

THE INFLUENCE OF pH ON SOLUBILITY OF COPPER IN SOILS CONTAMINATED BY COPPER INDUSTRY IN LEGNICA

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The aim of the study was to determine the influence of changes in pH on the solubility of copper in soils contaminated by copper industry. Soil samples were collected from the surface soil horizon (0-30 cm) at two sites situated in the vicinity of Legnica Copper Smelter. Soil material contained various concentrations of total Cu. Soil samples were treated with various doses of HCl and NaOH, in the presence of CaCl₂ as a background electrolyte. Copper concentrations and pH values were determined in the extracts obtained from the experiment. Buffering capacity curves were prepared on the basis of those results. The changes in pH affected the solubility of copper in contaminated soils. Addition of HCl resulted in increased copper solubility, particularly strong at the doses higher than 0,2 M HCl kg⁻¹.

Keywords: soil, copper, pH, mobility, copper mobility, soil pollution Legnica Copper Smelter

1. INTRODUCTION

Strategies of reclamation in Poland are based on the immobilization of contaminants, in particular heavy metals, and not on their removal from the environment. The choice of such solution results from economical and technical factors. Although the problem of soil pollution with heavy metals remains in Poland of local importance, in the surroundings of metal smelters, there are many multi-hectare polluted areas where soil decontamination would be very expensive and unprofitable [4, 11].

Toxicity and mobility of heavy metals in soil environment depends on soil properties and changes together with changing soil conditions. The most important factors that determine the mobility of heavy metals in soils include:

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the original geochemical form of the element, soil pH, sorption capacity, redox conditions, and the presence of competing ions or chelating compounds [4, 11].

Landscaping may cause the changes in soil conditions, for example it may affect soil pH, cation exchange capacity. A possible result of such changes may be mobilization of heavy metals and their migration to the groundwater or their uptake by soil organisms and plants [1, 5, 8, 10].

Legnica Copper Smelter was established in 1951 under the name of Legnica Metallurgical Plant. After the discovery of huge deposits of copper ore in Lubin by Jan Wyżykowski in 1957, the plant was modernized. The basic product of Legnica Smelter is electrolytic copper. For many years the plant remained on the black list of the biggest polluters in Poland. Nowadays the smelter produces 100 thousand tonnes of copper yearly [2, 3, 6, 7].

2. MATERIAL AND METHODS

Soil samples were collected at two afforested sites located in immediate vicinity of the Legnica Smelter at a distance of 50 m and 650 m from the smelter border – Fig. 1., fig. 2). These terrain are the most contaminated afforested areas in proximity of smelter. Dominant tree species are willow, birch-tree and juvenile pine. Samples of soil material were collected in 5 replicates. Dried soil material was sieved through a mesh with thickness of 1mm.

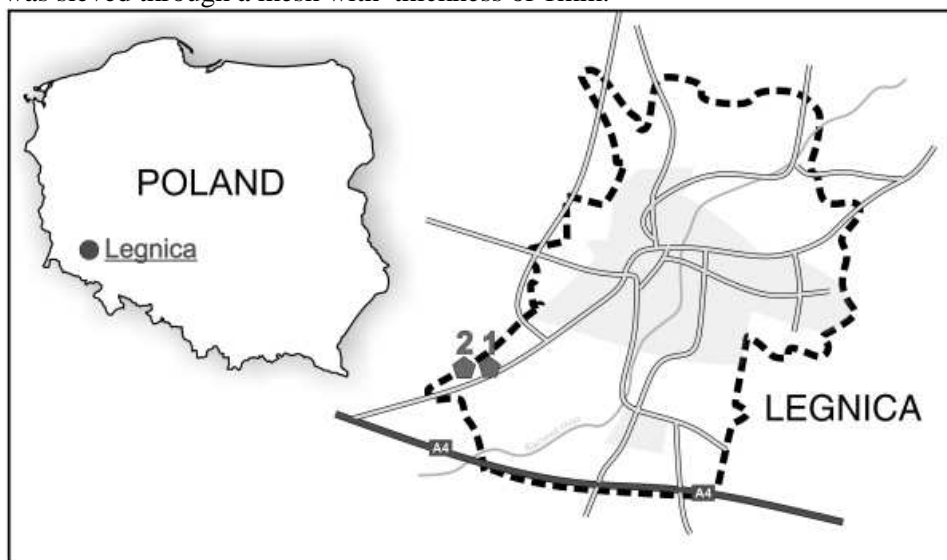


Fig. 1. Sampling locations (own elaboration)

Following parameters were determined: grain size distribution by areometric-sieve method modified by Prószyński, pH in H₂O and 1 M KCl by potentiometrical method, cation exchange capacity CEC by Kappen method,

organic carbon content by CS-Mat 5500 machine and the total content of copper by AAS - after soil digestion in perchloric acid [12].

Prepared samples were extracted with 0.01 M calcium chloride (CaCl_2) in three replicates. Two sets of samples were independently treated by solutions of 1 M NaOH and 1 M HCl. The suspension (5 g of soil and 25 cm^3 of CaCl_2) was supplemented with 0.1 cm^3 , 0.2 cm^3 , 0.5 cm^3 , 1 cm^3 , 2 cm^3 and 5 cm^3 of 1 M HCl or 1 M NaOH and was made up to 50 cm^3 of appropriate amount of distilled water. The suspension was shaken on an overhead shaker. The extraction time was 1 hour. The solution was then filtered through paper filter. In the obtained extract, the concentration of the copper was measured by atomic absorption spectrophotometry AAS. The concentration of Cu in extract is a measure of the mobility of copper in soil, related to a specific pH value. In addition, the pH of the suspension was measured for each of the additives and water (control solution) [12].

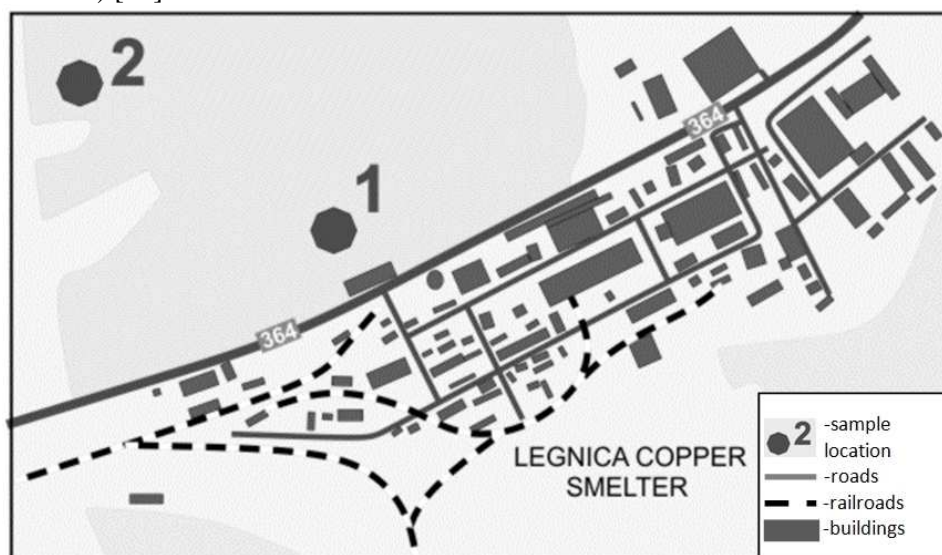


Fig. 2. Sampling locations (own elaboration)

3. RESULTS AND DISCUSSION

Both examined soils had a texture of silt loam. The reaction of both soils was acidic and their pH values, measured in KCl, were 5.3 and 4.5, in soils No.1 and No.2, respectively. Cation exchange capacity of soils was within the range of 6,36-6,56 $\text{cmol (+)} \cdot \text{kg}^{-1}$. Total copper content was 927 $\text{mg Cu} \cdot \text{kg}^{-1}$ in soil No. 1 and 566 $\text{mg Cu} \cdot \text{kg}^{-1}$ in soil No. 2.

Total concentrations of copper in soils was assessed as typical, and representative of the contaminated soil occurring in the surroundings of Legnica

Copper Smelter. Physical and chemical properties of both soils, shown in Tab. 1, are also typical for this area [6, 7].

3.1. The effects of HCl and NaOH addition on pH of soils

Analysis showed that there were significant differences in pH values between the analyzed soils and control solution (in H₂O – fig. 3).

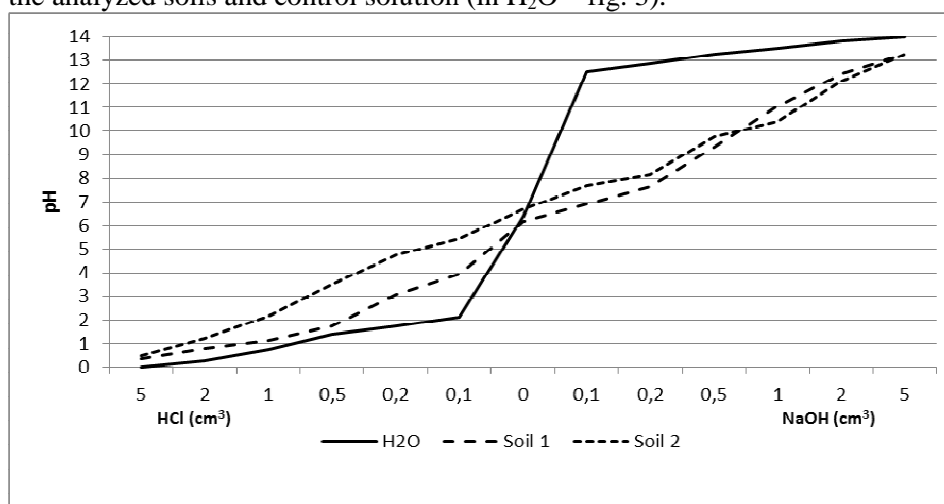


Fig. 3 The changes in pH after addition of various volumes of 1M HCl and 1M NaOH to analyzed soils.

The differences between pH values of contaminated soils and control sample proved relatively high buffering capacities against NaOH of soil No. 1 and soil No. 2. These capacities of both soils were similar.

On the other hand, addition of various doses of 1 M HCl showed higher buffering capacity of soil No. 2 against HCl if compared with soil No.1. These differences may be explained slightly higher content of organic carbon and a bit higher cation exchange capacity of soil No. 2 (Tab. 1).

Table 1. Basic properties of analyzed soils

Soil No.	Textural group	pH		CEC cmol(+) \cdot kg ⁻¹	C _{org} %	Fraction <0,002 mm content	Total Cu, mg \cdot kg ⁻¹
		KCl	H ₂ O				
1	SiL	5,3	5,9	6,36	1,2	7	927
2	SiL	4,5	5,3	6,56	1,8	10	566

3.2. The influence of pH on copper solubility

The application of different doses of 1 M HCl and 1 M NaOH caused changes in copper solubility in soils. Increasing doses of hydrochloric acid caused an increase in solubility of copper in both soils. The highest solubility of copper in

soil No. 1 was observed after application of the largest doses of acid, i.e. 1 and 5 cm³ HCl. These doses are equivalent of 0.2 and 1.0 M HCl per kg soil. This effect of Cu solubilization was associated with an extreme decline in the pH value of the suspensions, to the values below 1.0, when iron and manganese oxides dissolve. As a result of this process, chemically bound and occluded copper was released into solution. Extremely low pH values may also cause breakdown of the primary and secondary clay minerals, which normally effectively bind heavy metal cations. In the extracts with the addition of 1M NaOH, copper concentrations were significantly lower than those found in extracts without additives. Fig. 4 presents the effects of pH on copper solubility in soil No. 1. It is worth mentioning that a slight increase of Cu solubility was observed after addition of the largest amount (5 cm³) of NaOH. It could be a result of forming a negatively charged complex ions (Me[OH]ⁿ⁻), complex bonding of copper with ammonium ions or with low molecular weight organic compounds.

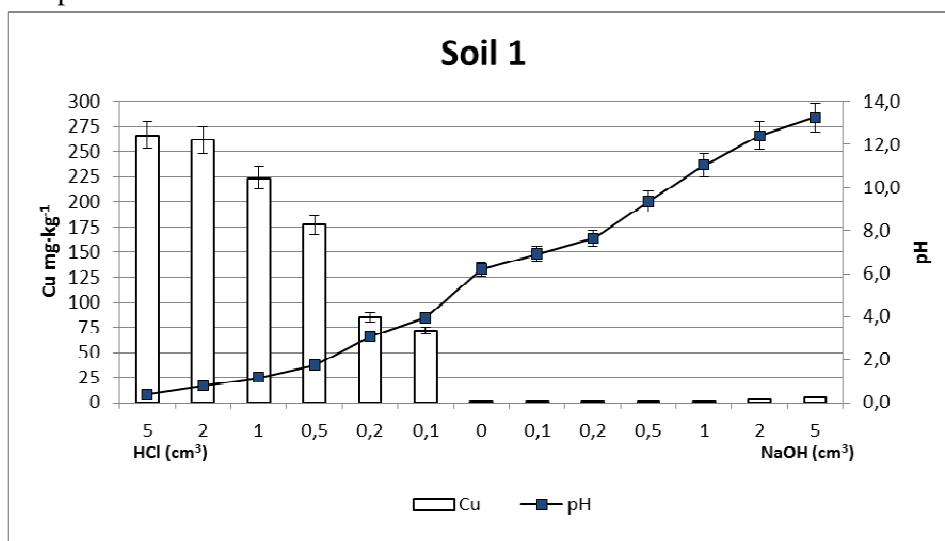


Fig. 4. The influence of pH on solubility of copper in soil No. 1.

The results obtained in the case of soil No. 2 were similar to those described above. Fig. 5 presents the effects of pH on solubility of copper in soil No. 2. Application of hydrochloric acid caused substantial increase in copper solubility in soil. There was a sharp increase in the amounts copper released to solution with the addition of 0,5 cm³ HCl. Absolute amounts of Cu released from soil No. 2 were lower than those solubilized from soil No 1, that contained higher total copper concentration.

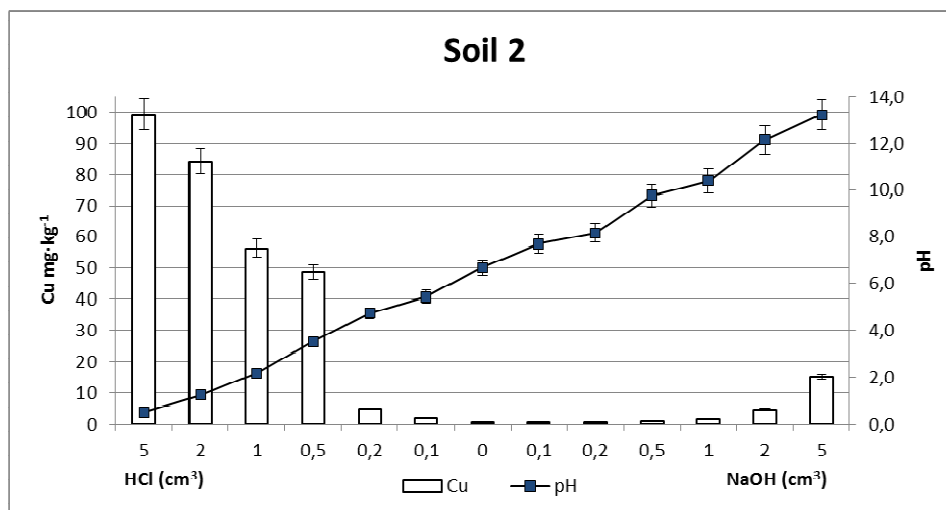


Fig. 5. The influence of pH changes on solubility of copper in soil No. 2.

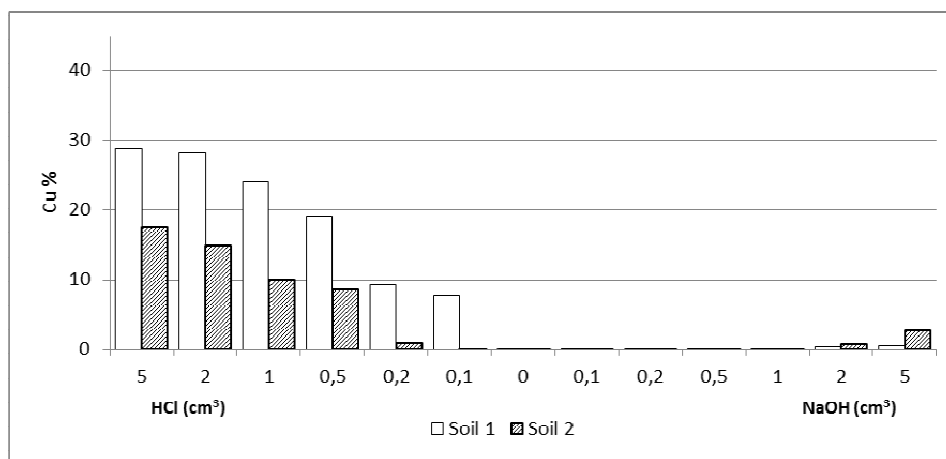


Fig. 6. Percentage of released Cu from contaminated soils, related to total Cu concentrations in soils No.1 and soil No. 2, as dependent on the rates of applied NaOH or HCl.

The maximum amount of copper released from soil No. 1 reached about 30% of total Cu, while in the case of soil No. 2 this quantity was about 18% (Fig. 6). This hypothesis is confirmed by the fact that higher contents of copper were leached by sodium hydroxide from soil No. 2. This indicates that the organic matter in soil No. 2 bonds higher quantities of copper. Further evidence of this is sharp increase of copper solubility in soil No. 1 with the 0,1 cm³ HCl dose.

3.3. Assessment of copper solubility in relation to soil reclamation

Total content of copper in soil No. 2 exceeds the permissible value established in Regulation by the Minister of Environment (DzU. 165, poz. 1359). At the same time, the content of soluble forms of copper is negligible. Therefore, copper remains in fact unavailable to plants and does not pose a real environmental risk. In addition, as a result of an effective flue gas desulphurization, there is no risk of severe soil acidification from that source. Flue gases discharged from Legnica Copper Smelter contain, apart from large amounts of copper and lead, also such compounds as: $\text{Ca}[\text{Mg}_{0.67}\text{Fe}_{0.33}][\text{CO}_3]$ – dolomite, $\text{Ca}[\text{FeMg}][\text{CO}_3]_2$ – ankerite, $\text{Ca}[\text{MgFe}]\text{Si}_2\text{O}_6$ – augite, which effectively neutralize the pH of dust [9].

There is, however, another source of potential risk, i.e. the presence of forest litter and its decomposition in afforested ecosystems. Low molecular weight organic acids can bind copper into a form of mobile complexes. This may result in leaching of contaminant into the soil profile. Another factor that should be considered as a potential source of soil acidification, is “physiologically acidic” fertilizers used in forestry. Therefore, various kinds of soil treatment that may lead to copper mobilization, should be banned. It is also important to keep monitoring of soil pH value in this area [5, 7, 8].

4. CONCLUSIONS

1. Soil No. 2 has better buffering properties against acidification compared with soil No. 1. This difference results most likely from higher content of organic matter.
2. Increasing HCl doses caused a significant increase in the solubility of copper in soils, particularly dramatic at the doses of 0.2 M HCl per kg soil and higher.
3. At extremely high pH of extracts, a slight increase of copper solubility was observed in the soil No. 2.
4. Despite very high total concentrations of copper in soils in the vicinity of Legnica Smelter, copper solubility in neutral or slightly acidic conditions remains very low, and thanks to high buffering capacity of soils it does not pose a real environmental risk.

REFERENCES

1. Alloway B.: *Heavy metals in soils*, Glasgow, Blackie Academic and Professional., 1995.
2. Dobrzański J., Brydziak H.: *Wpływ polskiego przemysłu miedziowego na środowisko naturalne*, Zesz. Probl. Post. Nauk Rol. **418** (1995), 383-389.

3. Kabała C., Singh BR.: *Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter*, Journal of Environmental Quality, 30(2) (2001), 485-492.
4. Kabata-Pendias A., Pendias H.: *Biogeochemia pierwiastków śladowych*, Warszawa, Wydawnictwo Naukowe PWN, 1999.
5. Karczewska A. 2002.: *Metale ciężkie w glebach zanieczyszczonych emisjami hut miedzi – formy i rozpuszczalność*, Rozprawa habilitacyjna, Zeszyty Naukowe AR we Wrocławiu, Rozprawy CLXXXIV, 432.
6. Karczewska A., Kabała C.: *The soils polluted with heavy metals and arsenic in Lower Silesia – the need and methods of reclamation*, Zeszyty Naukowe Uniwersytetu Przyrodniczego we Wrocławiu, Rolnictwo XCVI, **576**, (2010) 59-79.
7. Karczewska A., Kaszubkiewicz J., Jezierski P., Kabała C., Król K.: *Level of soil contamination with copper, lead, and cadmium within a protection zone of Copper Smelter Legnica in the years 1982 and 2005*, Roczniki Gleboznawcze tom LXI, **1** (2010), 45-51.
8. Karczewska A.: *Ochrona gleb i rekultywacja terenów zdegradowanych*, Wrocław, Wydawnictwo Uniwersytetu Przyrodniczego we Wrocławiu, 2012.
9. Konarski P., Iwanejko I., Mierzejewska A., Ćwil M., Diduszko R., *Analiza spektralna mikro- i nanocząstek zanieczyszczających środowisko w Legnicy*, II Krajowa Konferencja Naukowo-Techniczna „Ekologia w Elektronice”, Warszawa, 2002, 75-81.
10. McBride M.: *Environmental chemistry of soils*, New York, Oxford University Press, 1994.
11. Mercik S.: *Chemia rolna. Podstawy teoretyczne i praktyczne*, Warszawa, Wydawnictwo SGGW, 2002.
12. Ostrowska A., Gawliński Z., Szczubiałka Z.: *Metody analizy i oceny właściwości gleb i roślin*, Warszawa, IOŚ 1991.
13. Rozporządzenie Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi (Dz.U.Nr.165 poz. 1359).

WPŁYW PH NA MOBILNOŚĆ MIEDZI W GLEBACH ZANIECZYSZCZONYCH PRZEZ PRZEMYSŁ MIEDZIOWY W LEGNICY

Streszczenie

Celem niniejszych badań było określenie wpływu odczynu na mobilność miedzi w glebach zanieczyszczonych przez przemysł miedziowy. W doświadczeniu pobrano dwie próbki glebowe z poziomów powierzchniowych (0-30cm) z otoczenia Huty Miedzi

Legnica. Materiał glebowy różnił się całkowitą zawartością miedzi w glebie. Próbki gleby traktowane były różnymi dawkami HCl i NaOH w obecności CaCl₂ stanowiącego elektrolit podstawowy. W ekstraktach oznaczano stężenie miedzi i pH. Na tej podstawie wykreślono krzywe buforowe dla obu gleb. Zmiany wartości pH wpłynęły na rozpuszczalność miedzi w glebach zanieczyszczonych. Dodatek HCl w ilości przekraczającej 0,2 M kg⁻¹ spowodował radykalny wzrost rozpuszczalności miedzi.

