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Impact of Solvay Waste Alkalinity on the Leaching of Heavy Metals in A 100 Year-Old Landfill

Katarzyna Sutkowska, Leslaw Teper
Department of Applied Geology, Faculty of Earth Sciences, University of Silesia
Bedzinska 60, 41-200 Sosnowiec, Poland
katarzyna.sutkowska@us.edu.pl; leslaw.teper@us.edu.pl

Abstract -The present study was conducted in the northern outskirts of the Jaworzno town situated in the Upper Silesia, the most industrialized part of Poland, where the over hundred-year-old landfill site of soda ash waste is situated. The 10 waste samples and 10 topsoil samples were collected. Value of the pH and the total load of selected heavy metals (Cd, Cr, Pb and Zn) were determined for both types of samples. The atomic emission spectrometer ICP-OES was used to geochemical measurements. The wastes are characterised by low to very strong alkalinity, while the topsoil is near-neutral to slightly alkaline. Total loads of the selected heavy metals in the waste samples present the highest level in surface layer with lower but almost unchanged values through the profile length, caused by very strong alkalinity. Contents of Cr, Cd, Pb and Zn recognized in the meadow topsoil are significantly lower than those in the uppermost layer of the wastes. The alkaline nature of the post-Solvay tailings is what is responsible for limited heavy metal migration to adjacent soils.

Keywords: Solvay process, soil contamination, heavy metals, waste

1. Introduction

The Solvay process was implemented in the 19th century to reduce negative impact of the soda ash production on the natural environment (Steinhauser, 2008; Web-1). At present the Solvay technology constitutes almost 60% of soda ash world production and dominates in the Europe and Asia with capacities reaching over 15 and 9.7 million tonnes per year, respectively (Web-1). Despite of continuous technological improvement this manufacturing method requires large amounts of raw materials: sodium chlorite (NaCl), limestone ($CaCO_3$), ammonia (NH_3) and plenty of the energy (Steinhauser, 2008; Web-1). Moreover, the soda-ash industry sector generates lots of solid and liquid waste (Jadeja and Tewari, 2007; Steinhauser, 2008; Web-1). The magnitude of the solid waste value fabricated in the Solvay technology is estimated at 10 to 300 kg per each tone of soda ash (Web-1). These post-production slurries are overloaded by inorganic chlorides, carbonates, sulphates, alkali, ammonia and suspended solids, including heavy metals derived from the raw materials, i.e. limestone, coke and brine (Hong et al., 2014; Web-1). The above let us to assume that in the vicinity of the currently and historically operating soda-ash plants, especially land-locked, handling with the objects of the waste storage is an important environmental issue.

In spite of ecological importance of the solid wastes of soda-ash industry for the environment components, there is the deficiency of scientific information about that effect. This motivated us to inspect the concentration of selected heavy metals in the over 100-years old soda-ash remains produced by the Solvay factory in Jaworzno town. The main aim of our research is to check the ecological hazard of the historical soda-ash tailings on the uppermost horizon of soil in proximity of the heap.

2. Material And Methods

The study field is located in the northern outskirts of the Jaworzno town situated in the Upper Silesia, the most industrialized part of Poland. In that area, the abandoned, over hundred-year-old landfill site of soda ash waste is situated. The meadows, forests, residential and industrial areas make a neighbourhood of the heap.

The relatively short time activity of soda-ash Solvay plant, late 19th to early 20th century (Web-2), had resulted in the three to five meters high dump which occupies an area of ca. 3.3 hectares (Fig. 1.). The top surface of the dump is covered by about 15 cm thick soil layer.

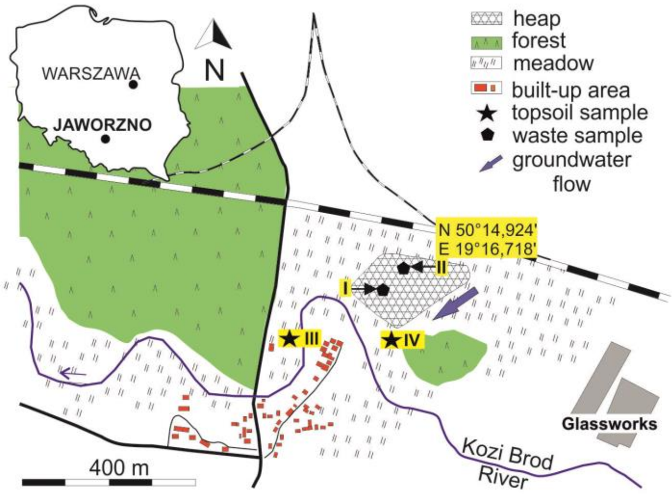

Fig. 1. The study area and sampling points situation in Jaworzno town

In the immediate neighbourhood, there is a build-up area and small river called Kozi Brod runs, what led us to control the heavy metal concentrations in two sites located on the waste dump and in other two locations where fallow topsoil (the podzol) developed on the fluvio-glacial sediments was sampled (Fig. 1.). The soil profiles are situated in the direction of local groundwater flow. Total number of studied samples is 20.

Analyses were conducted on dry samples of waste and soil sifted through a plastic sieve with 2 mm mesh. Value of the pH of all samples was measured potentiometrically in 1M KCl solution. Selected heavy metal (Cd, Cr, Pb and Zn) loads were determined in two replications by using atomic emission spectrometer ICP-OES Optima 7300 Dual View Perkin Elmer.

3. Results And Discussion

The authors intention was to consider if chemical properties of soda-ash leftovers abandoned almost 100-years ago are hazardous for environment. To provide such kind of information, the pH and the contents of Cd, Cr, Pb and Zn in waste and topsoil samples were analysed.

The wastes are characterised by low to very strong alkalinity. The pH values measured in the waste material vary from 7.45 to 11.75 (Fig. 2.), with median 9.13. Compatible results were received for similar wastes in Poland (Skrzypczak et al., 2009; Wojcik and Zawadzki, 2011) and India (Jadeja and Tewari, 2007). The topsoil is near-neutral to slightly alkaline as the topsoil pH varies between 6.93 and 7.92, with median 7.53 (Fig. 2.).

Total loads of the selected heavy metals in the waste samples equal 1.07–3.74 mg kg^{-1} for Cd, 2.72–8.22 mg kg^{-1} for Cr, 8.55–20.25 mg kg^{-1} for Pb and 82.87–178.85 mg kg^{-1} for Zn, with geometric means 1.91 mg kg^{-1}, 5.53 mg kg^{-1}, 13.80 mg kg^{-1} and 144.65 mg kg^{-1}, respectively. The soil covering the waste heap demonstrates higher level of metals content than in the waste: 3.72–9.89 mg kg^{-1} for Cd, 4.56–20.40 mg kg^{-1} for Cr, 61.20–146.05 mg kg^{-1} for Pb and 388.91–552.35 mg kg^{-1} for Zn, with geometric means 6.84 mg kg^{-1}, 12.89 mg kg^{-1}, 109.95 mg kg^{-1} and 460.78 mg kg^{-1}, appropriately.

Abundance of the same elements in the topsoil specimens achieves values 0.045–1.21 mg kg^{-1} of Cd, 7.99–103.62 mg kg^{-1} of Cr, 14.56–36.33 mg kg^{-1} of Pb and 93.05–153.87 mg kg^{-1} of Zn, with geometric means 0.87 mg kg^{-1}, 21.68 mg kg^{-1}, 25.67 mg kg^{-1} and 119.81 mg kg^{-1}, consequently.

Considering the vertical distribution of the metals content in profiles from the heap, the highest contamination level is observed in the surface soil layer and the strong reduction of metal concentrations is detected in the deeper horizons. Moreover, in horizons over the depth of 15 cm, contents of the heavy metals remain almost unchanged through the profile length (Fig. 2.). The retention of cadmium, chromium, lead and zinc observed in waste samples seems to be analogous to heavy metals behaviour/immobility in soils characterized by alkaline pH (Kabata-Pendias and Pendias, 1999; Kabata-Pendias, 2001). The very strong alkalinity of the Solvay process tailings tightly holds heavy metals in insoluble state as a part of suspended solids. In that way both the soil and water environment are protected against heavy metals pollution until the heap will not be broken.

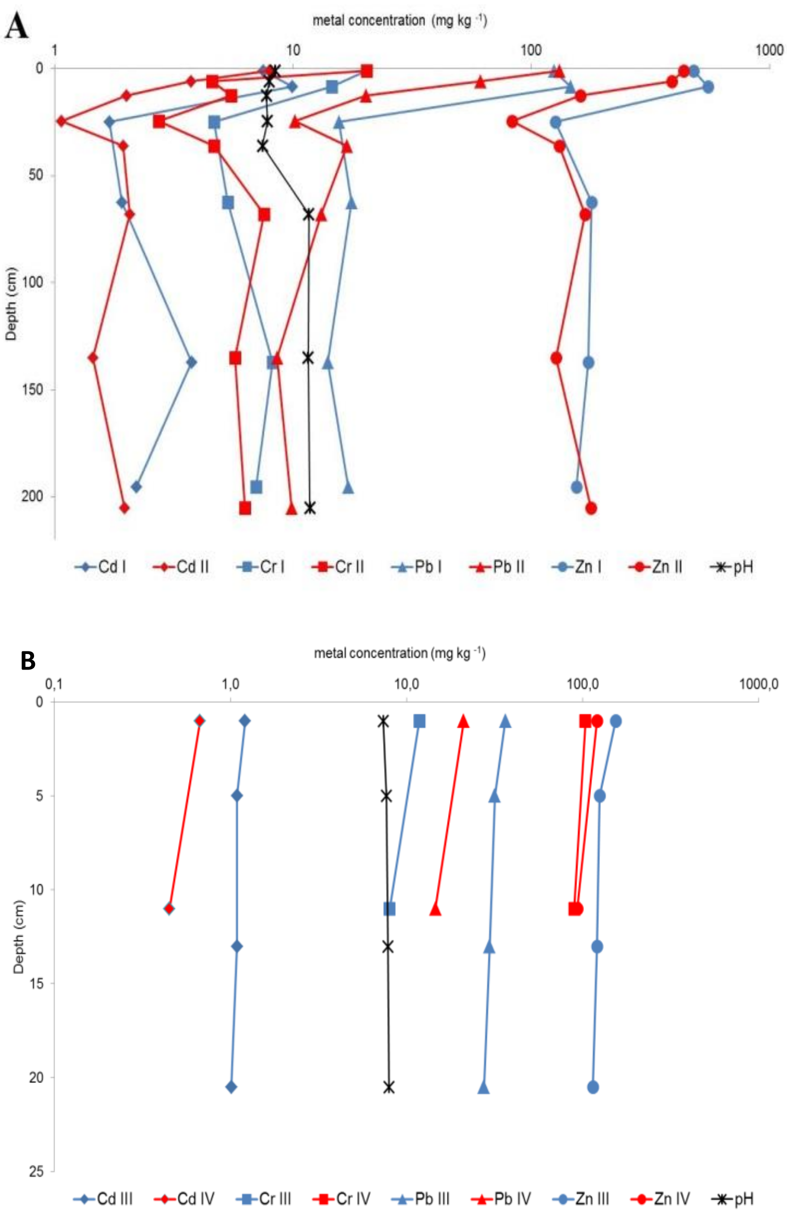

Fig. 2. Distribution of heavy metal concentrations in waste material (A) and soil profiles (B). Values of soil and waste pH are also shown

Unquestionably, the greatest heavy metal loads identified in the dump topsoil (Fig. 2.) are consequence of the cumulative impact of pollution provided from the raw material, especially from the limestone, and the fuel used for burning the limestone. Even 94% of the total amount of heavy metal contamination from present soda-ash industry can be derived from both mentioned materials (Web-1). On the other hand, the concentrations of Cr, Cd, Pb and Zn recognized in the meadow topsoil are significantly lower than those in the uppermost layer of the wastes (Fig. 2.). We believe that in this case the coke burning is where the only source of metals should be sought. Similar levels of heavy metals were found in topsoils from neighbouring industrial area affected mostly by combustion (Sutkowska et al., 2013).

The industrial influence on the dump vicinity is confirmed by the comparison of geometric means and medians of the heavy metal contents in the studied soils to topsoils all over Poland. Such analysis shows strong contamination of examined topsoils, expressed by even 98 times higher metal contents in the dump soils and up to 12.5 times higher metal quantities in the meadow topsoil compare to other Polish topsoils reported (Lis and Pasieczna, 1995; Kabata-Pendias, 2001; Pasieczna, 2008).

4. Conclusion

Outcomes of geochemical study reported in this paper indicate that industrial activity has noticeable impact on soil environment in the vicinity of the historical soda-ash plant. The highest heavy metal contents are detected in the anthropogenic soil overlaying soda-ash waste, while soil in neighbourhood of the waste dump is only slightly affected. It is suggested that bulk of heavy metals occurring in the wastes came from the raw materials. In contrast, heavy metals existing in the meadow topsoil were derived mainly from the coke combustion processes.

It is proposed that strong alkaline nature of the tailings produced by the Solvay plant prevents heavy metals originated from material deposited on the dump from being translocated in adjacent soils.

Finally, it is recommended to leave the industrial waste in untouched state to protect local environment against spontaneous heavy metal migration and excessive alkalization.

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References

Hong, J., Chen, W., Wang, Y., Xu, C., & Xua, X. (2014). Life Cycle Assessment Of Caustic Soda Production: A Case Study In China. *Journal of Cleaner Production,* 66, 113–120.

Jadeja, R. N., & Tewari, A. (2007). Effect Of Soda Ash Industry Effluent On Bioaccumulation Of Metals By Seaweeds Of Coastal Region Of Gujarat, India. *Journal of Hazardous Materials,* 147, 148–154.

Kabata-Pendias, A. (2001). *Trace Elements In Soil And Plants*. Third edition. USA: CRC Press.

Kabata-Pendias, A., & Pendias, H. (1999). *Biogeochemistry of trace elements.* Warsaw: Polish Scientific Publishers PWN, in Polish.

Lis, J., & Pasieczna, A. (1995). *Geochemical atlas of Poland 1:2 500 000.* Warsaw: Polish Geological Institute, in Polish.

Pasieczna, A. (2008). Impact Of Industry On Environment In Silesia-Cracow Region. *Mineral Resources Management,* 24(2/2), 67–82.

Skrzypczak, R., Sroczyński, W., Syposz-Łuczak, B., & Wota, A. (2009). Krakow „Białe Morza" – Chosen Problems Of Management And Revitalization. *Bulletin of the Mineral and Energy Economy Research Institute the Polish Academy of Science,* 76, 31-42.

Steinhauser, G. (2008). Cleaner Production In The Solvay Process: General Strategies And Recent Developments. *Journal of Cleaner Production,* 16(7), 833-841.

Sutkowska, K., Czech, T., Teper, L., & Krzykawski, T. (2009). Heavy Metals Soil Contamination Induced By Historical Zinc Smelting In Jaworzno. *Ecological Chemistry and Engineering A,* 20(12), 1441-1450.

Wojcik, R., & Zawadzki, L. (2011). Anion Leachability From The Top Layer Of The Cracow Soda Waste Dumps. *Environmental Protection and Natural Resources,* 49, 433-442.

Web sites:

Web-1: http://eippcb.jrc.ec.europa.eu/reference/BREF/lvic-s_bref_0907.pdf, consulted 3 Mar. 2015.

Web-2: http://www.jaworzno.pl/downloads/2013-02-19_12-22-19-917670/Waloryzacja_Jaworzno _2011.pdf, consulted 3 Mar. 2015.