E3S Web of Conferences **1**, 19009 (2013)
DOI: 10.1051/e3sconf/20130119009

Soils from sites of historical metal mining in western Małopolska (S Poland) are strongly contaminated with Zn, Pb and Cd

A. M. Stefanowicz[1], M. W. Woch[2] and P. Kapusta[1]

[1] Department of Ecology, Institute of Botany, Polish Academy of Sciences, Lubicz 46, 31-512 Kraków, Poland, a.stefanowicz@botany.pl, p.kapusta@botany.pl
[2] Department of Botany, Institute of Biology, Pedagogical University of Kraków, Podchorążych 2, Kraków 31-054, Poland, jurania@o2.pl

Abstract. Concentrations of Cd, Pb and Zn in soils developed at 63 sites of historical metal mining in western Małopolska (S Poland) were estimated. Heavy metal concentrations were measured with an atomic absorption spectrometer after wet digestion in hot $HClO_4$ (total forms), extraction in 0.1 M $BaCl_2$ (exchangeable forms) or in water (water-soluble forms). Basic soil properties such as texture, C, N, Ca contents and pH were also measured. Total concentrations of Cd in soil varied from 4.4 to 392, Pb from 72.8 to 16931 and Zn from 322 to 41860 mg kg^{-1}. Exchangeable Cd, Pb and Zn extended from 0 to 19.3 %, from 0 to 0.2 % and from 0 to 3.5 % of the total metal forms, respectively, indicating that Cd is the most mobile and potentially bioavailable metal. In turn, water-soluble metal forms did not exceed 1 % of the total. Our study showed that soils developed at sites of historical metal mining are severely polluted with heavy metals. Old heaps threaten not only the environment, but also local inhabitants, as they are often located in a close proximity to houses or agricultural fields.

Keywords*:* Historical Ag-Pb-Zn mining, metal pollution, old heaps, soil

Introduction

Western Małopolska is a part of one of the oldest region of non-ferrous metal mining in central Europe (Molenda 1963). Mining of Zn-Pb ores in western Małopolska dates back to 12^{th} century, although earlier exploitation cannot be excluded (Molenda 1963). During a few centuries, Pb and Ag were being used, whereas Zn ores were deposited in the form of heaps or left in mine shafts. Excavation of Zn ores started in the 16^{th} century, and since the 19^{th} century Zn has been the most important metal mined and processed in this region (Molenda 2000). Contemporary metal industry in this area developed after World War II, when modern metal mines and smelters had been built. High Cd, Pb and Zn concentration in soils in the nearby of these modern mines and smelters in western Małopolska is an effect of deposition of mining and flotation wastes as well as smelting emissions; the contamination is evident and well-studied by many authors (e.g. Chrastný et al. 2012, Stefanowicz et al. 2010, Verner et al. 1996). Relics of historical Pb-Zn mining (small, inconspicuous, probably at least 100 years old heaps) are more problematic. Most of them are spread in vast areas covered by forests. However, they can be also found in the immediate vicinity of houses, gardens or agricultural fields, potentially posing a threat to local inhabitants. The aim of our study was to identify objects of historical Ag-Pb-Zn mining (old mine waste heaps) in non-forested areas in western Małopolska and measure Cd, Pb and Zn concentrations in their soils.

Materials and Methods

Sixty-three study sites were established in the area of historical Ag-Pb-Zn mining between Krzeszowice, Libiąż, Jaworzno and Olkusz in western Małopolska (S Poland). They were located on S, SW or SE slopes of old mining heaps (Fig. 1). From each site, 3 samples of the top mineral layer to a depth of 15 cm were collected (2-3 m apart) and bulked to obtain one composite soil sample. Concentrations of Cd, Pb and Zn were measured by flame atomic absorption spectrometry (Varian 220 FS) after wet digestion in hot $HClO_4$ (total forms), extraction in 0.1 M $BaCl_2$ (exchangeable forms) or in water (water-soluble forms). Additionally, some basic soil properties were estimated. The particle size distribution (sand, silt and clay fractions) was determined by a combination of sieving and sedimentation. The content of organic C was measured with Leco RC-612 instrument, whereas total N by the Kjeldahl method using a Kjeltec 2300 (Foss

Tecator). Soil pH was measured electrometrically after extraction with H_2O. Concentration of total Ca was measured by flame atomic absorption spectrometry after wet digestion in hot $HClO_4$. The data were transformed with a logarithmic or exponential function, standardized and subjected to correlation/regression analysis.

Results

Total concentrations of metals in soils varied widely: Cd from 4.4 to 392, Pb from 72.8 to 16931 and Zn from 322 to 41860 mg kg^{-1} (Table 1). Similarly, exchangeable and water-soluble metal concentrations also varied across a wide range (Table 1). Exchangeable Cd, Pb and Zn extended from 0 to 19.3 %, from 0 to 0.2 % and from 0 to 3.5 % of the total metal forms, respectively. In turn, water-soluble metal forms did not exceed 1 % of the total. Other soil properties such as texture, nutrient content or pH did not differ between soils as much as did heavy metal concentrations (Table 1). The soils were similar with respect to pH, which was relatively high in all samples, ranging from 7.1 to 8.1. It was positively correlated with Ca concentration in soil ($r = 0.66$, $p < 0.0001$), which was also high, reaching up to 323 g kg^{-1}. Although studied soils were all neutral or alkaline, pH significantly ($p < 0.0001$) affected the amount of exchangeable Cd ($r = -0.61$) and Zn ($r = -0.66$) concentrations in soil. Relations between pH and the ratio of exchangeable to total Zn and Cd are shown in Figs 2 and 3. The amount of water-soluble metals was not affected by pH ($p > 0.1$).

Discussion

Concentrations of Cd, Pb and Zn in almost all tested soils exceeded the maximum permissible guideline values (Cd: 1-3, Pb: 50-300, Zn: 150-300 mg kg^{-1}; Commission of European Communities 1986). Metal concentrations in the most polluted soils from old mining areas exceeded the maximum permissible values from 56 (Pb) to 140 times (Zn). The soils developed on heaps were characterized by high Ca concentrations and high pH, as mining wastes contain large amounts of dolomite and calcite. Ore deposits near Olkusz comprise 69 % of dolomite and calcite (Cabała 2009). However, despite high pH, concentration of exchangeable, potentially bioavailable and toxic Cd form, exceeded in many soils 10-19 % of total Cd. Mobility of Zn and particularly Pb was low. The results are in accordance with those obtained by Kapusta et al. (2011) and Vaněk et al. (2005), indicating that Cd is the most mobile of the three metal tested.

Our study showed that many relics of historical mining in western Małopolska are heavily contaminated with Cd, Pb and Zn. Therefore, old heaps may threaten not only the environment, but also local inhabitants, as they are often located close to houses or agricultural fields. The question remains to what extent the metals are taken up by plants growing on old heaps and in their vicinity, and incorporated into the trophic chain. Pyatt et al. (2001) found that metal may affect the environment for many centuries after cessation of the industrial activities. It should be taken into account that metal mining remnants, such as hillocks and mining shafts, as well as social awareness of metal pollution at such sites will probably disappear with time, while heavy metals – as elements – remain in soil, constantly posing a threat to the surroundings.

Fig.1 A highly metal-polluted (Cd: 82.4, Pb: 4135, Zn: 14300 mg kg^{-1} soil) relic of historical Ag-Pb-Zn mining in western Małopolska (S Poland) surrounded by a pasture

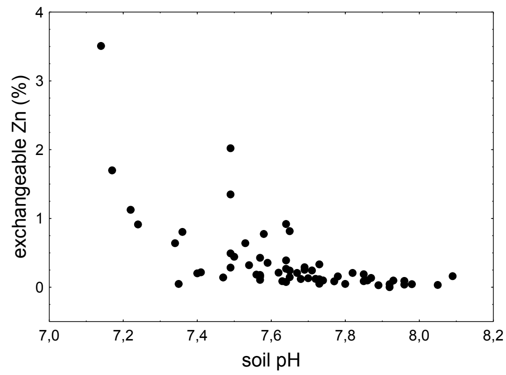

Fig.2 Relation between soil pH and exchangeable Zn (non-transformed data)

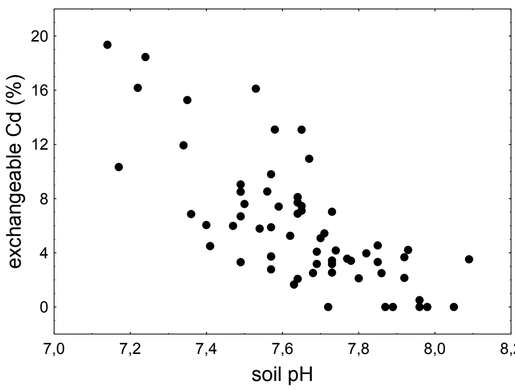

Fig.3 Relation between soil pH and exchangeable Cd (non-transformed data)

Tab.1 Physicochemical characteristics of metal-polluted soils developed at sites of historical Ag-Pb-Zn mining in western Małopolska (S Poland); org – organic, tot – total, ex – exchangeable, ws – water-soluble (N = 63)

	minimum	mean	median	maximum	variation coefficient (%)
sand (%)	44.0	65.4	66.0	81.0	13.2
silt (%)	5.0	20.5	20.0	42.0	37.7
clay (%)	5.0	14.1	14.0	35.0	42.0
C_{org} (%)	0.2	4.2	4.0	10.3	53.9
N_{tot} (%)	0.1	0.3	0.3	0.7	41.0
pH (H_2O)	7.1	7.6	7.6	8.1	2.7
Ca_{tot} (g kg^{-1})	6.1	105	88	323	70.5
Cd_{tot} (mg kg^{-1})	4.4	71.0	27.2	392	122
Pb_{tot} (mg kg^{-1})	72.8	2092	890	16931	143
Zn_{tot} (mg kg^{-1})	322	10168	4820	41860	104
Cd_{ex} (mg kg^{-1})	0.0	4.5	1.4	32.0	138
Pb_{ex} (mg kg^{-1})	0.0	0.7	0.0	16.3	355
Zn_{ex} (mg kg^{-1})	0.0	54.3	9.1	656	228
Cd_{ws} (µg kg^{-1})	0.0	9.6	0.0	207	368
Pb_{ws} (µg kg^{-1})	5.8	915	595	7480	127
Zn_{ws} (mg kg^{-1})	0.2	8.0	5.0	51.6	122

Acknowledgements

The study was financially supported by the National Science Centre in Poland (grant No N305 018040). The statutory fund of the Institute of Botany of the Polish Academy of Sciences also provided partial funding.

References

Cabała J. Metale ciężkie w środowisku glebowym olkuskiego rejonu eksploatacji rud Zn-Pb. Katowice: Wydawnictwo Uniwersytetu Śląskiego; 2009 (in Polish).

Commission of the European Communities (1986) Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal of the European Communities L 181 (86/278/EEC): 6-12.

Chrastný V, Vaněk A, Teper L, Cabala J, Procházka J, Pechar L, Drahota P, Penížek V, Komárek M, Novák M. Geochemical position of Pb, Zn and Cd in soils near the Olkusz mine/smelter, South Poland: effects of land use, type of contamination and distance from pollution source. Environ Monit Assess 2012;184:2517-36.

Kapusta P, Szarek-Łukaszewska G, Stefanowicz AM. Direct and indirect effects of metal contamination on soil biota in a Zn-Pb post-mining and smelting area (S Poland). Environ Pollut 2011;159:1516-22.

Molenda D. Górnictwo kruszcowe na terenie złóż śląsko-krakowskich do połowy XVI wieku. Wrocław-Warszawa-Kraków: PAN;1963 (in Polish).

Molenda D. Wydobycie i handel galmanem w Polsce od połowy XVII do schyłku XVIII wieku. Kwartalnik Historii Kultury Materialnej 2000;48:11-40 (in Polish).

Pyatt FB, Gilmore G, Grattan JP, Hunt CO, McLaren S. An imperial legacy? An exploration of the environmental impact of ancient metal mining and smelting in southern Jordan. J Archaeol Sci 2000;27:771-8.

Stefanowicz AM, Niklińska M, Kapusta P, Szarek-Łukaszewska G. Pine forest and grassland differently influence the response of soil microbial communities to metal contamination. Sci Total Environ 2010;408:6134-41.

Vaněk A, Borůvka L, Drábek O, Mihaljevič M, Komárek M. Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry. Plant Soil Environ 2005;51:316-21.

Verner JF, Ramsey MH, Helios-Rybicka E, Jędrzejczyk B. Heavy metal contamination of soils around a Pb-Zn smelter in Bukowno, Poland. Appl Geochem 1996;11:11-6.