Revealing the Distribution and Bioavailability of Zn, Pb, and Cd in Soil at an Abandoned Zn Processing Site: The Role of Spectrometry Techniques

K. Sutkowska[a], L. Teper[a,*], A. Vaněk[b] and T. Czech[c]

[a]Department of Applied Geology, Faculty of Earth Sciences, University of Silesia,
Bedzinska 60, 41-200 Sosnowiec, Poland

[b]Department of Soil Science and Soil Protection, Faculty of Agrobiology, Food and Natural Resources,
Czech University of Life Sciences Prague, Kamycka 129, Prague 6, Czech Republic

[c]Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow,
al. A. Mickiewicza 21, 31-120 Kraków, Poland

The focus of this study is the potential geochemical hazard in the soil system affected by historical zinc processing in Jaworzno, southern Poland. Total Zn, Pb, and Cd concentrations for soil samples determined by inductively coupled plasma optical emission spectrometry are reported. The modified three-step BCR sequential extraction procedure for analysis of the soil was successfully applied to obtain critical information on the heavy metal bioavailability and toxic impact on the natural environment. Exchangeable-, reducible-, oxidizable-, and residual fractions obtained using the sequential extraction procedure were separated and the heavy metal contents in each fraction were determined using inductively coupled plasma optical emission spectrometry. The results of the partitioning study provide information on the mobility of heavy metals in the soil profiles. Most of the Zn in the topsoil is related to the exchangeable-, reducible- and organic/oxidizable phases. The Zn fractionation in the whole soil profiles looks slightly different, with depletion of exchangeable- and reducible phases and enrichment of residual- and organic fractions. The greatest amount of Pb is associated with the reducible fraction. Cadmium is mainly found in the exchangeable- and reducible fraction. The spectrometry techniques applied are helpful in metal-level assessment and useful for evaluating the fate of contaminants and their bioavailability in soil systems. They show that 40 years since Zn processing ceased, the total concentrations of Zn, Pb, and Cd in the investigated soils are extremely high. Due to the high proportions of the metals in the easily soluble fraction, it is evident that the Jaworzno area has been strongly affected by the historical zinc industry and that the topsoil is heavily contaminated or even toxic.

1. Introduction

The focus of this study is the potential geochemical hazard in the soil system affected by historical zinc processing in Jaworzno, southern Poland. In 1865, a Zn smelter founded in the Jaworzno area in 1822 was replaced by another plant producing white zinc (ZnO). This was finally closed in 1976 as obsolete technology was harming the environment [1]. The raw material used for the production of zinc was non-sulfide ore from local mines [2]. The ore consists of zinc carbonates — smithsonite and/or monheimite, goethite (FeO(OH)), hemimorphite $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$, galena PbS, dolomite, calcite, and clay minerals. The old reclaimed waste heap, which is a relic of abandoned Zn processing, is nowadays situated in the immediate vicinity of a residential district and community gardens (Fig. 1).
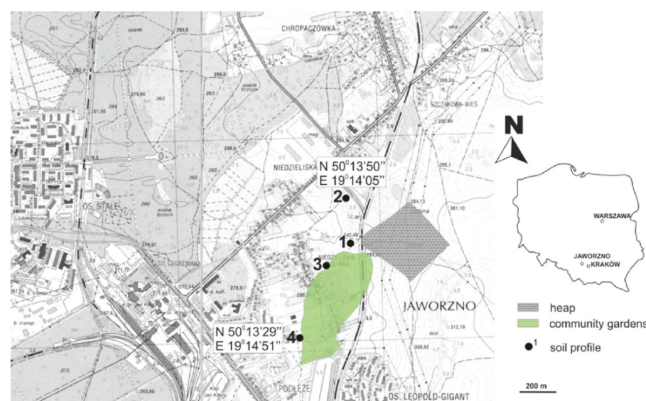

Fig. 1. Location of the study area and sampling sites in Jaworzno.

2. Material and methods

The research was conducted on 4 forest-soil profiles of the podzol located in the industrial- and anthropogenically-altered city space of Jaworzno in the NE part of the Upper Silesia, southern Poland (Fig. 1).

———————

*corresponding author; e-mail: leslaw.teper@us.edu.pl

The soil profiles developed on Pleistocene fluvio-glacial sediments, mainly sand and clay. Each soil profile was divided into separate horizons which were sampled, giving a total of 22 samples in all. Total Zn, Pb, and Cd concentrations were measured using inductively coupled plasma optical emission spectrometer ICP-OES Optima 7300 Dual View Perkin Elmer (Fig. 2). Each soil analysis was replicated twice. The modified three-step BCR sequential extraction procedure (SEP) [3]was

used to obtain basic information about chemical fractionation of trace elements in the tested soil samples. The operationally-defined fractions were as follows: acid-extractable/exchangeable, reducible, oxidizable and residual. The determination of element concentrations within the individual leachates of the SEP was carried out identically using the ICP-OES under standard analytical conditions.

3. Results

The Jaworzno soil samples contain 9.53–2307.52 of Zn, 3.07–531.09 of Pb and 0.16–17.62 of Cd [mg/kg in dry matter], with geometrical means of 91.76, 38.45 and 1.31, respectively. The highest combined Zn, Pb, and Cd values characterize the topsoil (Fig. 3). They decrease with depth. Downward trends of heavy-metal mobilization and translocation are known from other industrial regions. The total contents of Zn, Pb, and Cd in the soils, exceeding by 2–3 times the values of the background for southern Poland, reveal a moderate level of contamination [4, 5]. The Zn-, Pb-, and Cd contents exceed by 8-, 11-, and 28 times, respectively, median values for European soils [6]. However, compared to other long-lasting Zn-Pb mining- and smelting sites in Poland [7–11] and worldwide [12–14], the heavy-metal contents in the Jaworzno topsoil are lower by a factor of 2 at least.

Fig. 2. Inductively coupled plasma optical emission spectrometer ICP-OES Optima 7300 Dual View Perkin Elmer.
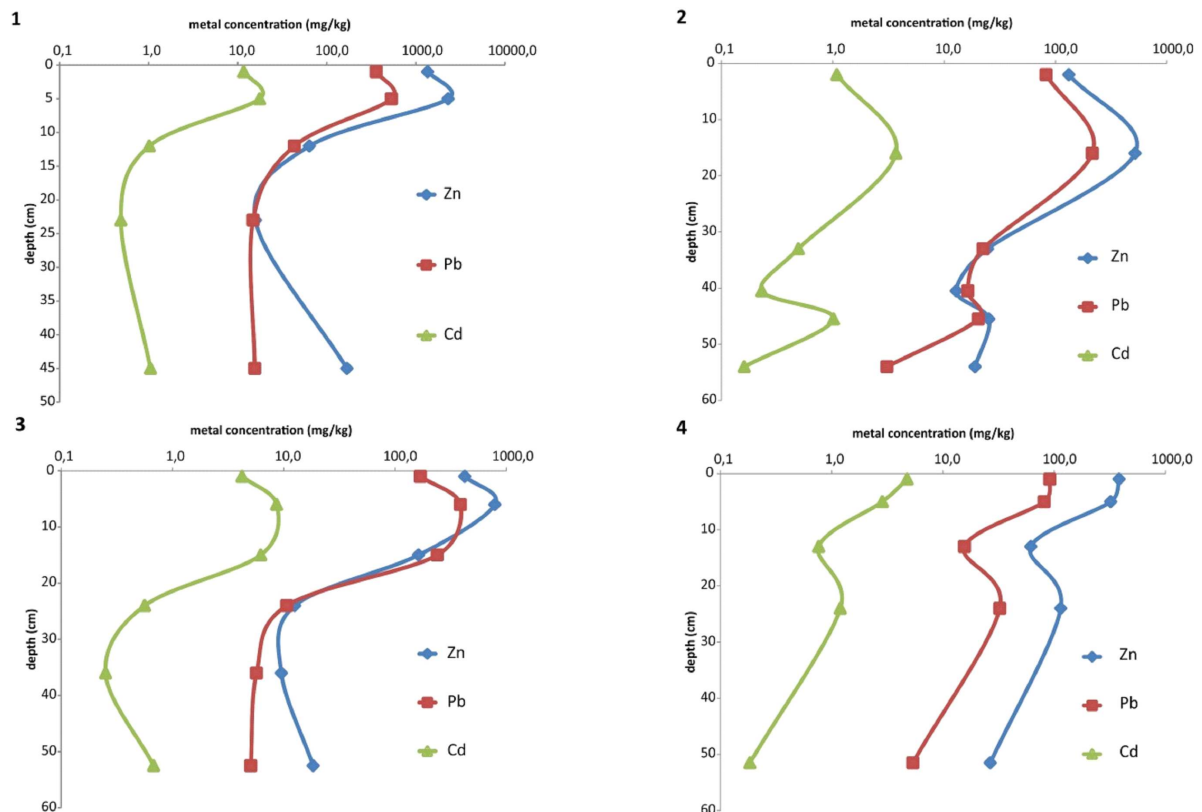

Fig. 3. Vertical distribution of heavy metal concentrations [mg/kg in dry matter] in the studied soil profiles. Metal concentration is given in log scale. 1, 2, 3, 4 — soil profile numbers (for localization see Fig. 1).
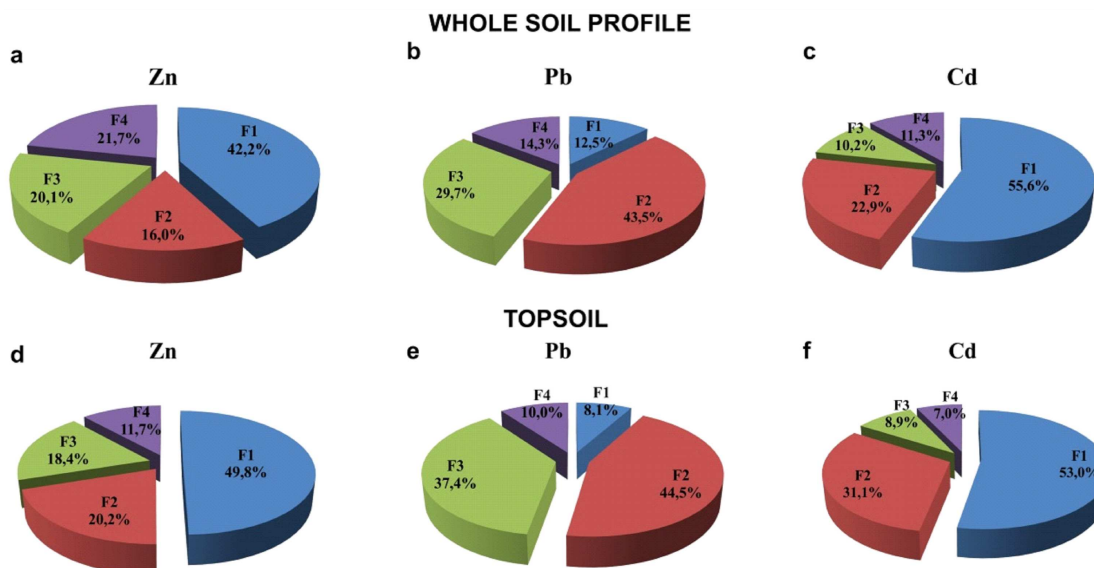
WHOLE SOIL PROFILE

Fig. 4.   Relative abundance of Zn, Pb, and Cd (%) in the sequentially extractable fractions.
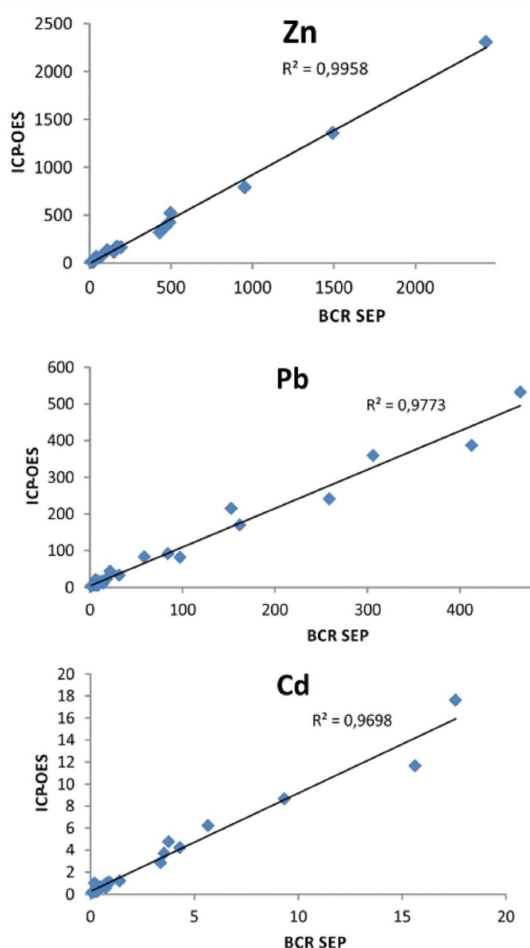

Fig. 5.   Correlation plots of metal contents in the studied soil samples determined by ICP-OES and the modified BCR sequential extraction procedure.

The results of the partitioning study provide information on the mobility of heavy metals in the soil profiles (Fig. 4). Most of the Zn in the topsoil (Fig. 4d) is related to the exchangeable (49.8%), reducible (20.2%) and organic/oxidizable (18.4%) phases. The Zn fractionation in the whole soil profiles looks slightly different (Fig. 4a), with depletion of exchangeable (42.2%) and reducible (15.9%) phases and enrichment of residual (21.7%) and organic (20.1%) fractions. The greatest amount of Pb is associated with the reducible fraction, accounting for about 44.5% in the topsoil (Fig. 4e) and 43.5% in whole profiles (Fig. 4b). Cadmium is mainly found in the exchangeable fraction (53% and 55.6% in the topsoil — Fig. 4f and whole profile — Fig. 4c, respectively) and in the reducible fraction (31.1% — Fig. 4f and 22.9% — Fig. 4c). Total metal contents (ICP-OES) and the summation of all fractions of the sequential extraction (modified BCR SEP) are strongly correlated (Fig. 5). The results suggest that the mobility and bioavailability of Zn, Pb and Cd in the topsoil decline in the order Cd >Zn >Pb. It is also evident that the participation of the residual fraction generally increases with depth. Moreover, the proportion of contaminants in the "labile" BCR SEP fractions, and subsequent vertical mobility, is generally higher for forest- than for agricultural soil, which is consistent with what has been observed in previous studies [11, 15].

4. Conclusion

The spectrometry techniques applied are helpful in metal-level assessment and useful for evaluating the fate of contaminants and their bioavailability in soil systems. They show that 40 years after Zn processing ceased, the total concentrations of Zn, Pb and Cd in the Jaworzno soils are extremely high, being *ca.* 8 to 28 times greater than in European topsoils [6] and twice greater

than the geochemical background for the extremely anthropogenically-altered soils of southern Poland [5]. Due to the high proportions of the metals in the very soluble fraction, it is evident that the Jaworzno area has been strongly affected by the past zinc industry and that the topsoil is heavily contaminated or even toxic.

Acknowledgments

References

[1] A.J. Wojcik, in: *Dzieje górnictwa — element europejskiego dziedzictwa kultury*, Eds. P.P. Zagożdżon, M. Madziarz, Oficyna Wydawnicza Polit. Wrocławskiej, Wrocław 2013, p. 379 (in Polish).

[2] K. Sutkowska, T. Czech, L. Teper, T. Krzykawski, *Ecol. Chem. Eng. A* **20**, 1441 (2013).

[3] G. Rauret, J.F. Lopez-Sanchez, A. Sahuquillo, E. Barahona, M. Lachica, A.M. Ure, C.M. Davidson, A. Gomez, D. Luck, J. Bacon, M. Yli-Halla, H. Muntau, P. Quevauviller, *J. Environ. Monit.* **2**, 228 (2000).

[4] J. Lis, A. Pasieczna, *Geochemical Atlas of Poland 1:2500000*, Polish Geological Institute, Warszawa 1995.

[5] A. Pasieczna, *Gospod. Surowcami Miner. — Mineral Resources Management* **24**, 67 (2008).

[6] R. Salaminen, *Geochemical Atlas of Europe*, Parts 1 and 2, Geological Survey of Finland, Helsinki 2005.

[7] J.F. Verner, M.H. Ramsey, E. Helios-Rybicka, B. Jedrzejczyk, *Appl. Geochem.* **11**, 11 (1996).

[8] S. Ullrich, M. Ramsey, E. Helios-Rybicka, *Appl. Geochem.* **14**, 187 (1999).

[9] J. Cabala, K. Sutkowska, *Prace Nauk. Inst. Górnictwa Polit. Wrocł. Studia i Materiały* **117**, 13 (2006).

[10] J. Cabala, L. Teper, *Water Air Soil Pollut.* **178**, 351 (2007).

[11] V. Chrastný, A. Vaněk, L. Teper, J. Cabala, J. Prochazka, L. Pechar, P. Drahota, V. Penizek, M. Komarek, M. Novak, *Environ. Monit. Assess.* **184**, 2517 (2012).

[12] Y.G. Yang, C.Q. Liu, W. Pan, G.P. Zhang, W.H. Zhu, *Water Air Soil Pollut.* **174**, 321 (2006).

[13] L. Rodríguez, E. Ruiz, J. Alonso-Azcárate, J. Rincón, *J. Environ. Manage.* **90**, 1106 (2009).

[14] H.Y. Zhan, Y.F. Jiang, J. Yuan, X.F. Hu, O.D. Nartey, B.L. Wang, *J. Geochem. Explor.* **147**, 182 (2014).

[15] V. Chrastný, E. Čadková, A. Vaněk, L. Teper, J. Cabala, M. Komárek, *Chem. Geol.* **405**, 1 (2015).