

Leszek Gersztyn\*, Anna Karczewska\*, Bernard Gałka\*

## Influence of pH on the solubility of arsenic in heavily contaminated soils

### Wpływ pH na rozpuszczalność arsenu w glebach silnie zanieczyszczonych

\* Mgr inż. Leszek Gersztyn, prof. dr hab. inż. Anna Karczewska, dr inż. Bernard Gałka, Department of Soil Sciences and Environmental Protection, Wrocław University of Environmental and Life Sciences, Grunwaldzka 53 St, 50-357 Wrocław, Poland; Phone: 071/3205604; E-mail: leszek.gersztyn@up.wroc.pl, anna.karczewska@up.wroc.pl, bernard.galka@up.wroc.pl

**Keywords:** arsenic, pH, contaminated soils, solubility

**Słowa kluczowe:** arsen, pH, gleby zanieczyszczone, rozpuszczalność

#### Abstract

The aim of this study was to determine the impact of pH on arsenic solubility in soils heavily contaminated by the former arsenic industry. For the purpose of the study, three soil samples were collected from the area affected by ore processing in Złoty Stok. Soils differed in initial pH, calcium carbonate content, organic matter content and total arsenic concentration. The amounts of arsenic released from soils at various pH were measured using extraction tests, where soil samples were shaken with various doses of HCl and NaOH in the presence of  $0.01 \text{ mol} \cdot \text{dm}^{-3} \text{ CaCl}_2$  as the background solution. Arsenic solubility in soils was considerably low at neutral or slightly acidic pH and increased considerably in both strongly acidic and alkaline conditions. The importance of these effects for environmental risk was discussed.

© IOŚ-PIB

## 1. INTRODUCTION

The natural concentration of arsenic in soils is very low, usually below  $5 \text{ mg} \cdot \text{kg}^{-1}$  [Kabata-Pendias, Pendias 2000]. Elevated arsenic concentrations in soils may be caused by human activities, including arsenic and gold mining and processing [Smith et al. 1998, Krysiak, Karczewska 2007]. Złoty Stok, a former centre for the gold and arsenic industry, remains the most arsenic-polluted area in Poland. For many centuries, Złoty Stok was a centre of industrial activity, until 1962 when all such activity ceased [Dziekoński 1972, Łuszczkiewicz, Muszer 1997]. Mining operations in the Złoty Potok valley generated large quantities of waste materials that were spread over a forested hilly area. Weathering of this material, together with the emissions from local smelting facilities, resulted in high concentrations of arsenic in soils. Large amounts of arsenic-rich tailings were disposed in landfills north of the town, from where they occasionally spilled into the valley of the Trująca river. Arsenic concentrations in soils exceed Polish soil quality standards on the large area of both valleys [Karczewska et al. 2013]. Because of the wide spread of polluted areas, decontamination of soils is not a viable option; therefore, it is important to effectively immobilise arsenic and prevent it from being released. Although soil arsenic is usually hardly mobile and poorly available to most plant species [Kabata-Pendias, Pendias 2000, Smith et al. 1998], its solubility and availability were reported as being highly dependent on soil properties, and, particularly, on soil pH [Masscheleyn et al. 1991,

#### Streszczenie

Celem badań było określenie wpływu zmian pH na rozpuszczalność arsenu w glebach silnie zanieczyszczonych przez dawny przemysł arsenowy. W doświadczeniu badano trzy różne gleby z obszaru zanieczyszczonego przez procesy przetwórcze rud w Złotym Stoku. Gleby różniły się początkowym odczynem pH, zawartością  $\text{CaCO}_3$  i materii organicznej oraz całkowitą zawartością As. Badano ilości As uwalniane z gleb przy różnych wartościach pH. W tym celu próbki gleby poddano testom ekstrakcji z użyciem różnych dawek HCl i NaOH, w obecności  $0,01 \text{ mol} \cdot \text{dm}^{-3} \text{ CaCl}_2$  jako elektrolitu podstawowego. Rozpuszczalność arsenu w glebach w warunkach obojętnego i lekko kwaśnego odczynu była niewielka, natomiast radykalnie wzrastała zarówno w warunkach odczynu silnie kwaśnego jak i alkalicznego. Dyskusji poddano znaczenie tych efektów dla oceny ryzyka środowiskowego.

Bayard et al. 2006, Al-Abes et al. 2007, Krysiak 2007]. The objective of this study was to determine the impact of pH on the solubility of arsenic in various soils contaminated by the arsenic industry in Złoty Stok.

## 2. MATERIALS AND METHODS

Three soil samples were collected from the surface layer (0–20 cm) of contaminated soils in three representative sites (Fig. 1): a fallow land in the Trująca valley (sample 1: S1), a forested slope in the Złoty Potok valley, strongly transformed by previous mining (sample 2: S2), and from the foreground of tailings landfill (sample 3: S3).

Soil samples were homogenised, air-dried and sieved to 2 mm prior to the experiment. The basic properties of the soils were determined using standard methods applied in soil science [Mocek et al. 2006]. Soil texture was determined by the sedimentary hydrometer method (according to ISO 11277). Soil pH was determined potentiometrically in  $1 \text{ mol} \cdot \text{dm}^{-3} \text{ KCl}$ . Calcium carbonate content was determined using Scheibler's method, based on the measurement of the volume of  $\text{CO}_2$  released from soil treated with HCl. The organic carbon content ( $C_{\text{org}}$ ) was determined using Tiurin's oxidometric method [Mocek et al. 2006]. For the analysis of total arsenic and total iron, the soil samples were digested with concentrated

perchloric acid in digestion tubes capped by reflux condensers. Arsenic concentrations in the digests were measured by inductively coupled plasma atomic emission spectrometry, while flame atomic absorption spectrometry was used to determine iron concentrations in the digests. Two certified reference materials were used for analytical control of soil arsenic determination: WEPAL RSM 2709 (San Joaquin Soil) and RSM 2711 (Montana Soil).

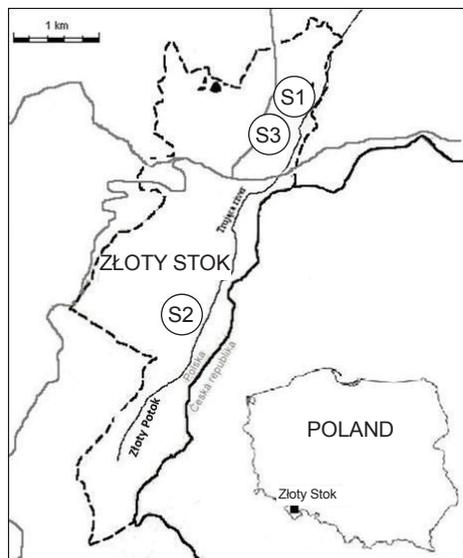


Fig. 1. Location of soil sampling sites.

The effect of pH on arsenic solubility was determined in a series of batch extraction tests (1:5 m/v), in which 5 g of air-dried soil was mixed with various doses of  $1 \text{ mol} \cdot \text{dm}^{-3}$  HCl or  $1 \text{ mol} \cdot \text{dm}^{-3}$  NaOH, diluted in appropriate amounts of distilled water to obtain a volume of 12.5 ml, to which 12.5 ml of  $0.02 \text{ mol} \cdot \text{dm}^{-3}$   $\text{CaCl}_2$  was added so that all the extracts contained  $0.01 \text{ mol} \cdot \text{dm}^{-3}$   $\text{CaCl}_2$  as the background electrolyte. The volumes of acid or base added were in the range  $0.1\text{--}5.0 \text{ cm}^3$ , which corresponded to  $20\text{--}1000 \text{ mmol H}^+$  or  $\text{OH}^-$  per 1 kg of soil. The samples were shaken overhead for 2 hours; thereafter, the suspensions were centrifuged and filtered. The concentrations of arsenic, as well as pH values, in the extracts were determined as described before. All the procedures were carried out in triplicate. For each treatment, the mean values, standard deviations and 95% confidence intervals were calculated. The significance of differences between the means was checked by Duncan's test.

Table 1. Selected properties of soils

Property	S1	S2	S3
Soil textural group	Sandy loam	Sandy loam	Sandy loam
Clay (<0.002 mm) (%)	6	3	3
Silt (0.002–0.05 mm) (%)	40	34	24
pH ( $1 \text{ mol} \cdot \text{dm}^{-3}$ KCl)	5.5	3.7	7.8
$\text{CaCO}_3$ (%)	0	0	2.7
$C_{\text{org}}$ ( $\text{g} \cdot \text{kg}^{-1}$ )	29.5	35.8	0.10
CEC ( $\text{cmol}^+ \cdot \text{kg}^{-1}$ )	13.6	15.8	7.5
Total Fe ( $\text{mg} \cdot \text{kg}^{-1}$ )	35100	47500	33400
Total As ( $\text{mg} \cdot \text{kg}^{-1}$ )	1970	1843	6520

S1, sample 1; S2, sample 2; S3, sample 3.

### 3. RESULTS AND DISCUSSION

#### 3.1 Basic soil properties

All soils used for the experiment had similar textures of sandy loams (Table 1), with low clay content (3–6%). Soil S3 had a neutral reaction and contained 2.7% of calcium carbonate. The other two soil samples were slightly acidic (S1) and strongly acidic (S2). Soil S3 contained only trace amounts of organic matter ( $0.10 \text{ g} \cdot \text{kg}^{-1} C_{\text{org}}$ ), whereas the other two soils were much richer in organic matter. Sample S3 contained extremely high amounts of arsenic ( $6520 \text{ mg} \cdot \text{kg}^{-1}$ ). The concentrations of arsenic in samples S1 and S2 were lower, below  $2000 \text{ mg} \cdot \text{kg}^{-1}$  (Table 1); however, all these values should be considered as very high.

#### 3.2 Soil buffering properties

The final pH of the suspension, after the addition of HCl or NaOH, depended on the buffering properties of the soil. The shapes of the buffering curves (Fig. 2) indicate that sample 3 had considerably high buffering capacity against acidification, due to the high calcium carbonate content. The results for buffering capacity against alkalinisation are much more ambiguous. When considering the slope of the curves in the alkalinisation range, samples S1 and S2 had lower buffering capacities against alkalinisation compared with S3, despite having higher content of organic matter and comparable or higher clay content. However, because of the very high natural pH of soil S3, the amounts of NaOH required to obtain extremely high pH (over 10 or higher) were much lower than those required in the case of soils S1 and S2. The volumes of bases required only to neutralise soils S1 and S2, that is, to adjust their pH values to 7.0, were  $0.09$  and  $0.30 \text{ cm}^3$  of  $1 \text{ mol} \cdot \text{dm}^{-3}$  NaOH per 5 g soil, respectively, that is, 18 and 60 mmol OH per 1 kg soil.

#### 3.3 The influence of changing pH on arsenic solubility in soils

The results of the extraction tests indicated that arsenic solubility in all investigated soils was very low at neutral or slightly acidic pH. The solubility of arsenic increased drastically in strongly acidic conditions (Fig. 3). Intensive arsenic mobilisation from soils due to their acidification started at pH below 3.0. This effect was undoubtedly caused by the dissolution of iron oxides that are the main components that bind to arsenic in soils [Bowell 1994, Bose, Sharma 2002, Krysiak 2007]. Unfortunately, the total concentrations of iron present in the soils, particularly in S1 and S3, did not differ very much, and, therefore, it was not possible to directly

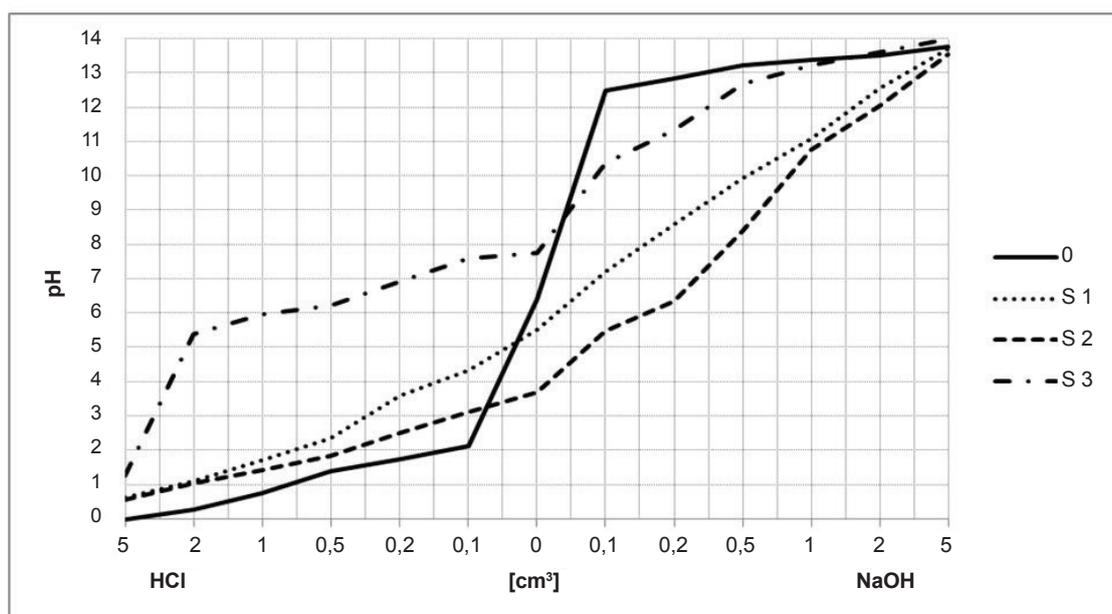


Fig. 2. Soil buffering curves. Changes in pH after the addition of various volumes of  $1 \text{ mol} \cdot \text{dm}^{-3}$  HCl and  $1 \text{ mol} \cdot \text{dm}^{-3}$  NaOH to the suspension containing 5 g of soils. 0 – control curve with distilled water.

assess the buffering effects of iron oxides in relation to the rate of arsenic solubilisation from various soils. The maximum amounts of arsenic released at  $\text{pH} < 1.0$  were as high as over 10% of the total arsenic in soils S1 and S2, and almost 40% of the total arsenic in soil S3. The highest dose of acid ( $5 \text{ cm}^3$  of  $1 \text{ mol} \cdot \text{dm}^{-3}$  HCl per 5 g, i.e.  $1000 \text{ mmol H}^+$  per kg) was necessary to bring down the pH of soil S3 to such low values. The effects of arsenic mobilisation at pH below 2 should be considered as practically and ecologically negligible, as it does not seem likely that soils might become acidified so strongly in natural conditions. However, these results, which may be attributed to the relatively high contributions of iron-bound arsenic in soils, may be important for the assessment of potential ecological risks that might be caused by long-lasting soil flooding [Burton et al. 2008, Krysiak, Karczewska 2011].

The effect of arsenic mobilisation from soils was also observed in alkaline conditions, at pH above 8.0 (Fig. 3). It was particularly well expressed in the case of soils S1 and S2, whereas the amounts of arsenic released in alkaline conditions from soil S3 were considerably lower. The maximum amounts of arsenic released in strongly alkaline conditions exceeded 10% of the total arsenic in soils S1 and S2 and were lower than 2% of total in soil S3. Arsenic release from soils at high pH may be partly attributed to the mechanism of pH-related anion desorption, that is, replacement of arsenite and arsenate ions bound in the sorption complexes by hydroxide ions ( $\text{OH}^-$ ). Arsenate ( $\text{AsV}$ ) adsorption on oxides and clays is maximum at low pH and decreases rapidly at neutral or alkaline pH, that is, at pH ranging from 5 to 9, depending on the soil components: at pH 9 for aluminium oxides, pH 7 for iron oxides and pH 5 for clays. Arsenite ( $\text{AsIII}$ ) adsorption is maximum at pH 8–9 [Bowell 1994, Goldberg 2002, Al-Abes et al., 2007, Krysiak 2007]. The most important mechanism of arsenic release at high pH, however, seems to be that caused by the dissolution of the soil's organic components, including humic substances [Wang, Mulligan 2006, Sapek, Sapek 1996]. This interpretation provides an explanation for the differences between the ratio of arsenic released from soils S1 and S2, which are rich in organic matter, and from the humus-poor soil S3. The effects observed in extremely alkaline conditions are in fact only of theoretical importance, and are not applicable

for the prediction of a risk that might be caused by soil treatment and reclamation. However, considerable amounts of arsenic ( $0.3\text{--}20 \text{ mg} \cdot \text{kg}^{-1}$  (equivalent to 0.1–1% of total arsenic)) were released at a pH of about 9. This fact should be taken into account when planning the remediation of strongly polluted soils in the Trująca valley (represented in this study by sample S1). Soil treatment with active lime ( $\text{CaO}$ ) or with freshly limed sewage sludge may cause a strong local alkalisation of those soils, resulting in the release of arsenic and hence increased environmental risk. However, this statement needs closer investigation. In fact, soil alkalisation due to the addition of NaOH and the resulting release of high amounts of arsenic in the tests carried out in this study were mostly caused by the effect of dispersion and dissolution of humic substances by NaOH. Consequently, soluble organic compounds act as arsenic chelators. Thus, it is possible that soil liming with  $\text{Ca}(\text{OH})_2$ , which basically supplies calcium, will not result in arsenic solubilisation, as calcium humates are hardly soluble in alkaline conditions. This clearly explains the case of sample 3, which is poor in organic matter, where arsenic release was marginal despite the high pH value. Moreover, liming of acidic soils will enhance the formation of oxy-iron compounds, strongly sorbing arsenic. However, a series of experiments with arsenic-rich soils (unpublished data) or tailings [Karczewska et al. 2011], modified with  $\text{Ca}(\text{OH})_2$ -treated sewage sludge, showed a significant increase of arsenic solubility in soils or tailings. The mechanisms of arsenic sorption and desorption from soils at high pH in the presence of organic compounds, particularly low-weight organic fractions and calcium ions, are extremely complex and need further study.

#### 4. CONCLUSIONS

1. Arsenic solubility in polluted soils from Złoty Stok remains very low at neutral or slightly acidic conditions, but it may increase drastically both at very low pH (below 2.0) and at very high pH (above 9.0).
2. The maximal amounts of arsenic that might be released from soils in extremely acidic ( $\text{pH} < 2$ ) or extremely alkaline ( $\text{pH} > 9$ ) conditions depend on the total arsenic concentration

- and on soil properties, and may reach values over 10% of total soil arsenic or even more.
3. Arsenic mobilisation in strongly acidic conditions is probably caused by dissolution of soil iron oxides. Soil carbonates are responsible for the buffering capacity against acidification.
  4. The content of organic matter in the soil appears to be a crucial factor that affects the solubility of arsenic in extremely alkaline conditions. The release of arsenic probably involves a combination of organic matter dissolution, anion desorption and chelation.
  5. The practical and environmental importance of possible arsenic release from soils in extremely acidic or alkaline conditions should be considered to be negligible. However, further studies are needed to examine the risk of arsenic mobilisation at high pH in the presence of organic matter and calcium ions.

## ACKNOWLEDGEMENTS

This study was supported by the Polish Ministry of Science and Higher Education (Project No. N305 395538).

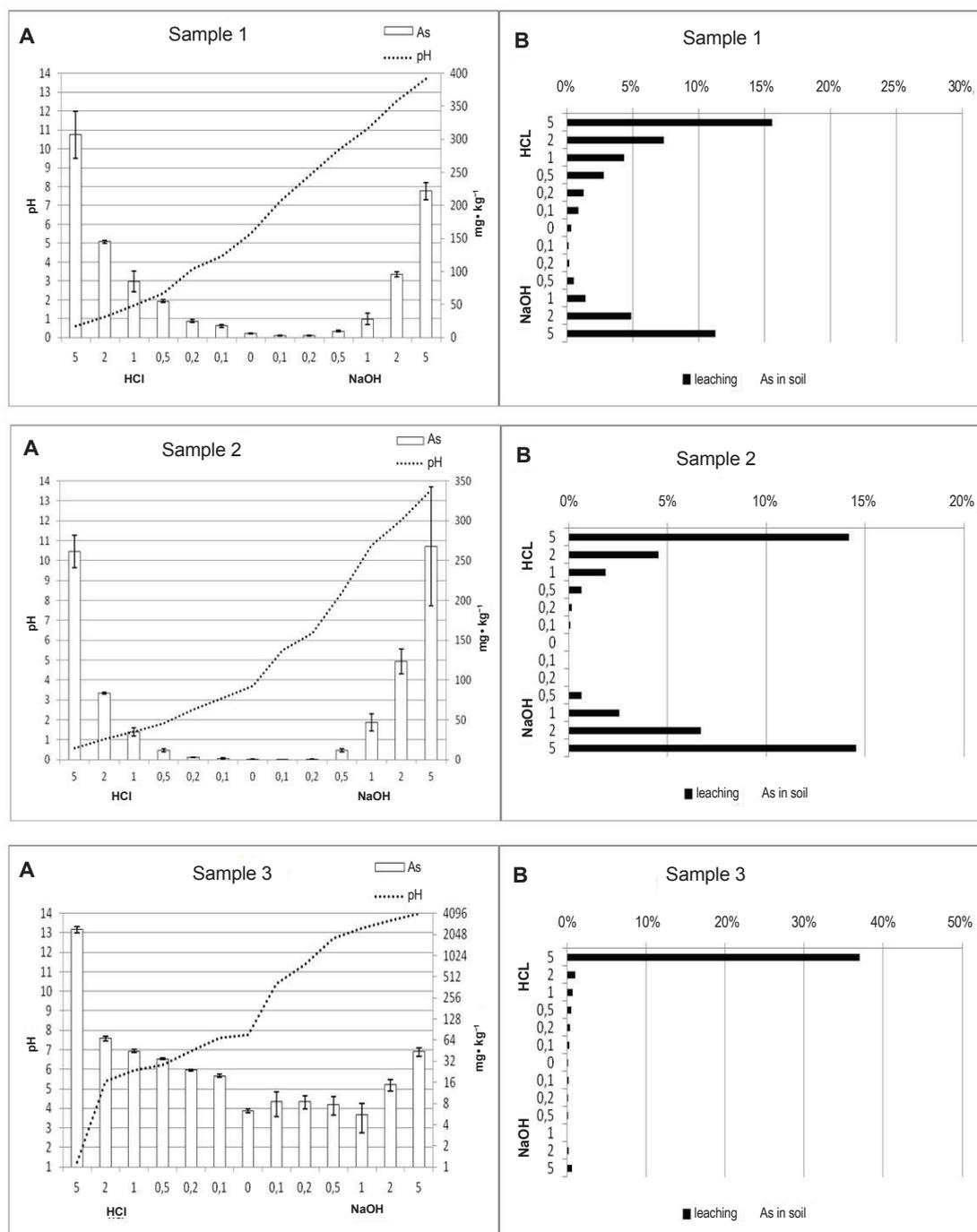


Fig. 3. Changes in pH and arsenic solubility in samples 1, 2 and 3 (S1, S2, S3), as affected by various doses of HCl and NaOH. Doses are expressed in cm<sup>3</sup> of 1 mol·dm<sup>-3</sup> HCl or 1 mol·dm<sup>-3</sup> NaOH per 5 g soil. Arsenic release is illustrated in mg·kg<sup>-1</sup> (A) and as a percentage of the total arsenic in soils (B).

## REFERENCES

- AL-ABES, SR, JAGADEESAN, G, PURANDARE, J, ALLEN D, 2007, Arsenic release from iron rich mineral processing waste: Influence of pH and redox potential. *Chemosphere*, vol. 66, pp. 775–782.
- BAYARD, R, CHATAIN, V, GACHET, C, TROADEC, A, GOURDON, R 2006, Mobilization of arsenic from a mining soil in batch slurry experiments under bio-oxidative conditions. *Water Research* vol. 40, pp. 1240–1248.
- BOSE, P, SHARMA, A 2002, Role of iron in controlling speciation and mobilization of arsenic in subsurface environment. *Water Research*, vol. 36, pp. 4916–4926.
- BOWELL, RJ 1994, Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Applied Geochemistry* 9, vol. 3, pp. 279–286.
- BURTON, ED, BUSH, RT, SULLIVAN, LA, JOHNSTON, SG, HOCKING, RK 2008, Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chemical Geology* 253, vol. 1–2, pp. 64–73.
- DZIEKONSKI, T 1972, *Wydobywanie i metalurgia kruszców na Dolnym Śląsku od XIII w. do połowy XX w.* Mining and processing of metal ores in Lower Silesia from 13<sup>th</sup> century until middle 20<sup>th</sup> century. Ossolineum: Wrocław (in Polish).
- GOLDBERG, S 2002, Competitive adsorption of arsenate and arsenite on oxides and clay minerals. *Soil Science Society of America Journal*, vol. 66, pp. 413–421.
- KABATA-PENDIAS, A, PENDIAS, H, 2000, *Trace Elements in Soils and Plants*, 3<sup>rd</sup> edn. CRC Press, Boca Raton, FL.
- KARCZEWSKA A., GERSZTYN L., GAŁKA B. 2011. Effect of differentially stabilized sewage sludge on the solubility of Cu, Pb and As in tailings produced by copper and arsenic industry. *Zeszyty Problemowe Postępów Nauk Rolniczych* 564: 103-113 (in Polish).
- KARCZEWSKA, A, KRYSIAK, A, MOKRZYCKA, D, JEZIERSKI, P, SZOPKA, K 2013, Arsenic distribution in soils of a former As mining area and processing. *Polish Journal of Environmental Studies* 22, vol. 1, pp. 175–181.
- KRYSIAK, A 2007, Arsenic solubility in soils as affected by pH changes on the area of former gold and arsenic mining at Złoty Stok. *Zeszyty Problemowe Postępów Nauk Rolniczych*, vol. 520, pp. 123–128 (in Polish).
- KRYSIAK, A, KARCZEWSKA, A 2007, Arsenic extractability in soils in the areas of former arsenic mining and smelting, SW Poland. *Science of the Total Environment* 379, vol. 2, pp. 190–200.
- KRYSIAK, A, KARCZEWSKA, A 2011, Effects of soil flooding on arsenic mobility in soils in the area of former gold and arsenic mining in Złoty Stok. *Rocz. Glebozn.*, vol. 62, pp. 240–248 (in Polish).
- ŁUSZCZYKIEWICZ, A, MUSZER, A 1997, Gold in mine wastes form Złoty Stok (SW Poland). *Physicochemical Problems of Mineral Processing*, vol. 31, pp. 197–209 (in Polish).
- MASSCHELEYN, PH, DLAUNE, RD, PATRICK JR, WH 1991, Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environmental Science and Technology*, vol. 25, pp. 1414–1419.
- MOCEK, A, DRZYMAŁA, S, MASZNER, P 2006, *Genesis, analysis and classification of soils*. Wyd AR Poznań (in Polish).
- SAPEK, B, SAPEK, A 1986, The use of 0.5M sodium hydroxide for characterizing humic substances from organic substances. *Rocz. Glebozn.*, vol. 37, pp. 139–147.
- SMITH, E, NAIDU, R, ALSTON, AM 1998, Arsenic in the soil environment: a review. *Advances in Agronomy*, vol. 64, pp. 149–195.
- WANG, S, MULLIGAN, CN 2006, Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environmental Geochemistry and Health* 28, vol. 3, pp. 197–214.