹*Institute of Plant Protection, Department of Ecology and Protection of Agricultural Environment, Miczurina 20, 60-318 Poznań, Poland, e-mail: J.Rosada@ior.poznan.pl*

²*Adam Mickiewicz University, Faculty of Chemistry, Poznań, Poland, e-mail: Schroede@amu.edu.pl*

From among various industrial contaminants which can pollute agricultural environment, heavy metals having the capacity of bioaccumulation deserve special attention. The total composition analysis of the heavy metals content in the polluted soils does not provide enough data about their accessibility to the crops cultivated on these soils. It is very important to have the information about the forms in which the examined element exists, because it decides about its mobility and toxicity for the environment. Using the sequential chemical extraction method of Zeien and Brümmer the fractions of Cu, Pb, Zn, Cd and As in the soils influenced by emissions from the Copper Smelter GŁOGÓW, were investigated. The aim of these investigations was to determine the availability assessment of the mentioned elements to the crops cultivated in this region.

Keywords: copper smelter, heavy metals, soil, pollution, sequential chemical extraction method.

Presented at VII Conference Wasteless Technologies and Waste Management in Chemical Industry and Agriculture, Międzyzdroje, 12 – 15 June, 2007.

INTRODUCTION

Dust emissions from the metallurgy of non-ferrous metals can be recognized as the main anthropogenic factors causing increased heavy metal concentrations in the agricultural environment. Metal-containing dusts emitted into the atmosphere by the metallurgical industry frequently contribute to the contamination of agrocenosis situated in the closest neighborhood of pollutant emitters. All the soils that are within the range of emission, demonstrate the increased accumulation of heavy metals, which is specific to the particular manufacturing process¹⁻².

In the case of the soils that are in the range of the Copper Smelter GŁOGÓW emission, the arable layer of these soils contains an increased concentration of copper and lead as well as zinc, cadmium and arsenic. The increased contents of heavy metals and arsenic in the soil pose hazard of their penetration to the subterranean waters, which are the potable water source, and to the plants cultivated in that soil. Consequently, allowing metals to enter the trophic chain of the ecosystem could threaten the health of humans and animals that consume the polluted plants, the products of their processing and drink the polluted water³⁻⁵.

Together with the risk scale estimation of the agricultural environment pollution by the increased concentration of heavy metals in the soil, it is also necessary to determine both: the potential solubility of metals in the short period of time and the long-term changes. In order to run such analysis, it is necessary to know each metal form that is present in the soil. The type of the mentioned form depends on the metal, its chemical properties, the initial form in the soil and the soil characteristics^{1 and 6}.

Heavy metals that occur in soil as soluble and exchangeable forms are considered as easily accessible for plants, easily displaced in the trophic chain and the most dangerous for the human being. The accessibility of these metal forms depends to a large extent on the intensity of the adsorption and desorption processes in the soil¹.

Metals from anthropogenic sources are less soluble, compared to the metals from the lithogenic ones, due to their chemical forms in which they are introduced into the environment. Heavy metals, emitted from non-ferrous smelters, usually occur as oxides and sulphates⁶⁻⁷.

The heavy metal amount, absorbed through the plant radical system, from the soil depends on the degree of each element's accumulation and its immobilization by the soil sorption complex. The soil sorption capacity is determined by the quality and quantity of the colloids that form the soil sorption complex. As the amount of the floatable elements (mostly colloidal clay), organic matter (mostly humus) and the pH index increase, the heavy metal accessibility for plants is significantly limited. In such case metals undergo binding by the beneficial soil buffer system and they become unavailable for plant roots¹.

The absorption mechanism of metals by plant roots is complicated and depends on such processes like: the cation exchange through the plasma membrane, the intracellular transport, processes occurring in the rhizosphere¹.

MATERIALS AND METHODS

The sequential analysis was applied to three different samples from the Copper Smelter GŁOGÓW emission area. Zeien and Brümmer's⁸ method was used for the sequential metal fractionation. This method allows a distinction of seven fractions with different activity in the soil environment. It is due to the fact that metals are bound with the soil components to a different degree. This method is based on the extraction of heavy metals bound with the soil components, by the application of different solutions on the same soil sample. The obtained extracts are separated from the solid phase by centrifugation and the residue is subjected to the next step of extraction. This method might be used for different kind of soils with various degrees of pollution (fig. 1).

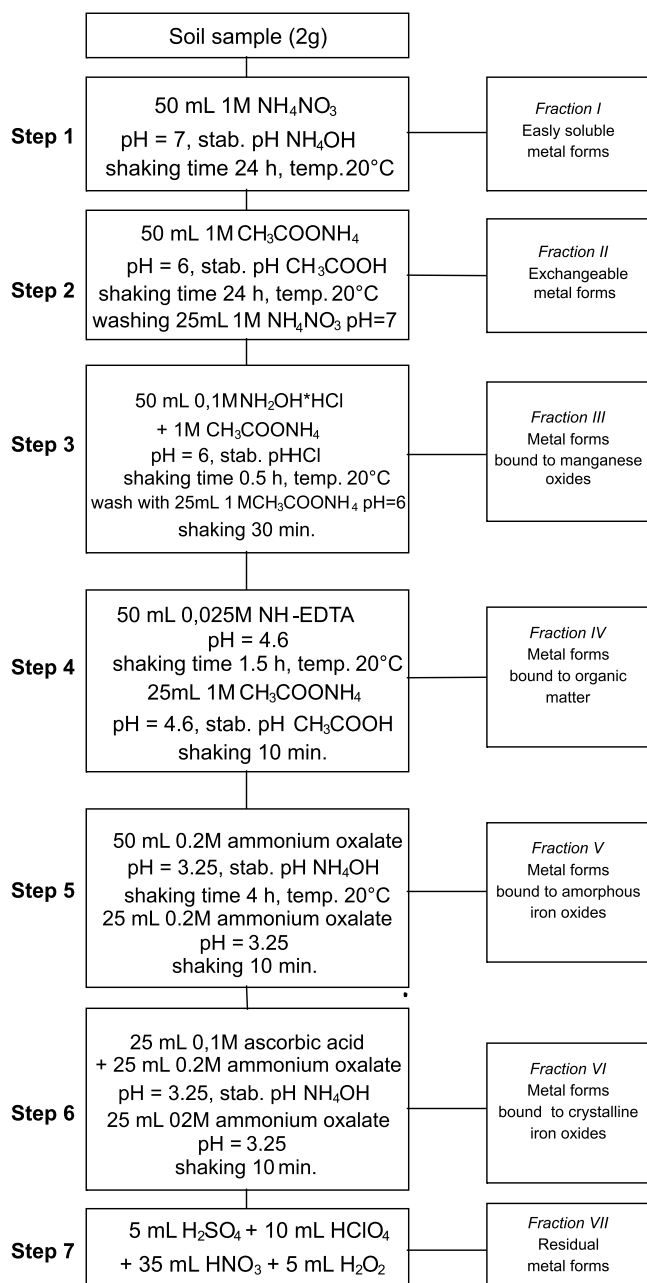


Figure 1. Metal fractions in Zeien-Brummer's sequential extraction technique

The description of the sequential analysis:

2g of dry and sifted soil sample were prepared for examination. In each step of sequential extraction, the solution's acidity was stabilized in accordance with the methodology. Between each extraction, the sediment was once or twice washed with the reagent from a previous extraction. Moreover, between each extraction, the separation was effected by centrifuging at 2500G (G – acceleration of gravity). The analytical procedure is presented in Figure 2. In extraction step II, the residue was washed with 25 ml 1 M NH_4NO_3 , subjected to centrifugation again and filtered; the filtrates were joined. In extraction step III, the residue was washed with 25 ml 1M NH_4OAc (pH 6.0), centrifuged again and filtered; the filtrates were joined. In extraction step IV, the residue was washed with 25 ml 1M NH_4OAc (pH 4.6), centrifuged again and filtered; the filtrates were joined. In extraction steps V and VI, the residue was washed with 25 ml of ammonium oxalate (pH 3.25), centrifuged again and filtered, the filtrates were joined. In extraction step VII, both the residual soil sam-

ple and the filter were mineralized separately. It was carried out in mineralization cells through maceration (5 cm³ sulfuric acid (VI) and 10 cm³ chloric acid (VII)) for 18h. After that the samples were put into the mineralization furnace for 2h. During the mineralization process at 150°C, 35 cm³ of nitric (V) acid and 5 cm³ hydrogen peroxide solution were added to each cell. The blank tests were also carried out. The mineralized samples were transferred into measuring flasks (50 cm³), which were made up to the mark by the redistilled water.

Concentration of Cu, Pb, Zn, Cd and As was determined by the ASA and ICP-AES techniques. In order to compare the results, an independent measurement of the total concentration of the analyzed elements in the soil was also conducted by mineralization with nitric acid.

RESULTS AND DISCUSSION

The fractional distribution of Cu, Pb, Zn, Cd and As in the soil samples to a large degree depended on the type of the studied element. Relatively the highest contents of heavy metals (Cu, Pb, Zn, Cd) were determined in the fractions with a difficult access for plants (IV-VII fractions). Those fractions include the metal forms that are bound with organic matter (fr. IV), amorphous iron oxides (fr. V), crystalline iron oxides (fr. VI) and also the residual metal forms (fr. VII). Lower heavy metal degree was stated in fractions I and II (easily soluble metal forms – fr. I; exchangeable metal forms – specifically absorbed – fr. II), as well as fraction III (metal forms bound with manganese oxides). The highest arsenic content was determined in fractions III-V.

The analysis of heavy metals and arsenic concentration by ASA and ICP methods was repeated three times. The results are presented as average values in Figures 2 – 6 (1% difference between a particular result). The results, repeated three times, are characterized by very good compatibility. The concentration in ppm for all heavy metals and arsenic are presented in the paper published by Rosada et al.⁹.

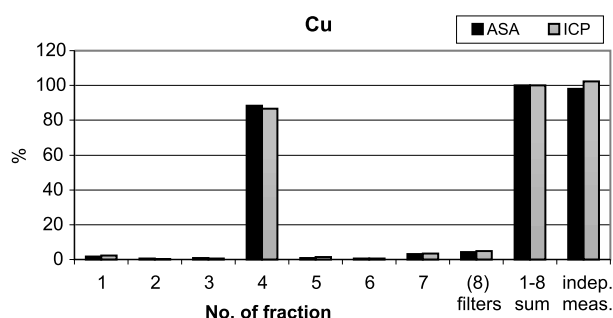


Figure 2. Copper content (%) in the soil, insulated by Zeien-Brumer's sequential extraction (seven steps of extraction), determined by the ASA and ICP methods. Explanation: 1 – 7 – the content of heavy metal in seven fractions of Zeien-Brumer's method; (8) – the content of heavy metal in mineralized filters used for the filtration of successive fractions; 1 – 8 – summary content of heavy metal (fractions + filters); indep. meas. – independent measure of the total content of metal in the analyzed sample.

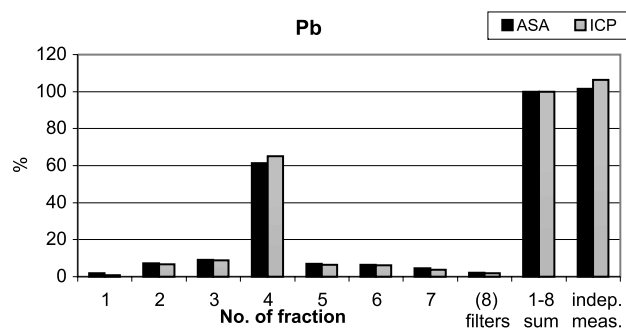


Figure 3. Lead content (%) in the soil, insulated by Zeien-Brümer's sequential extraction (seven steps of extraction), determined by the ASA and ICP methods

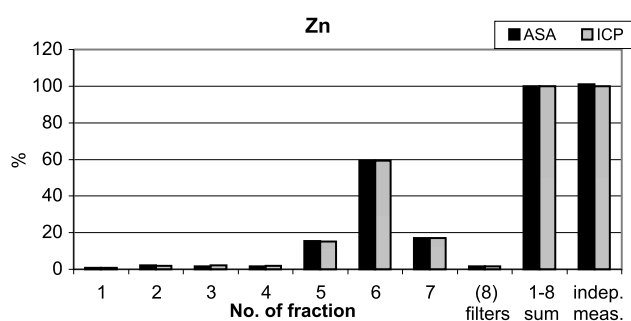


Figure 4. Zinc content (%) in the soil, insulated by Zeien-Brümer's sequential extraction (seven steps of extraction), determined by the ASA and ICP methods

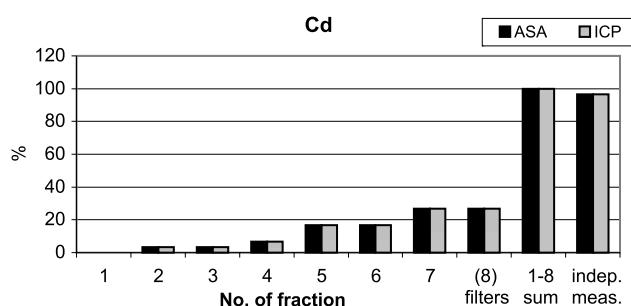


Figure 5. Cadmium content (%) in the soil, insulated by Zeien-Brümer's sequential extraction (seven steps of extraction), determined by the ASA and ICP methods

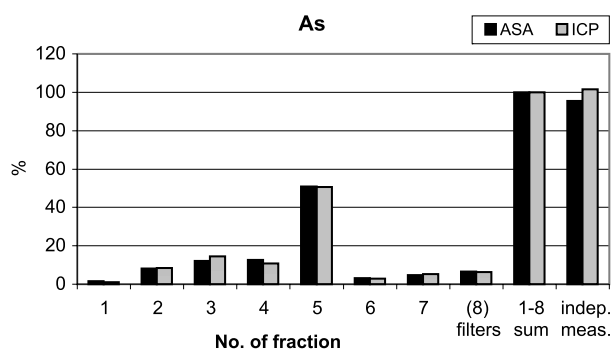


Figure 6. Arsenic content (%) in the soil, insulated by Zeien-Brümer's sequential extraction (seven steps of extraction), determined by the ASA and ICP methods

The research studies demonstrated that all determined elements in the soils from the Copper Smelter GŁOGÓW emission area are strongly bound in the soil sorptive complex and its accessibility for the cultivable plants is significantly reduced. The low contents of heavy metals

and arsenic in the cultivable plants, during the annual studies run by The Institute of Plant Protection in that area, is a testimony to that statement¹⁰⁻¹³.

CONCLUSIONS

1. The results of the speciation of Cu, Pb, Zn, Cd and As in the soil by the ASA and ICP analytical procedure are comparable for both: each soil fraction and the total element concentration.

2. The total concentration of metals and arsenic in all fractions in Zeien-Brümer seven-step method is comparable with the total concentration of these elements determined after mineralization with nitric acid.

3. Up to the results from the Zeien-Brümer seven-step extraction method, the highest concentration of individual elements is present in the following fractions:

- Copper – fraction 4 (>80% of the total concentration of Cu in all fractions);
- Lead – fraction 4 (>60% of the total concentration of Pb in all fractions);
- Zinc – fraction 6 (~60% of the total concentration of Zn in all fractions);
- Cadmium – fractions 5 – 7 (~60% of the total concentration of Cd in all fractions);
- Arsenic – fractions 3 – 5 (~80% of the total concentration of As in all fractions).

4. 3 – 7 fractions, in which the highest heavy metals and arsenic concentration was observed, are characterized by weak and slow elution under natural conditions; therefore the examined metals are stationary.

LITERATURE CITED

- (1) Kabata-Pendias A., Pendias H.: *Biogeochemia pierwiastków śladowych*. PWN Warszawa, **1999**.
- (2) Karczewska A.: Metal species distribution in the areas affected by copper smelter. *Appl. Geochem.* **1995**, 11, 35 – 42.
- (3) Rosada J., Chudziński B.: Copper and Lead – the Main Reasons for Plants Pollution in the Emission Region of Copper Foundry „Głogów”. *Biological Bulletin of Poznań*, **1996**, Vol. 33: 53 – 54.
- (4) Rosada J., Chudziński B.: The Potential Pathways of Plants Contamination in the Emission Region of Copper Foundry „Głogów”. In *Contaminated Soils: Third International Conference on Biogeochemistry of Trace Elements*, Paris 15 – 19 May **1995**, INRA Editions, ISBN: 2-7380-0775-9. **1997**.
- (5) Pilc L., Rosada J., Siepak J.: The Influence of Dust Emission from the „Głogów” Copper Foundry on Heavy Metal Concentrations in Agrocenoses. *Polish Journal of Environmental Studies*, **1999**, Vol. 8., No. 2: 111 – 114.
- (6) Karczewska A.: Metale ciężkie w glebach zanieczyszczonych emisjami hut miedzi – formy i rozpuszczalność. *Zesz. Nauk. AR Wrocław*, **2002**, Nr 432, Rozprawy CLXXXIV.
- (7) Pacyna J. M.: **1987**: Atmospheric emissions of arsenic, cadmium, lead and mercury from high temperature processes in power generation and industry. [W:] Hutchinson T.C., Mecma K.M. (ed.) *Lead, mercury, cadmium and arsenic in the environment*. SCOPE 31, J. Wiley, New York., 69 – 87.
- (8) Zeien, H., Brümmner G. W.: **1989**: Chemische Extraktionen zur Bestimmung von Schwermetallbindungsformen in Boden. *Mit. Dtsch. Bodenk. Gesellsch.*, 19/I, 505 – 510.

(9) Rosada J., Grzesiak J., Grzesiak P., Schroeder G., Ratajczak J., Orlicka A., Rissmann I.: Oznaczanie w glebach metodami ASA i ICP metali ciężkich izolowanych metodą ekstrakcji sekwencyjnej. 163 – 199. W monografii: „Chemiczne aspekty badań środowiska”. (G. Schroeder red.) Uniwersytet im. A. Mickiewicza, Poznań, **2004**. Tom 2, 215 ss. ISBN-83-89936-02-X.

(10) Rosada J.: Influence of Eco-friendly Activities of Copper Foundry „Głogów” on Condition of Agricultural Environment. In: Chemicals in Sustainable Agriculture (Edited by H. Górecki, Z. Dobrzański, P. Kafarski) Chemistry for Agriculture, Printed in Czech Republic, ISBN 80-239-0963-0, **2003**, Vol. 4, 780 pp, 426 – 429.

(11) Rosada J.: Positive changes in agricultural environment as a result of reduction of industrial emissions. In: New Agrochemicals and their Safe Use for Health and Environment (Edited by H. Górecki, Z. Dobrzański, P. Kafarski) Chemistry for Agriculture, Printed in Czech Republic, ISBN 80-239-3289-6, **2004**, Vol. 5, 850 pp, 704 – 707.

(12) Rosada J., Grzesiak J.: Condition of agrocenoses in the protective zone and external belt threatened by emissions of Copper Foundry „Głogów”. In: New Agrochemicals and their Safe Use for Health and Environment (Edited by H. Górecki, Z. Dobrzański, P. Kafarski) Chemistry for Agriculture, Printed in Czech Republic, ISBN 80-239-3289-6, **2004**, Vol. 5, 850 pp, 698 – 703.

(13) Rosada J.: Concentration of heavy metals (Cu, Pb, Zn, Cd) and arsenic (As) in soils and plants in agricultural areas threatened by emissions from non-ferrous metallurgy. Polish Journal of Chemical Technology, **2005**, 7, 2, 50 – 53.