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ORIGINAL PAPER

RECOVERY AND LEACHABILITY OF ANTIMONY FROM MINE- AND SHOOTING RANGE SOILS*

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Abstract

Little is known about the problem of soil contamination with antimony in Poland. Soil samples examined in this study represented two different kinds of Sb-enriched areas: military shooting ranges and historical mining sites in south-western Poland. Total Sb concentrations in soils, determined after fusion with lithium borate, were in the range 17.3-427 mg kg^{-1}. The amounts of Sb recovered as "near total concentrations" were determined after soil digestion with concentrated nitric acid and *aqua regia*. The study confirmed very low recovery of Sb in soils digested with nitric acid (mean 20.9% of total), significantly lower in mine soils (7.6 ±3.4%) than in shooting range soils (34.2±17.5%). *Aqua regia* digestion proved to ensure satisfactory recovery of Sb, circa 90% of its total concentrations, independently of the soil origin. Additionally, toxicity characteristic leaching procedure (TCLP), developed by the US EPA, was applied to determine leachability of Sb from soils. The concentrations of Sb in TCLP leachates: 0.001-0.281 mg L^{-1}, remained at a level considered as ecologically safe, but considerably exceeded the threshold values for underground and drinking water. The amounts of Sb leached from the shooting range soils in the TCLP procedure, expressed as percentage of total Sb, were determined as 6.2±2.0%, i.e. significantly higher compared to mine soils (0.74±0.42%). These results should be considered as a premise for further risk- and remediation-oriented examination of shooting range soils.

Keywords: digestion, nitric acid, aqua regia, TCLP, leachability.

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INTRODUCTION

Soil enrichment with heavy metals has already been well recognized in the areas affected by ongoing ore mining and processing (Medyńska et al. 2009, Jaworska, Dąbkowska-Naskręt 2012, Miśkowiec et al. 2015), as well as in some historical sites such as Złoty Stok or Miedzianka (Karczewska et al. 2006, 2013). There are, however, several other sites of historical ore mining in the Sudetes where the problem of soil contamination with heavy metals, including antimony, is hardly known. Similarly, the knowledge on soil pollution with metals within shooting ranges in Poland remains insufficient, despite the increasing interest in this issue across the world (Evangelou et al. 2012). Shooting range soils are often highly enriched with metals, in particular antimony and lead. Antimony, a potentially toxic metalloid, attracts increasing attention (Filella et al. 2009, Maher, 2009, Wilson et al. 2010, Clemente 2013). It occurs in the environment at trace concentrations, usually in association with arsenic or various metallic elements, sometimes more toxic than Sb itself (Tschan 2009). The median Sb content in European topsoils is 0.60 mg kg^{-1} and the concentrations range from 0.02 to 31.1 mg kg^{-1} (Salminen et al. 2005). The most spectacular cases of soil enrichment with antimony are those found in sites of contemporary or historical mining and processing of antimony or arsenic ores (Clemente 2011, Okkenhaug et al. 2011). Literature reports also high concentrations of antimony in soils in areas affected by mining, processing and metallurgy of other metals, in military and sport shooting ranges (Evangelou et al. 2012, Sanderson et al. 2014), as well as in the environs of landfills and waste incinerators (Filella et al. 2009). The data on antimony concentrations in Polish soils are quite scarse. A general geochemical survey of farmlands in Poland (Pasieczna 2012) revealed Sb concentrations in the range 0.06-1.3 mg kg^{-1}, and did not indicate any soils highly enriched with Sb. The data obtained from a local study on farmland soils affected by industry in southern Poland were in the range 0.34-2.26 mg Sb kg^{-1} (Loska et al. 2004). However, the local occurrence of soil enrichment with antimony may be expected for instance in several sites of Sudety Mountains where stibnite (antimonite) was acquired in the past (Mączka, Stysz 2008) and in the areas of former arsenic ore mining and processing, such as Złoty Stok, Czarnów and Radzimowice (Karczewska et al. 2007, 2013, Krysiak, Karczewska 2007). Soil enrichment with antimony may also be expected in numerous Lower Silesian areas of military and sport shooting ranges, but there are few published data concerning environmental contamination in such sites in Poland (Rauckyte et al. 2009). This work presents preliminary results of a study aimed to identify the sites in south-western Poland where soils are considerably enriched with Sb.

Geochemical interpretation of environmental enrichment with particular elements should based on their total concentrations, which means that either the silicate matrix should be fully dissolved by mixed acid digestion before instrumental analysis, or the techniques capable to analyse solid samples, such as X-ray fluorescence, need to be used. However, the methods most commonly used in environmental chemistry that address legal requirements are those that provide the data on “near total” or “pseudototal” concentrations, based on soil digestion with concentrated nitric acid or *aqua regia*. These methods, believed to provide the data on the maximum concentrations of elements that can be liberated in the natural environment, have been approved as international or national standards: ISO 11466 (*aqua regia*), US EPA 3050 (hot-plate, *aqua regia*), 3051 (microwave, HNO_3), and 3051a (microwave, *aqua regia*), and are commonly used for geochemical surveys (Salminen et al. 2005, Pasieczna 2012). The recovery of Sb, determined in soils by these methods, remains sometimes very low, particularly when nitric acid is used alone (Kimbrough, Wakakuwa 1989, Chen, Ma 1998), mainly because of the formation of insoluble Sb-silicate complexes or other insoluble compounds (Nash et al. 2000). Hewitt and Cragin (1991) pointed out that the more HCl is present in the digestion mixture, the better the recoveries. However, no systematic study has been performed to indicate the factors that determine the amounts of Sb recovered from soils as “near total” concentrations. Low or variable recoveries of total antimony from solid samples may additionally result from the loss of antimony by volatilization, and therefore a closed vessel methods of digestion should be used (Nash et al 2000, Hjortenkrans et al. 2009).

It is obvious that ecological effects of heavy metals and metalloids present in soils depend both on their total concentrations and potential and present solubility or leachability. Numerous investigations have been carried out to examine the relationships between extractability of toxic elements from soils and their bioavailability, toxicity and environmental hazards (McLaughlin et al. 2000, Rao et al. 2008), and various standard methods have been worked out based on those investigations. They include a TCLP procedure (US EPA 1311), prepared originally for waste materials, but often used for contaminated soils (Cao et al. 2003, Sun et al. 2006). In fact, Sb in not on the list of elements with permissible TCLP values, although the knowledge of its leachability may be useful as an indicative parameter of an environmental hazard.

The aim of this study was to compare total and digestion-based, referred to as “near total”, concentrations of Sb, in soil samples highly enriched with Sb, collected from historical mining sites and shooting ranges in south-western Poland. Additionally, the leachability of Sb from those soils, determined according to the TPLC procedure, was examined and discussed.

MATERIAL AND METHODS

Soil samples examined in this study were chosen from a larger collection, gathered under the project: “Antimony speciation in soils of selected areas in Lower Silesia, as related to environmental risk”, which was carried out in south-western Poland. Based on the analysis of the data set, twelve soil samples with the highest content of Sb were selected, which represented two different sources of antimony in soils. Six samples were collected from shooting ranges in a military complex in Wroclaw and six others were obtained from three historical mining sites situated in various ranges of the Central Sudetes: Dębowina in the Bardzkie Mts., Bystrzyca Górna in the Sowie Mts., and Czarnów in the Rudawy Janowickie Mts. (Figure 1)

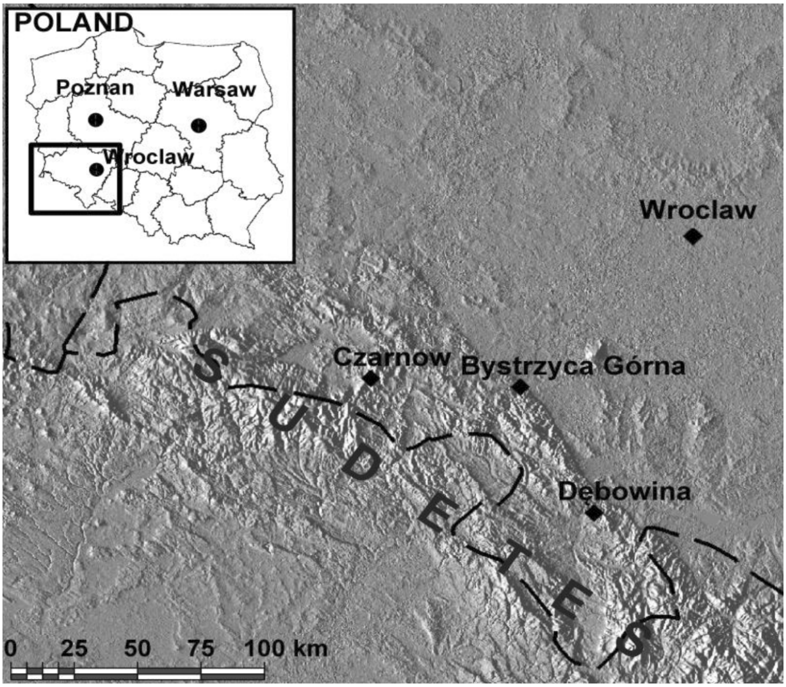

Fig. 1. Location of soil sampling sites

Samples 1 and 2 represented the surface (0-10 cm) layer of soils at firing posts, classified according to the FAO-WRB (2014) as Urbic Technosols (Arenic, Brunic, Skeletic), samples 3 to 5 – the surface (0-10 cm) and subsoil (10-25 cm) layers of earthy stop butts (Protic Arenosols, Technic, Transportic), and sample 6 – the surface layer of soil (Urbic Technosol, Arenic, Skeletic) in front of a wooden bullet protecting screen (first stop butt) – Table 1.

Soil samples 7-12, which represented historical mining sites, were collected both from the native soils and from mine spoils remaining in the vici-

Table 1

Basic properties of soils and total concentrations of Sb and selected elements, determined after fusion with lithium borate, followed by *aqua regia* digestion

Sample	Depth (cm)	pH (1M KCl)	Corg (%)	Clay (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_3 (%)	Sb (mg kg^{-1})	As (mg kg^{-1})	Pb (mg kg^{-1})
Shooting ranges										
1	0-10	6.5	2.6	4	2.5	3.7	86	23.5	5.1	47.9
2	0-10	5.6	1.9	4	1.8	3.6	87	26.8	3.9	47.9
3	0-10	7.5	1.3	6	2.0	2.9	89	67.3	2.3	9350.1
4	0-10	6.5	3.5	4	2.8	3.6	85	30.6	5.0	3637.2
5	10-25	6.8	5.8	3	3.6	5.3	79	90.7	9.5	5860.9
6	0-10	6.1	2.7	4	3.4	4.2	81	116.1	8.1	>10 000
Mining sites										
7	0-10	3.0	13.5	1	5.1	11	48	42.6	615.1	210.4
8	0-10	3.2	17.4	1	3.6	8.1	43	186.3	473.7	401.5
9	10-25	3.3	4.0	7	6.5	13	61	427.1	2839.7	231.2
10	0-10	5.4	1.5	3	5.4	12	53	82.8	62.0	>10 000
11	0-10	4.4	0.5	6	5.1	15	65	81.2	160	6088.4
12	0-10	2.9	2.8	0	20	8.9	45	17.3	>10 000	309.7

nities of adits. Soil samples 7 - 8 were collected from the top soil (0-10 cm) in two sites of Reiche Silber Glück: next to the entrance to an adit, and the sample 9 represented the subsoil (15-25 cm) in one of those sites. The second historical mine of interest, Bystrzyca Górna (Beathe mine), provided the following samples: soil samples 10 and 11 collected from the top layer (0-10 cm) of soils that developed on mine spoils situated close to the upper and middle adits of Beathe mine, on a hill called Widna Góra. Soil sample 12 was collected from the third mining site, Czarnów, from a site apparently changed by the mining activity and waste rock disposal, in a forested area. All the soils from historical mining sites were classified as Spolic Technosols (Dystric, Skeletic), partly with Umbric features FAO-WRB (2014).

Soil material was air-dried and sieved to 2 mm prior to the experiment and analyses. Basic soil properties: grain size distribution, pH, organic carbon and total Fe content, were determined with common methods The content of organic carbon in soils was determined by wet oxidation, according to the Walkley-Black method. Total concentrations of Sb, as well as total concentrations of some other elements: Al, Fe, Si, Pb and As (Table 1), were determined after fusing the samples with lithium borate, which effectively decomposes mineral soil matrices, including those considered as refractory. Lithium borate fusion was followed by *aqua regia* digestion, and the concentrations of Sb and other elements in the digests were determined by ICP-MS.

The analysis was performed by AcmeLabs (Bureau Veritas Commodities Canada Ltd.). “Near total” (“pseudototal”) concentrations of Sb were determined by ICP-MS, after microwave digestion of samples according to two procedures: in concentrated nitric acid and in *aqua regia* (suprapure, Merck). Analytical quality control was performed by the analysis of three certified reference materials provided by Sigma-Aldrich. The toxicity characteristic leaching procedure (TCLP), developed by the US EPA, was used to determine leachability of Sb from soils. Soil samples were shaken overhead for 18 hr with CH_3COOH (m:v 1:20) at pH 4.93±0.05. The results were expressed as the concentrations in leachates (mg L^{-1}), and re-calculated to determine the amounts of Sb leached from soils, mg kg^{-1}.

The percentage of Sb recovered from soils by all the procedures was calculated versus the total soil Sb. The recovery of Sb in two groups of soils: shooting range and mining sites, were compared. Statistical analysis (T-student test for comparison of the means) was carried out using Statistica (StatSoft) software. The differences between the groups of samples were considered statistically significant at $P < 0.05$.

RESULTS AND DISCUSSION

Two sets of soils representing shooting ranges and mining sites, differed in their basic properties. The soils from the shooting ranges represented the textural groups of sands and loamy sands, with the clay content of 3-6%, whereas the soils from the mining sites contained various amounts of skeleton (gravels and stones), and their fine fractions were predominantly classified as sands and sandy loams, containing 0 - 7% of clay (Table 1). The organic carbon content was relatively high in the mining site soils, up to 17%, which should be attributed to the specific conditions typical for forested mountain soils. The content of Corg in the shooting range soils was lower (1.3 - 5.8%). Soil samples 7 - 12, mainly of weathering origin, collected from the former mining areas, contained much higher amounts of iron and aluminum oxides than soils 1 - 6, developed from alluvial and fluvioglacial sands, from which iron compounds were apparently washed out. The two groups of soils differed also significantly in their pH values: neutral in the samples from the shooting ranges and acidic in the samples collected from the mining sites.

The samples analysed in this study were chosen from a larger collection on the basis of their highest total content of antimony. The concentrations of Sb in the shooting range soils were in the range 23.5-116.1 mg kg^{-1} and in the soils collected from historical mining sites ranged from 17.3 to 427.1 mg kg^{-1}. All the soils, regardless of their origin, contained also high, or even extremely high, concentrations of lead, up to over 10 000 mg kg^{-1}. The mining site soils were also very rich in arsenic (62->10 000 mg kg^{-1}), thus confirming the knowledge about the co-occurrence of Sb and As in ores. Arsenic concentrations in the shooting range soils were much lower (2.3-9.5 mg kg^{-1}), although slightly enhanced in comparison to unpolluted areas. Very high total concentrations of Sb and Pb in the soils of the shooting ranges provide more evidence to the well-documented data on soil contamination of these areas. Similar data were achieved elsewhere, e.g. OKKENHAUG et al. (2016) reported even higher concentrations of Sb in Norwegian and Australian shooting ranges, up to 123 and 325 mg kg^{-1}, respectively, and very high concentrations of Pb reaching 12 000 mg kg^{-1}. Proportions between concentrations of both metals varied considerably among the samples. The maximum concentrations of Sb in soils of our historical mining sites, although higher than those in the shooting ranges, remain much lower than the ones reported in the world literature from the surroundings of antimony mines, which sometimes exceed 1% (OKKENHAUG et al. 2011).

The concentrations of Sb in our soils should be assessed as very high compared to the geochemical background. It is not easy, however, to estimate potential environmental effects that may be caused by such enrichment and potential hazards posed to the human health or soil biota, as such effects obviously depend on the solubility and bioavailability of toxic elements rather than on their total concentrations. Moreover, the data on Sb threshold values or standards in soils, if established, differ among the countries. Relatively low "intervention value" of 15 mg kg^{-1}, established in the modified Dutch list (VROM 2000), is much lower than the minimum hazardous concentrations of Sb provided by ecotoxicological studies. OORST et al. (2008) and OORST and SMOLDERS (2009) proved that the lowest concentrations of chronic Sb toxicity to biota were at least 370 mg kg^{-1} or even higher. Various authors pointed out, however, that antimony can pose a threat to ecosystems at much lower concentrations in soils because of its proneness to leaching and potential bioavailability being highly dependent on soil properties and conditions such as redox potential, pH value or the content of carbonates (WILSON et al. 2004, CORNELIS et al. 2012, HOCKMANN et al. 2014).

The "pseudototal" concentrations of antimony in soils, determined after microwave digestion with concentrated HNO_3 and alternatively with *aqua regia*, differed considerably. The mean recovery of Sb after digestion with HNO_3 was very low, i.e. 20.9% of total (Table 2), and did not exceed 12.5% in the mine soils. Such results stay in agreement with previous findings by various authors, who reported very low recovery of Sb, in some cases below 10%, in samples digested with concentrated nitric acid (HEWITT, CRAGIN 1991, CHEN, MA 1998, HJORTENKRANS et al. 2009). Comparison of two soil groups: shooting range versus mining site soils (Figure 2) shows that Sb recovery in the latter group was much lower (mean: 7.6%) than that in the former one (mean: 34.2%), and this difference proved statistically significant. This observation confirms relatively high potential solubility of Sb of missile- and ammunition-related origin and, reversely, low digestibility of Sb minerals present in its ores. The recovery of Sb from all the soils in the digestion tre-

Table 2

Mean recovery of Sb from soils in various procedures, and results of the TCLP test

Sample	*Aqua regia* digestion		Nitric acid digestion		TCLP		
	(mg kg^{-1})	(%) of total	(mg kg^{-1})	(%) of total	leachates (mg L^{-1})	(mg kg^{-1})	(%) of total
1	17.4	74.0	16.4	69.8	0.078	1.55	6.60
2	22.1	82.5	7.97	29.7	0.059	1.18	4.42
3	48.7	72.4	7.73	11.5	0.281	5.62	8.35
4	28.1	91.8	15.4	50.3	0.150	3.01	9.83
5	89.6	98.8	17.03	18.8	0.152	3.04	3.35
6	93.4	80.5	29.1	25.1	0.265	5.29	4.56
7	35.1	82.4	4.68	11.0	0.021	0.43	1.00
8	178.6	95.9	20.1	10.8	0.141	2.83	1.52
9	437.2	102.3*	11.25	2.6	0.180	3.60	0.84
10	80.8	97.6	5.02	6.1	0.001	0.03	0.04
11	79.8	98.3	2.39	2.9	0.011	0.23	0.28
12	16.6	95.9	2.13	12.3	0.007	0.13	0.75

* The asterisk indicates a value with a mean recovery >100%. In this case, the result obtained for one of three replicates was exceptionally high, which may be explained by high heterogeneity of mine waste material and likely presence of Sb-rich mineral grains in some sub-samples.

atment with *aqua regia* was much higher, with the mean value 89.4% of total, and did not differ significantly between the two soil groups of various Sb origin (Figure 2).

The concentrations of Sb in leachates obtained from TCLP tests were in a broad range of 0.001 - 0.281 mg L^{-1}, and the highest results were reported

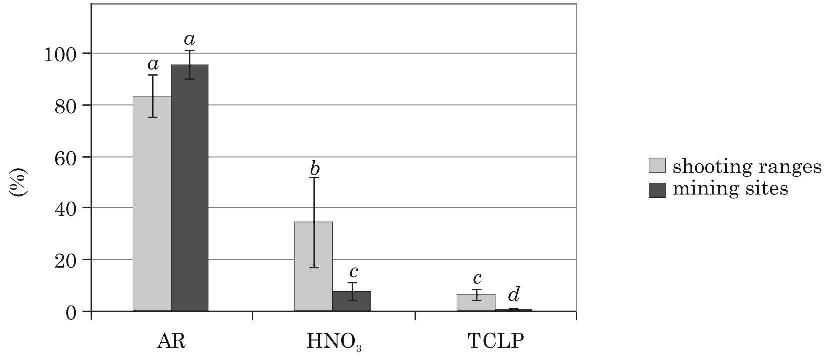

Fig. 2. Mean recovery of Sb in various analytical procedures ($n = 12$): AR – microwave digestion with *aqua regia*, HNO_3 – microwave digestion with concentrated nitric acid, TCLP – leaching according to TCLP procedure. The data expressed as a percentage of total Sb, determined by ICP-MS after fusing the samples with lithium borate, and subsequent digestion with *aqua regia*. Error bar indicates confidence intervals, $p = 0.95$. Same letters stand for the groups that do not differ significantly at $p = 0.95$

for the soils from the military area with the highest total Sb (Table 2). Regrettably, US EPA has not included Sb in the list of contaminants for which permissible concentrations in TCLP leachates are defined, therefore our results cannot be juxtaposed with such values. However, they may be operationally related to the data of underground or drinking water standards or to the results of ecotoxicological tests. Our results of TCLP tests were by 3 orders of values lower than the extreme values (up to 203 mg L^{-1}) reported by Guo et al. (2014) in leachates of slag material that contained 31.6% of Sb. The results of our study were generally slightly lower than those reported by Sanderson et al. (2015) from Australian military ranges, and lower than the concentrations of *ca* 1 mg L^{-1} referred to as those suppressing microbiological activity in natural water (Flynn et al. 2003, Oorts, Smolders 2009). On the other hand, however, the comparison of Sb concentrations in TCLP leachates from this study with permissible Sb concentrations in drinking water established by US EPA (0.006 mg L^{-1}) or by the Directive 98/83/EC for EC countries, including Poland (0.005 mg L^{-1}), may raise some concern. In spite of the fact that only some of antimony leached by TCLP procedure could be actually released into underground water, the amounts of Sb leachable from shooting range soils should be considered as relevant.

The amounts of Sb leached in the TCLP procedure, expressed as a percentage of total Sb, were significantly higher in soils from the shooting ranges than in those collected from the former mining sites, as illustrated by the mean values: of 6.2% and 0.76%, respectively (Figure 2). Relatively high amounts of Sb leached from the shooting range soils indicate that there is a need to examine those soils with particular focus on rationally designed remediation. On the contrary, low amounts of Sb potentially leachable from soils of the historical mining sites, confirm that antimony remains in chemically stable forms, probably bound in primary or secondary minerals, strongly associated with Fe and Al-oxides. Similar results, and very low contributions of the potentially soluble Sb fraction in mine soils, were reported by other authors: Gal et al. (2007), Denys et al. (2008) and Okkenhaug et al. (2011).

CONCLUSIONS

Considerable enrichment with Sb is observed locally in soils of Lower Silesia, in the shooting range soils and in soils of former mining sites. The results of this study confirm very low recovery of Sb determined in soils after digestion with concentrated HNO_3, which was much lower in mine soils than in shooting range soils. *Aqua regia* digestion proved to ensure satisfactory recovery, of circa 90%, independently of Sb origin. Although Sb concentrations in soil leachates obtained in the TCLP procedure remained at a level considered to be safe for soil biota, they considerably exceeded the values of permissible Sb concentrations in underground and drinking water. This fact, as well as a relatively high percentage of Sb leached from the shooting range soils in the TCLP procedure, creates a strong premise for further risk- and remediation-oriented examination of those soils.

REFERENCES

Cao X., Ma L. Chen Q.M., Hardison D.W., Harris W.G. 2003. *Weathering of lead bullets and their environmental effects at outdoor shooting ranges*. J. Environ. Qual., 32(2): 526-534.

Chen M., Ma L.Q. 1998. *Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils*. J. Environ. Qual., 27(6): 1294-1300.

Cornelis G., Van Gerven T., Vandecasteele C. 2012. *Antimony leaching from MSWI bottom ash: Modeling of the effect of pH and carbonation*. Waste Mat., 32: 278-286.

Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

Danys S., Tack K., Caboche J., Delalain P. 2008. *Bioaccessibility, solid phase distribution, and speciation of Sb in soils and in digestive fluids*. Chemosphere, 74: 711-716.

Evangelou M.W., Hockmann K., Pokharel R., Jakob A., Schulin R. 2012. *Accumulation of Sb, Pb, Cu, Zn and Cd by various plants species on two different relocated military shooting range soils*. J. Environ. Manage., 108: 102-107.

FAO-WRB, 2014. *World Reference Base for Soil Resources 2014. World soil resources report No. 106*. Rome.

Feng R., Wei C., Tu S., Ding Y., Wang R., Guo J. 2013. *The uptake and detoxification of antimony by plants: A review*. Environ. Exp. Bot., 96: 28-34.

Filella M., Williams P.A., Belzile N. 2009. *Antimony in the environment: Knowns and unknowns*. Environ. Chem., 6(2): 95-105.

Flynn H.C., Meharg A.A., Bowyer P.K., Paton G.I. 2003. *Antimony bioavailability in mine soils*. Environ Pollut., 124(1): 93-100.

Gal J., Hursthouse A., Cuthbert S. 2007. *Bioavailability of arsenic and antimony in soils from abandoned mining area, Glendinning (SW Scotland)*. J. Environ. Sci. Health Part A, 42: 1263-1274.

Guo X., Wang K., He M., Liu Z., Yang H., Li S. 2014. *Antimony smelting process generating solid wastes and dust: Characterization and leaching behaviors*. J. Environ. Sci., 26(7): 1549-1556.

Hewitt A.D., Cragin J.H. 1991. *Comment on "Acid digestion for sediments, sludges, soils, and solid wastes. A proposed alternative to EPA SW 846 Method 3050"*. Environ. Sci. Technol., 25(5): 985-986.

Hjortenkrans D.S., Mänsson N.S., Bergbäck B.G., Häggerud A.V. 2009. *Problems with Sb analysis of environmentally relevant samples*. Environ. Chem., 6(2): 153-159.

Hockmann K., Lenz M., Tandy S., Nachtegaal M., Janousch M., Schulin R. 2014. *Release of antimony from contaminated soil induced by redox changes*. J. Hazard Mater, 275: 215-221.

Jaworska H., Dąbkowska-Naskręt H. 2012. *Influence of the Głogów copper works on the content of mobile forms of copper and zinc in arable soils*. J. Elem., 17(1): 57-66.

Karczewska A., Krysiak A., Mokrzycka D., Jezierski P., Szopka K., 2013. *Arsenic distribution in soils of a former As mining area and processing*. Pol. J. Environ. Stud., 22(1): 175-181.

Karczewska A., Bogda A., Krysiak A. 2007. *Arsenic in soils in the areas of former mining and mineral processing in Lower Silesia, southwestern Poland*. Trace Metals and other Contaminants in the Environment, 9: 411-440.

Karczewska A., Bogda A., Gałka B., Szulc A., Czwarkiel D., Duszyńska D. 2006. *Natural and anthropogenic soil enrichment in heavy metals in areas of former metallic ore mining in the Sudety Mts*. Pol J Soil Sci, 39: 131-142.

Kimbrough D.E., Wakakuwa J.R. 1989. *Acid digestion for sediments, sludges, soils, and solid wastes. A proposed alternative to EPA SW 846 Method 3050*. Environ. Sci. Technol., 23(7): 898-900.

Krysiak A., Karczewska A. 2007. *Arsenic extractability in soils in the areas of former arsenic mining and smelting, SW Poland*. Sci. Tot. Environ., 379(2): 190-200.

Loska K., Wiechuła D., Korus I. 2004. *Metal contamination of farming soils affected by industry*. Environ Intern., 30(2): 159-165.

Mączka M., Stysz M. 2008. *The mine „Reiche Silber Glück" in Dembowina – the relic of past antimony mining in the Bardzkie Mountains*. In: *History of mining – the part of European cultural heritage*. (eds P.P. Zagożdzon, M. Madziarz), Wyd. P.Wr. Wrocław, 213-226. (in Polish, with English abstract)

Maher W.A. 2009. *Antimony in the environment – the new global puzzle*. Environ. Chem., 6(2): 93-94.

McLaughlin M.J., Zarcinas B.A., Stevens D.P., Cook N. 2000. *Soil testing for heavy metals*. Commun. Soil Sci. Plant Anal., 31(11-14): 1661-1700.

Medyńska A., Kabała C., Chodak T., Jezierski P. 2009. *Concentration of copper, zinc, lead and cadmium in plants cultivated in the surroundings of Żelazny Most copper ore tailings impoundment*. J. Elem., 14(4): 729-736.

Miśkowiec P., Łaptaś A., Zięba K. 2015. *Soil pollution with heavy metals in industrial and agricultural areas: A case study of Olkusz District*. J. Elem., 20(2): 353-362.

Nash M.J., Maskall J.E., Hill S.J. 2000. *Methodologies for determination of antimony in terrestrial environmental samples*. J. Environ. Monit., 2(2): 97-109.

Okkenhaug G., Grasshorn K.-A., Gebhardt, Amstaetter K., Lassen Bue H., Herzel H., Mariussen E., Rossebø Almås Å., Cornelissen G., Breedveld G. D., Rasmussen G., Mulder J. 2016. *Antimony (Sb) and lead (Pb) in contaminated shooting range soils: Sb and Pb mobility and immobilization by iron based sorbents, a field study*. J. Hazard Mater, 307: 336-343.

Okkenhaug G., Zhu Y.G., Luo L., Lei M., Li X., Mulder J. 2011. *Distribution, speciation and availability of antimony (Sb) in soils and terrestrial plants from an active Sb mining area*. Environ. Pollut., 159(10): 2427-2434.

Oorts K., Smolders E. 2009. *Ecological threshold concentrations for antimony in water and soil*. Environ. Chem., 6(2): 116-121.

Oorts K., Smolders E., Degryse F., Buekers J., Gascó G., Cornelis G., Mertens J. 2008. *Solubility and toxicity of antimony trioxide (Sb_2O_3) in soil*. Environ. Sci. Technol., 42(12): 4378-4383.

Pasieczna A. 2012. *Contents of antimony and bismuth in agricultural soils of Poland*. Pol. J. Agron., 10: 21-29.

Rao C.R.M., Sahuquillo A., Sanchez J.L. 2008. *A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials*. Water Air Soil Pollut., 189(1-4), 291-333.

Rauckyte T., Żak S., Pawlak Z., Oloyede A. 2009. *Lead leachability from shooting Range Soils*. Ecol. Chem. Eng. A, 16(4): 419-426.

Salminen R., Plant J. A., Reeder S. 2005. *Geochemical Atlas of Europe*. Part 1. *Background information, methodology and maps*, Espoo: Geological survey of Finland, pp. 526.

Sanderson P., Naidu R., Bolan N. 2014. *Ecotoxicity of chemically stabilised metal (loid)s in shooting range soils*. Ecotox. Environ. Saf., 100: 201-208.

Sanderson P., Naidu R., Bolan N. 2015. *Effectiveness of chemical amendments for stabilisation of lead and antimony in risk-based land management of soils of shooting ranges*. Environ. Sci. Pollut. Res., 22: 8942-8956.

Sun Y., Xie Z., Li J., Xu J., Chen Z., Naidu R. 2006. *Assessment of toxicity of heavy metal contaminated soils by the toxicity characteristic leaching procedure*. Environ. Geochem. Health, 28(1-2): 73-78.

Tschan M., Robinson B. H., Schulin R. 2009. *Antimony in the soil–plant system – a review*. Environ. Chem., 6(2): 106-115.

VROM. 2000. *Circular on target values and intervention values for soil remediation: DBO/1999226863*. Netherlands Government Gazette, 39: 1-51.

Wan X.M., Tandy S., Hockmann K., Schulin R. 2013. *Changes in Sb speciation with waterlogging of shooting range soils and impacts on plant uptake*. Environ. Pollut., 172: 53-60.

Wilson N.J., Craw D., Hunter K. 2004. *Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand*. Environ. Pollut., 129(2): 257-266.

Wilson S.C., Lockwood P.V., Ashley P.M., Tighe M. 2010. *The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review*. Environ. Pollut., 158(5): 1169-1181.