



© 2022. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-ShareAlike 4.0 International Public License (CC BY SA 4.0, <https://creativecommons.org/licenses/by-sa/4.0/legalcode>), which permits use, distribution, and reproduction in any medium, provided that the article is properly cited.

Antimony speciation in soils in areas subjected to industrial anthropopressure

Magdalena Jabłońska-Czapla*, Katarzyna Grygoyć, Marzena Rachwał

Institute of Environmental Engineering, Polish Academy of Sciences, Poland

*Corresponding author's e-mail: magdalena.czapla@ipispan.edu.pl

Keywords: soil, Sb(III), antimony speciation, Sb(V), SbMe₃, industrial anthropopressure

Abstract: The aim of the study was optimization of antimony speciation methodology in soils in areas subjected to industrial anthropopressure from traffic, metallurgy and recycling of electrowaste (e-waste) sources. Antimony speciation was carried out using the hyphenated HPLC-ICP-MS (High-Performance Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometry) technique for the determination of antimony species ((Sb(III), Sb(V), SbMe₃). The extraction and determination of antimony species in soil was optimized and validated, taking into account the matrix effects. The best results in antimony extraction from soils were obtained using a mixture of 100 mM citric acid and 20 mM Na₂EDTA. Ions were successfully separated in 6 minutes on Hamilton PRPX100 column with 0.11 µg/L, 0.16 µg/L, 0.43 µg/L limit of detection for Sb(III), Sb(V), SbMe₃, respectively. The oxidized antimony form (Sb(V)) predominated in the soil samples. The reduced antimony form (Sb(III)) was present only in a few samples, characterized by the lowest pH. The methyl derivative of antimony (SbMe₃) was present in the samples with the lowest redox potential from the area around WEEE (Waste of Electrical and Electronic Equipment) treatment plant. The methodology of extraction and determination of three antimony species in soils was developed, achieving low limits of quantification and very good recovery. The research showed a large variation in antimony content in the soils impacted by type of industrial anthropopressure. The antimony content was the highest in the area of the WEEE treatment plant, indicating this type of industrial activity as a significant source of soil contamination with antimony.

Introduction

Antimony (Sb) is commonly in natural environment. It comes from natural processes and anthropogenic activity. Over the years, human activity has caused a large increase in the antimony concentration in the environment (Nishad and Bhaskarapillai 2021). Antimony has an increasing range of applications, and its emission into environment, which mainly results from anthropogenic activities such as mining, traffic, industrial applications and shooting, continues to increase (He et al. 2019). Antimony is similar to arsenic and bismuth in its geochemical behavior. Sb is one of the main elements of interest of the USEPA (Environmental Protection Agency of the United States 2021) and European Union (Commission of the European Communities Directive 2020). The concentration limit for antimony in Europe is 10 µg/L (Commission of the European Communities Directive 2020), while in the United States it is 6 µg/L. Antimony is on the list of harmful substances after the Basel Convention (Filella et al. 2002). There are two stable oxidation states of Sb in the environment, Sb(III) and Sb(V). Under aerobic conditions, the dominant species is Sb(V) occurring as the anion Sb(OH)₆⁻ in soil solution, while under reducing conditions it is Sb(III) occurring as Sb(OH)₃. The biological role of antimony is not fully understood, but

just like arsenic, it is toxic at a low level, trivalent antimony has about 10 times more toxic properties than pentavalent, hence great interest in speciation analysis of this element. Antimony compounds are readily absorbed by plants, and the easy phytoavailability of this element increases its concentration in plants, especially in contaminated areas. Antimony in animal and human tissues accumulates mainly in the kidneys, hair, liver and thyroid gland (Muhammad Shahid et al. 2019). Earlier studies have shown the effect of mining dump on an increase in antimony concentration in the environment (Jabłońska-Czapla et al. 2014a).

It turns out that the element form, rather than its total content, determines the Sb influence on living organisms. Trivalent antimony compounds accumulate mainly in red blood cells and liver, while pentavalent compounds accumulate in plasma. The symptoms of poisoning caused by antimony are similar to those caused by arsenic. Headaches, weakness, breathing disorders, vomiting, and diarrhea are observed. Antimony and its salts are toxic mainly to the central nervous system and blood. They also cause conjunctivitis and skin inflammation, and damage the heart muscle and liver. Antimony compounds show mutagenic and carcinogenic effects (Muhammad Shahid et al. 2019).

Analyzing elements and their species requires more sophisticated analytical methods and techniques such as high

performance liquid chromatography-inductively coupled plasma-mass spectrometry HPLC-ICP-MS (Jabłońska-Czapla et al. 2014b). Along with the development of analytical techniques allowing for the determination of lower and lower concentrations of analytes, a number of studies have been carried out on the content of antimony and its species in the environment (Ge et al. 2013, Kozak and Niedzielski 2008, Wu et al. 2022, Quiroz et al. 2013, Zhang et al. 2021). However, it is still unclear whether different sources of antimony have an influence on the ionic form in which it occurs in soil. There is a knowledge gap about antimony concentration levels and its species in brownfield soils. Research on the content of antimony species allows us to learn more about the geochemistry of this element (He et al. 2019, Herath et al. 2017, Ji et al. 2018, Jia et al. 2022). For the first time, the study investigated different antimony species (Sb(III), Sb(V), SbMe₃) in soils originating from three sources: traffic, metallurgy and recycling of e-waste, which allowed for the multi-parameter analysis. Additionally, the methodology of determination of antimony species using the HPLC-ICP-MS technique was optimized, taking into account the matrix effects and various conditions. Different methods of antimony extracting from soils were also investigated. The methodology of soil extraction with the best leaching degree was optimized and developed.

Materials and methods

Characteristics of research objects

Three research objects located in the Silesia region in southern Poland were selected for investigation. (1) The area around the town of Piekary Śląskie was chosen because of the closed

dump of slag remaining after Zn and Pb mining and smelting activity lasting for 150 years. This area has been monitored during recent years mainly for heavy metals such as Pb, Zn, Cd, As (Kulka and Gzyl 2008, Rachwał et al. 2017, Warchulski et al. 2005). (2) The Waste Electric and Electronic Equipment (WEEE) plant area located in the southern, heavily forested district of Katowice (Figure 1). The company collects worn out devices and components from electrical and electronic devices. Additionally, the subject of the company's interest is any waste containing precious metals such as gold, silver, palladium, platinum, rhodium, and iridium. Waste is segregated and collected according to the type, stored in containers and big bags on a hard surface. The storage site is covered, which protects the waste from contact with rainfall and prevents the leakage of metal compounds and hazardous substances directly into the soil. So far, no metal/metalloid content studies have been conducted in the area around this plant. (3) The area in the vicinity of the A4 Motorway – the longest motorway in Poland, 672.75 km long, running from west to east through southern Poland. It belongs to the 3rd Pan-European Transport Corridor. Over one hundred thousand cars pass the A4 motorway in Katowice every day. The research area includes a park near the A4 motorway. In addition, the investigation was carried out in an agriculture area not subjected to industrial anthropopressure, near Lublin (Poland) treated as a background. Figure 1 shows the location of the research objects.

Sampling

Topsoil samples (the uppermost 5–6 cm layer) were taken in 6 sites from each investigated area at different distances from



Fig. 1. The location of the research objects

the pollution source. At each distance two subsamples were collected and then mixed into one representative sample. The same procedure was used for background soil samples from areas near Lublin (Poland). In the laboratory, soil samples after standard preparation, i.e. air drying, averaging and sieving through a sieve with a diameter of 0.2 mm, were subjected to chemical analysis.

Measurements of basic physicochemical parameters of soils like pH and Eh (redox potential) were made after the samples were delivered to the laboratory. Eh was performed with the ERPt-111 electrode (Elmetron, Poland), and the pH with the ERH-111 electrode (Elmetron, Poland) (PN-ISO 10390 Soil quality. Determination of pH).

Reagents

High purity reagents were used in all preparation steps including preparation of dilutions, digestion and extraction of samples, cleaning of vials, vessels and containers. The Merck (Darmstadt, Germany) suprapur nitric acid (65%), suprapur hydrofluoric acid (40%) and hydrogen peroxide (30%) EMSURE® purity were used for microwave digestion. For the mobile phase and extraction studies ethylenediaminetetraacetic acid disodium salt dihydrate (Na_2EDTA , $\geq 98\%$), ammonium nitrate (NH_4NO_3 , $\geq 95\%$) were obtained from Sigma-Aldrich (USA), ammonium tartarate dibasic ($(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$, $\geq 99.0\%$) and citric acid (99.5%, Sigma Aldrich, USA) from Fluka (Munich, Germany), and methanol (CH_3OH , 99.8%) from Avantor Performance Materials Poland S.A. (Gliwice, Poland). Commercial solution of Sb ($1.000 \pm 0.003 \text{ mg L}^{-1}$ in 2% HNO_3), periodic table mix 1 for ICP ($10.00 \pm 0.03 \text{ mg L}^{-1}$ in 10% HNO_3), metalloid and non-metal mix for ICP ($100.1 \pm 0.3 \text{ mg L}^{-1}$ in 10% HNO_3 and 0.02% HF) were purchased from Sigma-Aldrich (Buchs, Switzerland). Rhodium ICP standard (10 mg L^{-1} in 0.5 mol L^{-1} HNO_3) was acquired from Merck (Darmstadt, Germany). Standard stock solutions for antimony(III) ($1000 \text{ mg Sb L}^{-1}$), antimony(V) ($1000 \text{ mg Sb L}^{-1}$) and methyl antimony were prepared by dissolving the appropriate amount of antimony(III) oxide (Sb_2O_3 , $\geq 99\%$), potassium hexahydroxoantimonate ($\text{KSb}(\text{OH})_6$, $\geq 99\%$) and trimethylantimony(V) bromide ($\text{Sb}(\text{CH}_3)_3\text{Br}_2$, 98%) purchased from Sigma-Aldrich (USA) in water. All solutions were prepared in ultrapure water obtained from a Milli-Q-Gradient ZMQ5V001 water purification system (Millipore, Corporation, USA).

Determination of total antimony concentration

Microwave digestion method (Anton Paar 3000, Switzerland) was used for digestion of the soil samples. 0.2 g of the soil samples was accurately weighted into a digestion vessels. 5 ml of HNO_3 , 2 ml of H_2O_2 and 3 ml of HF were added and the sample was dissolved with a power of 1400W for 35 minutes. Total antimony content was determined using ICP-MS Elan 6100 DRC-e Perkin Elmer spectrometer. The spectrometer was equipped with a standard ICP quartz torch, cross nebulizer, nickel cones, samples and standards fed by a peristaltic pump. The spectrometer was optimized daily using 1% HNO_3 Elan 6100 Solution by Perkin Elmer. Analyzes were performed using ^{103}Rh as internal standard.

In order to validate the analytical method, the NCS DC 73324 (China National Analysis Center for Iron and Steel)

reference material was digested under the same conditions as other soil samples. In the ICP-MS analysis, the isotope ^{121}Sb was determined, with the limit of detection (LOD) and quantification (LOQ) of 0.01 and 0.03 $\mu\text{g/L}$, respectively. The recovery of antimony from a certified soil sample was 104%. The limit of quantification was assumed to be three times the limit of detection.

Results and discussion

Optimization of antimony extraction of soil samples

The selection of the extractant was initially based on a thorough literature review. In the work (Hammel et al. 2000) various eluents were used to extract marine fauna, the authors obtained the best extraction efficiency using EDTA. In road dust and municipal dust aerosol (Quiroz et al. 2013), antimony was extracted with oxalic acid. However, Zhang et al. (2021) extracted antimony from soil using 100 mM citric acid and 20 mM Na_2EDTA pH = 3.8. The development of extraction methodology involved the use of shaking or ultrasound while using various extractants. Initially, the efficiency of soil extraction for the content of antimony species was checked by shaking 1 g of the Certified Soil Reference Material (NCS DC73324, NCS DC73322) for 2 hours on a shaker (145 rpm) using 10 ml of extractants such as 100 mM citric acid, 20 mM Na_2EDTA , 300 mM ammonium tartrate and water. Soil extraction efficiency was insufficient and it was decided to change the extraction method. Then, an ultrasonic cleaner was used, in which the extraction degree of certified soil samples was tested by checking the effect of the extraction time and the type of extracting agent at a constant temperature (30°C) after 1, 2, 3 and 4 hours of extraction time. After each hour of extraction, the sample was centrifuged by Beckman Coulter Avanti JXN-26 (20,000 rpm, time 8 min, temperature 4°C), the supernatant was decanted and filtered through a PES syringe filter with a pore diameter of 0.22 μm .

Optimization of the antimony species determination using the HPLC-ICP-MS technique

Selection of the chromatographic column

The research carried out in previous years and the analysis of the literature on the separation of antimony species in soil samples allowed for the selection of two anion exchange columns for further research, which allowed for the simultaneous separation of Sb(III), SbMe_3 and Sb(V): Dionex IonPac AS7 and Hamilton PRP-X100. Initially, the separation of antimony species was carried out using a Dionex IonPac AS7 column (200 mm \times 4 mm, particle size 10 μm , Dionex). A necessary condition was a good chromatographic separation of all antimony species extracted from soils with the help of the extracting agent. Separation in the HPLC-ICP-MS system with the use of various extractants was checked. The use of the Dionex IonPac AS7 column did not allow for the proper separation of antimony forms. Therefore, it was decided to test another anion exchange column, which was the Hamilton PRPX100 column (150 mm \times 4.6 mm, particle size 5 μm). Due to the better resolution of the peaks, further studies were carried out using a Hamilton PRP-X100 column. Table 1 presents the optimized parameters of the antimony speciation in soils. Calibration curves were obtained by measuring five times the

standard solutions, which were a mixture of Sb(V), Sb(III) and SbMe₃ standards. Solutions of 1, 5, 10, 25, 50 µg/L were prepared each time from 1 g/L stock standards before analysis. The results of these tests are shown on chromatograms with calibration curves (Fig. 2 and 3).

Eluent selection

The selection of the mobile phase was initially based on a literature review. The methodology used in the work (Ge and Wei, 2013) in the HPLC-ICP-MS system assumed the selection of the Hamilton PRPX100 column, while the eluent in this analysis was a mixture of 200 mM ammonium tartrate and 4% methanol. The authors also studied three antimony ionic forms. A similar column was used by the authors of another

work (Quiroz et al. 2013), but the analysis was carried out in a different combination of hyphenated techniques, namely in the HPLC-HG-AFS system. They investigated two antimony species: Sb(III) and Sb(V). They used two different eluents as the mobile phase, which in the gradient method allowed for the determination of two ionic forms of antimony: 20 mM EDTA, 2 M KHP pH = 4.5 and 50 mM sodium phosphate pH = 8.3. The authors extracted the dust with oxalic acid. In the work (Zhang et al. 2021), the separation of Sb(III) and Sb(V) in the HPLC-ICP-MS system was carried out using a Hamilton PRPX100 column, and the mobile phase was 10 mM Na₂EDTA, 80 mM ammonium nitrate, 25 mM ammonium tartrate, 2% methanol, pH = 4.5. Similarly, De Gregori et al. (2007), used a Hamilton PRPX100 column, but the separation of three antimony forms

Table 1. The basic parameters of the ICP-MS spectrometer

Parameter	Value
RF power [W]	1125
Plasma gas flow [L/min]	15
Nebulizer gas flow [L/min]	0.76–0.82
Auxiliary gas flow [L/min]	1.15–1.16
Nebulizer type	Cross flow
Plasma torch	Quartz
Scanning mode	Peak hopping
Dwell time [ms]	100
Sweeps/reading	20
Number of replicates	3

Table 2. Optimized detection and separation conditions for the antimony speciation in the HPLC-ICP-MS system

Parameter	Value
ICP-MS	
RF power [W]	1125
Plasma gas flow [L/min]	15
Nebulizer gas flow [L/min]	0.73–0.79
Auxiliary gas flow [L/min]	1.15
Nebulizer type	Cross flow
Plasma torch	Quartz
Scanning mode	Peak hopping
HPLC	
Separation column	Hamilton PRP-X100
Temperature [°C]	30
Mobile phase	7.5 mM disodium ethylenediaminetetraacetate dihydrate (Na ₂ EDTA), 60 mM ammonium nitrate (NH ₄ NO ₃), 35 mM ammonium tartrate ((NH ₄) ₂ C ₄ H ₄ O ₆), 2% methanol (CH ₃ OH), pH = 4.5
Elution program	isocratic
Retention time of Sb species [min]	1.35 for Sb(V) 2.43 for SbMe ₃ 4.0 for Sb(III)
Flow rate during analysis [mL/min]	1.9
Flow rate during the rinsing [mL/min]	1.9
Volume of sample [µL]	150

was carried out in the system of combined techniques HPLC-(UV)-HG-AFS, and the mobile phase was used as by Quiroz et al. (2013). Based on these articles, the concentration of mobile phase was optimized to obtain a good separation of the three antimony species: Sb(III), Sb(V), and SbMe₃. Various mobile phases and in different concentrations were tested: phthalic acid, Na₂EDTA, methanol, ammonium tartrate, ammonium nitrate.

The most optimal mobile phase was the mixture of 7.5 mM Na₂EDTA, 60 mM NH₄NO₃, 35 mM ammonium tartrate, 2% methanol, pH = 4.5, which allowed for an isocratic elution, in a short time of 6 minutes, and quantitative

analysis of the three antimony species in soil using HPLC-ICP-MS system. As shown in Figure 2, the selection of such conditions allowed for the separation of three antimony species with retention times: Sb(V) 1.35 min; SbMe₃ 2.43 min; Sb(III) 4.15 min.

The extraction of soils with a mixture of citric acid and Na₂EDTA at pH 3.8 resulted in a shift in antimony species elution and a change in retention times, while maintaining the order of elution, so that the forms finally eluted with time, respectively: Sb(V) 2.67 min; SbMe₃ 3.32 min; Sb(III) 4.61 min. Finally, the three antimony species were separated in soil extracts within 6 minutes.

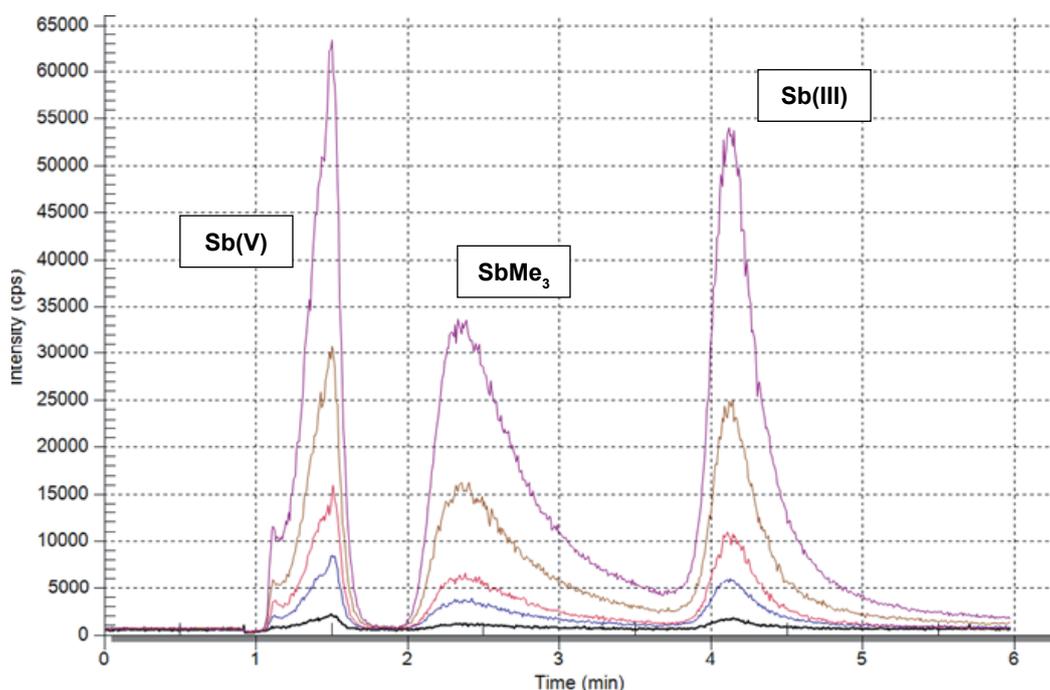


Fig. 2. Superimposed chromatograms for antimony speciation. Calibration curves obtained with measurement of 1 µg/L, 5 µg/L, 10 µg/L, 25 µg/L and 50 µg/L Sb(V), SbMe₃ and Sb(III) standard solution

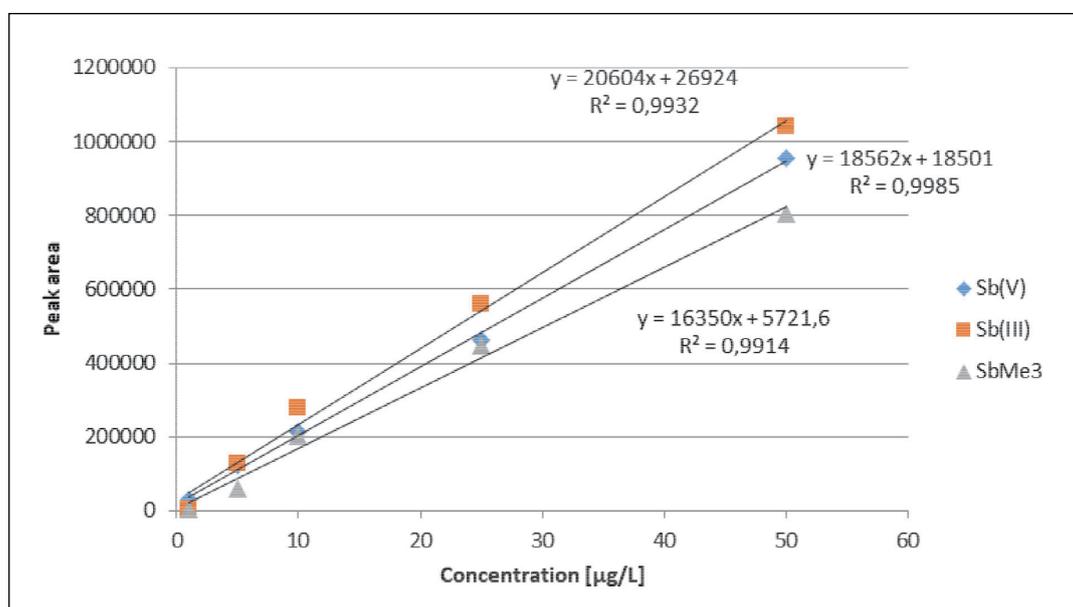


Fig. 3. Calibration curves for the determination of three antimony species using HPLX-ICP-MS system

Quality control of antimony speciation

Due to the lack of certified reference materials containing three antimony species available on the market, the quality control of the antimony speciation was carried out with the use of certified reference material of soil (NCS DC 73324), to which 10 µg/L of the standard mixture containing Sb(V), SbMe₃ and Sb(III) was added. Moreover, the matrix effects were tested by adding the mixture of antimony standards to the real soil sample No. E25.

Table 3 shows the basic validation parameters such as the limits of detection (LOD) and the limits of quantification LOQ. For this purpose, a series of standard solutions Sb(V), Sb(III), SbMe₃ with a concentration of 1 µg/L, 5 µg/L, 10 µg/L, 25 µg/L, 50 µg/L was prepared. The LOD of Sb species and the method repeatability were calculated on the basis of multiple calibration curves. The LOD calculation was based on the following dependence:

$$\text{LOD} = (3.3 \times S) / b$$

where S – standard deviation value, b – linear coefficient of calibration line.

The standard deviation value can be determined as a standard deviation for a free factor of the obtained calibration curve. The measurement uncertainty, understood as Type A uncertainty, was determined with multiple measurements of diversified real samples (n>30). The method recovery was established with the measurement of the real samples to which the known amount of the specific analyte was added (Table 3).

Total antimony content in soil samples

The obtained results indicate a large variation in the degree of soil contamination in the areas impacted by various objects. The results of chemical analyzes of the antimony content show its excessive amounts in all the studied areas. The results of the quantitative analysis of antimony in soils from the areas surrounding the metallurgical slag dump are presented in Table 5. The metallurgical slag dump becomes a source of metals, including antimony, during weathering. The dump material in the form of dust is transported with the wind to the adjacent areas, hence the concentration of antimony in the immediate vicinity of the dump, especially in the prevailing winds direction in this area, is increased. In all the tested soil samples near the dump, the antimony content was high and averaged 11.31 mg/kg. The highest antimony content amounting to 33.35 mg/kg of antimony was found in the soil sample no. P17 collected closest to the heap. In samples collected near the dump, a high content of this element (21.32 mg/kg) was also found in sample P06, lying in the prevailing wind direction, east of the landfill.

For comparison, in the soils treated as the background area, near Lublin, the antimony content did not exceed 1 mg/kg. Unfortunately, Polish legislation does not define the maximum content of antimony in soil (Regulation of the Minister of the Environment 2016). The antimony content in most soils in Poland reaches a maximum of 0.52 mg/kg, and on average in the areas of permanent grasslands, it is 0.17 mg/kg (Pasiczna 2012). Even in the areas enriched with antimony in the region of Pszczyna, the content of this element did not exceed 3 mg/kg (Loska et al. 2004). Hence, the antimony content in the studied areas differs significantly from the amount of antimony naturally occurring in soils of geogenic origin.

According to the world literature, the content of antimony in soils contaminated with anthropogenic activity may be very high. In urban areas subject to pressure from zinc and lead smelters, the Sb content in the topsoil was 2.5–175 mg/kg (Loska et al. 2004), while in areas contaminated by mining activities, the antimony content was in the range of 441–1472 mg/kg (Wei et al. 2015). Analyzing soil samples collected from the vicinity of an Anhui coal mine in China, Qi et al. (2011) it was found that more than 75% of the soil samples showed a significant degree of Sb contamination with an average Sb content of 4 mg/kg.

As in the soils of the area surrounding the heap in Piekary Śląskie, large amounts of antimony were found in the soils around the WEEE processing and collection plant (Table 4). In the soil sample no. E05 collected in the immediate vicinity of this plant, the antimony content was 27.39 mg/kg. Taking into account all the results of the quantitative analysis of antimony in the tested soil samples, it turns out that the WEEE processing and sorting plant has the greatest impact on the content of antimony in the soil. In the vicinity of this plant, the average Sb content in the soil reached 16.3 mg/kg. The increased concentration of antimony in the soil in the areas surrounding the electrowaste treatment plant is related to the material that is stored, dismantled and recovered in this plant, namely wasted printed circuit boards (Barragan et al. 2020). In the WEEE plant there were large amounts of big bags in which used electronic boards were stored, which were then mechanically shredded and components were removed from them in order to recover the stuck and so-called critical elements.

Our results confirm previous studies carried out in e-waste processing areas. Sb pollution was concentrated mainly in the surface and middle layers of soil, where its content was as high as 16.3 and 20.2 mg/kg (Quan et al. 2015). Similar results were also obtained by Bi et al. (2011).

In addition to the high antimony content in the soil, the e-waste treatment and sorting plant is a source of metals such as lead, manganese and cadmium. The lead content in

Table 3. Limits of detection and quantification of antimony species in soil using HPLC-ICP-MS system

Antimony form	Limit of detection LOD [µg/L]	Limit of quantification LOQ [µg/L]	Limit of quantification LOQ [mg/kg]	Relative standard deviation of repeatability [%]	Uncertainty [%]
Sb(V)	0.16	0.48	0.12	2.9	13
SbMe ₃	0.43	1.30	0.33	3.5	12
Sb(III)	0.11	0.33	0.08	3.1	15

the soils surrounding this source was higher than in the soils surrounding the dump in Piekary Śląskie. The lead content in the topsoil was even 1476.21 mg/kg Pb in sample E05 (closest to the WEEE plant). At this collection point, apart from lead, there were also found high contents of Cd, Mn, Co (Jabłońska-Czapla et al. 2022).

The results of the antimony content in soils taken from the areas surrounding the A4 motorway are presented in Table 4. Increased car traffic causes additional environmental pollution, which, after being removed from the road surface by wind or rainfall, accumulate in the soil. Brake pads from cars can pose a serious threat to the environment. High temperatures can develop on the contact surfaces and inside the brake pads during braking. Sb_3S_2 , as a type of solid lubricant, plays an important role in brake performance, but it can react, oxidize or decompose when exposed to high temperatures of up to about 600°C (Martinez and Escheberría 2016).

In the case of the research area near the A4 motorway, the highest antimony content, 9.98 mg/kg Sb, was found in the soil sample no. S07, the average Sb content in this area was 3.88 mg/kg. This is the smallest content compared to other research objects. This means that the impact of road traffic and brake pad wear, i.e. traffic anthropopression in general, has little effect on the surrounding soil in terms of antimony content. Unfortunately, research has shown that car traffic has a large impact on the increase in the content of manganese and zinc in the soil (Jabłońska-Czapla et al. 2022).

Antimony speciation

Extraction

The soil extraction was optimized based on the NCS DC 73324 Certified Reference Material. Initially, the soil was extracted by shaking for 2 hours and the obtained extraction efficiency was: 0.03% for water, 0.17% for 300 mM ammonium tartrate, 0.12% for 20 mM Na_2EDTA 0.12%, and 0.37% for 100 mM citric acid. This efficiency was very low, so ultrasound assisted extraction was applied. Figure 4 shows the results of soil extraction depending on the duration of extraction, using 100 mM citric acid, 20 mM Na_2EDTA , 300 mM ammonium tartrate, 100 mM citric acid with 20 mM Na_2EDTA pH 3.8. Based on the obtained results, the ultrasound-assisted extraction time was selected for 4 hours. The highest extraction efficiency of antimony from soils was obtained with the use of a mixture of 100 mM citric acid with 20 mM Na_2EDTA pH 3.8 and it was 15.4% in total for 4 hours of extraction. Despite the use of ultrasounds for extraction, the yield was still low. However, as reported by other authors (Hammel et al. 2000), the antimony associated with the mobile fraction is a small part extractable from soils. According to the authors, the efficiency of antimony extraction from some types of soil was only 0.06–0.59%. The authors reported that some of the soils studied by them were characterized by low antimony mobility due to poor solubility of antimony sulphides. Moreover, in these soils, more than 90% of antimony was bound to Fe-Mn oxides and organic matter. Sb(V) was sorbed on humic acids of soils, especially at low pH (3.1–5.4), hence the efficiency of antimony extraction may be low.

Table 4 shows the results of the quantitative analysis of antimony in soils after microwave digestion, and the basic physicochemical parameters of soils, such as pH and Eh,

collected from three research objects. Soil pH plays a key role in the mobilization of antimony. The tested soils with low antimony mobility had a pH in the range of 6.3–7.2.

Figure 4 shows the extraction efficiency of the soils of real samples using a mixture of 100 mM citric acid with 20 mM Na_2EDTA at pH 3.8. In soil samples collected from the areas around e-waste treatment plants, the efficiency of antimony extraction was the lowest (21–30%). This correlates with the lowest pH values of these soils (from 3.35 to 3.85). In the case of soils collected from the areas around the dump of metallurgical waste or the areas around the motorway, the extraction efficiency was higher (even 80% in sample no. S6). On average, the extraction efficiency of soils from Piekary Śląskie was 23%, and from Katowice (near the A4 motorway) 48%.

Antimony speciation analysis results

Table 4 presents the results of the quantitative analysis of the antimony speciation in soils.

The oxidized antimony form predominated in the tested soil samples. The reduced antimony form Sb(III) was present only in samples no. P01, S7, and S10. These samples originate from the vicinity of the metallurgical dump and the motorway. In these samples, no methyl antimony derivative was found (below the detection limit). Soil samples collected from the vicinity of the e-waste treatment plant contained large amounts of humic substances, they were forest soils, significantly different from soils from other research areas. Extracts of soil samples from the area around the e-waste treatment plant were dark brown in color and contained, apart from Sb(V), also a methyl antimony derivative. The form of antimony in soils is related to soil conditions such as pH, redox potential and soil methylation processes.

Barker et al. (2020) found that Sb(V) in soils usually constitutes > 99% of water-soluble Sb (up to 5 mg/L), and that in contaminated soils near shooting ranges antimony concentration was even 13.8 g/kg. However, a comparative study using Japanese mine-contaminated soils showed that the dependence of solute concentration against depth or Eh was very different. Wei et al. (2015) found that Sb(V) was a stable oxidation state even under reducing conditions. Thus it confirms that the stable form of antimony in the environment is Sb(V). The authors showed that the dissolved Sb concentrations did not increase with the decrease in Eh.

Diquattro et al. (2021) showed that antimony extracted from soil was present mainly in the oxidized form Sb(V). Only forest soils, strongly acidified, containing large amounts of organic matter, contained a maximum of 34% of Sb(III). Interaction with humic material can have a significant effect on the mobility of antimony. Sb(III) may be more soluble over a wider pH range. This was confirmed in the work on dissolved Sb(III) in water systems (Filella et al. 2002). The relationship of antimony with soil organic matter in environmental samples was confirmed previously (Bagherifam et al. 2021).

The results on the content of antimony species in soil are in agreement with the results obtained by other researchers. The reduced antimony form appeared in soil samples with the lowest pH, as in the case of the sample no. P01 collected in Piekary Śląskie, the pH of which was the lowest among those studied in this area. Similarly, in the case of sample no. S12,

Table 4. Basic physicochemical parameters of studied soil, total antimony concentration after digestion and extraction, extraction efficiency and antimony species concentration after extraction. Abbreviations: P – soil samples collected from the area around the Plekary Śląskie smelting slag heap; S – soil samples collected from the area near the A4 Katowice motorway; E – soil samples collected from the area of the WEEE plant in Katowice)

Sampling point	Total antimony concentration after digestion [mg/kg]	Total antimony concentration after extraction [mg/kg]	Extraction efficiency [%]	Sb(V) [mg/kg]	SbMe ₃ [mg/kg]	Sb(III) [mg/kg]	pH in H ₂ O	pH in KCl	Redox potential (Eh) [mV]
P01	30.47±3.35	9.09±1.0	30	7.58±0.99	<0.32	0.15±0.02	6.5±0.5	6.5±0.5	183±5
P02	7.02±0.77	2.07±0.23	29	1.94±0.25	<0.32	<0.08	6.6±0.5	6.5±0.5	230±5
P06	21.32±2.34	2.90±0.32	14	2.09±0.27	<0.32	<0.08	6.1±0.5	6.0±0.5	293±5
P11	6.15±0.68	2.14±0.24	35	1.59±0.21	<0.32	<0.08	7.1±0.5	7.1±0.5	245±5
P12	12.14±1.33	1.99±0.22	16	1.30±0.17	<0.32	<0.08	6.3±0.5	6.2±0.5	258±5
P17	33.35±3.67	2.12±0.23	6	1.51±0.19	<0.32	<0.08	7.4±0.5	7.3±0.5	229±5
S5	2.13±0.23	0.98±0.11	46	0.93±0.12	<0.32	<0.08	6.9±0.5	6.8±0.5	262±5
S6	6.16±0.68	4.95±0.54	80	4.90±0.64	<0.32	<0.08	6.8±0.5	6.7±0.5	267±5
S7	5.27±0.58	2.48±0.27	47	2.13±0.28	<0.32	0.99±0.15	6.7±0.5	6.6±0.5	262±5
S8	3.00±0.33	1.07±0.12	36	0.85±0.11	<0.32	<0.08	6.8±0.5	6.6±0.5	255±5
S10	9.98±1.10	0.82±0.09	8	0.71±0.09	<0.32	<0.08	6.7±0.5	6.6±0.5	256±5
S12	6.61±0.73	4.56±0.50	69	4.11±0.53	<0.32	0.50±0.08	6.5±0.5	6.5±0.5	254±5
E05	27.39±3.01	5.73±0.63	21	3.01±0.39	0.74±0.09	<0.08	3.8±0.5	3.5±0.5	349±5
E09	14.47±1.59	3.30±0.36	23	1.42±0.18	<0.32	<0.08	3.9±0.5	3.6±0.5	384±5
E10	21.75±2.39	6.05±0.67	28	2.07±0.27	0.88±0.11	<0.08	3.4±0.5	3.1±0.5	425±5
E22	20.78±2.29	4.87±0.54	23	2.78±0.36	0.59±0.07	<0.08	4.3±0.5	3.7±0.5	376±5
E25	17.15±1.89	3.9±0.43	23	1.33±0.17	<0.32	<0.08	3.6±0.5	3.5±0.5	376±5
E27	20.89±2.30	6.25±0.69	30	1.65±0.21	0.89±0.11	<0.08	3.4±0.5	3.1±0.5	399±5
CRM 73324	62.7±6.90	9.5±1.05	15	7.11±0.92	<0.32	0.29±0.04	6.29±0.5	6.24	269±5

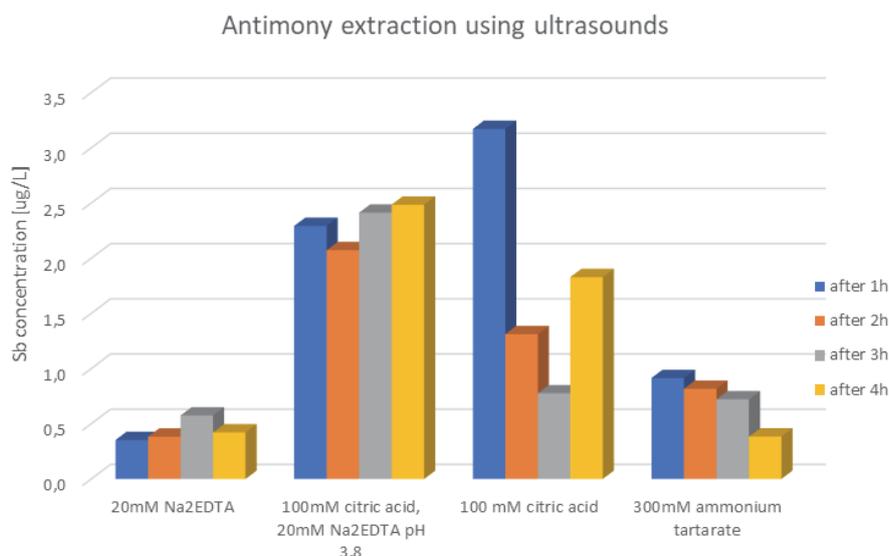


Fig. 4. Optimization of soil extraction using various extractants

taken from the vicinity of the motorway, the pH of this sample was the lowest (6.5) in the motorway area. If the content of antimony species was affected only by soil pH, then large amounts of the reduced antimony form in soil samples from the area around the WEEE plant would be expected. The content of antimony species is also influenced by redox potential. This is confirmed by the high correlation coefficient ($R^2 = 0.78$), which was found between the concentration of Sb(III) and the soil redox potential of soils around the WEEE plant. Moreover, these soils were characterized by the lowest Eh. However, in addition to the appropriate pH, Eh, methylation processes take place in forest soils, hence Sb(V) has been changed by methylation processes into a methyl derivative, namely SbMe₃. According to some researchers (Ji et al. 2018), the low redox potential of soils affects the mobility of the methyl antimony derivative. The research results obtained during the implementation of this study confirmed the influence of Eh on the content of methyl antimony derivative in soils. A dependence was found consisting in an increase in the concentration of methyl antimony derivatives with a decrease in soil redox potential.

Speciation analysis using the hyphenated HPLC-ICP-MS technique allows us to estimate the content of inorganic and organic speciation forms of antimony. Hence, the methodology used allows us to check the content of the forms of this element in various types of soils. The soil collected in the vicinity of the WEEE plant was typical undisturbed forest soil, whereas the soil around the inactive dump was technogenic soil, heavily anthropogenically changed, and the soil from the area surrounding the motorway was taken from the park where soil forming processes are in the initial stage.

Conclusions

The following conclusions can be drawn from the conducted research:

1. A large variation in the content of metals/metalloids in the soils impacted by individual pollution sources was found.

2. The most polluted were soils influenced by emissions from the metallurgical slag dump, then from the e-waste plant, and the lowest level of antimony contamination was found in the soils near the motorway.
3. The antimony content was the highest in the area of the electrical and electronic waste treatment plant, indicating this type of industrial activity as a significant source of soil contamination with antimony.
4. The methodology of extraction and determination of antimony ionic forms in soil samples using hyphenated HPLC-ICP-MS techniques was developed and optimized. The mixture of 7.5 mM Na₂EDTA, 60 mM NH₄NO₃, 35 mM ammonium tartrate, 2% methanol, pH = 4.5 turned out to be the most optimal mobile phase allowing for an isocratic elution, in a short time of 6 minutes.
5. The oxidized antimony form (Sb(V)) predominated in the tested soil samples.
6. The reduced antimony form (Sb(III)) was present only in a few samples, characterized by the lowest pH.
7. The methyl derivative of antimony (SbMe₃) was present in soil samples with the lowest redox potential from the area around the electrical waste treatment plant.
8. The form of antimony in soils is related to the soil conditions such as pH, redox potential and soil methylation processes.

Acknowledgements

The research was carried out in the frame of project which received funding from statutory research of the Institute of Environmental Engineering, Polish Academy of Sciences, for 2020, No. 1A-127/20 and project funding from the National Science Centre of Poland UMO-2018/ 29/B/ST10/01522 (tests of soil samples taken from Lublin).

Conflicts of Interest

The authors declare no conflict of interest.

References

- Bagherifam, S., Brown, T.C., Wijayawardena, A. & Naidu, R. (2021). The influence of different antimony (Sb) compounds and ageing on bioavailability and fractionation of antimony in two dissimilar soils, *Environmental Pollution*, 270, 1, pp. 116270. DOI: 10.1016/j.envpol.2020.116270
- Barker, A.J., Mayhew L.E., Douglas, T.A., Ilgen, A.G. & Trainor T.P. (2020). Lead and antimony speciation associated with the weathering of bullets in a historic shooting range in Alaska, *Chemical Geology*, 553, pp. 119797. DOI: 10.1016/j.chemgeo.2020.119797
- Barragan, J.A., Ponce de León, C., Alemán Castro, J. R., Peregrina-Lucano A., Gómez-Zamudio F. & Larios-Durán, E.R. (2020), Copper and Antimony Recovery from Electronic Waste by Hydrometallurgical and Electrochemical Techniques, *ACS Omega*, 5(21), pp. 12355–12363. DOI: 10.1021/acsomega.0c01100
- Bi, X., Li, Z., Zhuang, X., Han, Z. & Yang, W. (2011). High levels of antimony in dust from e-waste recycling in southeastern China, *Science of the Total Environment*, 409, pp. 5126–5128. DOI: 10.1016/j.scitotenv.2011.08.009
- De Gregori, I., Quiroz, W., Pinochet, H., Pannier, F. & Potin-Gautier, M. (2007). Speciation analysis of antimony in marine biota by HPLC-(UV)-HG-AFS: Extraction procedures and stability of antimony species, *Talanta*, 73, pp. 458–465. DOI: 10.1016/j.talanta.2007.04.015
- Directive (EU) 2020/2184 of the European Parliament and of the council of 16 December 2020 on the quality of water intended for human consumption <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32003L0040&from=EL>
- Diquattro, S., Castidi, P., Ritch, S., Juhasz, L.J., Brunetti, G., Scheckel, K.G., Garau, G. & Lombi, E. (2021). Insights into the fate of antimony (Sb) in contaminated soils: Ageing influence on Sb mobility, bioavailability, bioaccessibility and speciation, *Science of The Total Environment*, 770, pp. 145354. DOI: 10.1016/j.scitotenv.2021.145354
- Filella, M., Belzile, N. & Chen, Y. (2002). Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry, *Earth-Science Reviews*, 59, pp. 265–285. DOI: 10.1002/chin.200323280
- Ge, Z. & Wei, C. (2013). Simultaneous Analysis of SbIII, SbV and TMSb by High Performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry Detection: Application to Antimony Speciation in Soil Samples, *Journal of Chromatographic Science*, 51, pp. 391–399. DOI: 10.1093/chromsci/bms153
- Hammel, W., Debus, R. & Steubing, L. (2000). Mobility of antimony in soil and its availability to plants, *Chemosphere*, 41, pp. 1791–1798. DOI: 10.1016/s0045-6535(00)00037-0
- He, M., Wang, N., Long, X., Zhang, C., Ma, C., Zhong, Q., Wang, A., Wang, Y., Pervaiz, A. & Shan, J. (2019). Antimony speciation in the environment: recent advances in understanding the biogeochemical processes and ecological effects, *Journal of Environmental Sciences*, 75, pp. 14–39. DOI: 10.1016/j.jes.2018.05.023
- Herath, I., Vithanage, M. & Bundschuh, J. (2017). Antimony as a global dilemma: geochemistry, mobility, fate and transport, *Environmental Pollution*, 223, pp. 545–559. DOI: 10.1016/j.envpol.2017.01.057
- Jabłońska-Czapla, M., Rachwał M., Grygoyć K. & Wawer M. (2022). Identification of the antimony sources in soils in areas subject to industrial anthropopressure using geophysical-geochemical methods, *Chemosphere* (under review).
- Jabłońska-Czapla, M., Szopa, S. & Rosik-Dulewska, Cz. (2014a). Impact of mining dump on the accumulation and mobility of metals in the Bytomka River sediments, *Archives of Environmental Protection*, 40, 2, pp. 3–19. DOI: 10.2478/aep-2014-0013
- Jabłońska-Czapla, M., Szopa, S., Grygoyć, K., Łyko, A. & Michalski, R. (2014b). Development and validation of HPLC-ICP-MS method for the determination inorganic Cr, As and Sb speciation forms and its application for Pławniowice reservoir (Poland) water and bottom sediments variability study, *Talanta*, 120, pp. 475–483. DOI: 10.1016/j.talanta.2013.11.092
- Ji, Y., Mestrot, A., Schulin, R. & Tandy, S. (2018). Uptake and transformations of methylated and inorganic antimony in plants, *Frontiers in Plant Science*, 9, 140, pp. 1–10. DOI: 10.3389/fpls.2018.00140
- Jia, X., Ma L., Liu, J., Liu, P., Yu, L., Zhou, J., Li, W., Zhou W. & Dong, Z. (2022). Reduction of antimony mobility from Sb-rich smelting slag by *Shewanella oneidensis*: Integrated biosorption and precipitation, *Journal of Hazardous Materials*, 426, pp.127385. DOI: 10.1016/j.jhazmat.2021.127385
- Kozak, L. & Niedzielski, P. (2008). Determination of inorganic antimony species by hyphenated technique high performance liquid chromatography with hydride generation atomic absorption spectrometry detection, *Archives of Environmental Protection*, 34, 4, pp. 71–79.
- Kulka, E. & Gzyl, J. (2008). Assessment of lead and cadmium soil contamination in the vicinity of a non-ferrous metal smelter, *Archives of Environmental Protection*, 34, pp. 105–115.
- Loska, K., Wierchuła, D. & Korus, I. (2004). Antimony concentration in farming soil of southern Poland, *Bulletin of Environmental Contamination and Toxicology*, 72, pp. 858–865. DOI: 10.1007/S00128-004-0323-2
- Martinez, A.M. & Escheberria, J. (2016). Towards a better understanding of the reaction between metal powders and the solid lubricant Sb₂S₃ in a low-metallic brake pad at high temperature, *Wear*, 348–349, pp. 27–42. DOI: 10.1016/j.wear.2015.11.014
- Muhammad Shahid, N., Khalid, S., Dumat, C., Pierart, A. & Niazi N.K. (2019). Biogeochemistry of antimony in soil-plant system: Ecotoxicology and human health, *Applied Geochemistry*, 106, pp. 45–59. DOI: 10.1016/j.apgeochem.2019.04.006
- Nishad, P.A. & Bhaskarapillai, A. (2021). Antimony, a pollutant of emerging concern: A review on industrial sources and remediation technologies, *Chemosphere*, 277, pp. 130–252. DOI: 10.1016/j.chemosphere.2021.130252
- Pasieczna, A. (2012). The content of antimony and bismuth in the soils of agricultural lands in Poland, *Polish Journal of Agronomy*, 10, pp. 21–29. (in Polish)
- Qi, C., Liu, G., Kang, Y., Lam, P.K.S. & Chou, C. (2011). Assessment and distribution of antimony in soils around three coal mines, Anhui China, *Journal of the Air & Waste Management Association*, 61, pp. 850–857. DOI: 10.3155/1047-3289.61.8.850
- Quan, S.X., Yan, B., Yang, F., Li, N., Xiao, X.M. & Fu, J.M. (2015). Spatial distribution of heavy metal contamination in soils near a primitive e-waste recycling site, *Environmental Science and Pollution Research*, 22, pp. 1290–1298. DOI: 10.1007/s11356-014-3420-8
- Quiroz, W., Cortes, M., Astudillo, F., Bravo, M., Cereceda, F., Vidal, V. & Lobos, M.G. (2013). Antimony speciation in road dust and urban particulate matter in Valparaiso, Chile: Analytical and environmental considerations, *Microchemical Journal*, 10, pp. 266–272. DOI: 10.1016/j.microc.2013.04.006
- Rachwał, M., Wawer, M., Magiera T. & Steinnes, E. (2017). Integration of soil magnetometry and geochemistry for assessment of human health risk from metallurgical slag dumps. *Environmental Science and Pollution Research*, 24, pp. 26410–26423. DOI: 10.1007/s11356-017-0218-5
- Regulation of the Minister of the Environment of September 1, 2016 on the method of assessing pollution of the earth's surface,

- Journal of Laws No. 1395 (in Polish) <https://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=wdu20160001395>
- Warchulski, R., Gawęda, A., Kądziołka-Gaweł, M. & Szopa, K. (2015). Composition and element mobilization in pyrometallurgical slags from the Orzeł Biały smelting plant in the Bytom Piekary Śląskie area, Poland. *Mineralogical Magazine*, 79, 2, pp. 459–483. DOI: 10.1180/minmag.2015.079.2.21
- Wei, C., Ge, Z., Chu, W. & Feng, R. (2015). Speciation of antimony and arsenic in the soils and plants in an old antimony mine, *Environmental and Experimental Botany*, 109, pp. 31–39. DOI: 10.1016/j.envexpbot.2014.08.002
- Wu, T., Cui, X., Ata-Ul-Karim, S.T., Cui, P., Liu, C., Fan, T., Sun, Q., Gong, H., Zhou, D. & Wang Y. (2022). The impact of alternate wetting and drying and continuous flooding on antimony speciation and uptake in a soil-rice system. *Chemosphere*, 297, pp. 134147. DOI: 10.1016/j.chemosphere.2022.134147
- Zhang, Z., Lu, Y., Li, H., Zhang, N., Cao, J., Qui, B. & Yang, Z. (2021). Simultaneous Separation of Sb(III) and Sb(V) by High Performance Liquid Chromatography (HPLC) – Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) with Application to Plants, Soils and Sediments, *Analytical Letters*, 54, 6, pp. 919–934. DOI: 10.1080/00032719.2020.1788049

Specjacja antymonu w glebach na obszarach podlegających antropopresji przemysłowej

Streszczenie: Celem pracy była optymalizacja metodyki specjacji antymonu w glebach na obszarach poddanych antropopresji przemysłowej z transportu, hutnictwa i recyklingu elektroodpadów. Specjację antymonu przeprowadzono za pomocą techniki łączonej wysokosprawnej chromatografii cieczowej z spektrometrią mas ze wzbudzeniem w plazmie indukcyjnie sprzężonej (HPLC-ICP-MS) do oznaczania form specjacyjnych antymonu ((Sb(III), Sb(V), SbMe₃)). Zoptymalizowano i zwalidowano ekstrakcję oraz oznaczanie form specjacyjnych antymonu biorąc pod uwagę efekty matrycowe. Najlepsze wyniki w ekstrakcji antymonu z gleb uzyskano stosując mieszaninę 100 mM kwasu cytrynowego i 20 mM Na₂EDTA. Jony zostały rozdzielone w ciągu 6 minut na kolumnie Hamilton PRPX100 z granicami wykrywalności odpowiednio 0,11 µg/L, 0,16 µg/L, 0,43 µg/L dla odpowiednio Sb(III), Sb(V), SbMe₃. W próbkach gleb dominowała utleniona forma antymonu (Sb(V)). Zredukowana forma antymonu (Sb(III)) była obecna tylko w kilku próbkach, charakteryzujących się najniższym pH. Metylowa pochodna antymonu (SbMe₃) była obecna w próbkach o najniższym potencjale redoks z terenu wokół zakładu przetwarzania zużytego sprzętu elektrycznego i elektronicznego odpadów (ZSEiE). Opracowano metodykę ekstrakcji i oznaczania trzech form antymonu w glebach, osiągając niskie granice oznaczalności i bardzo dobry odzysk. Badania wykazały duże zróżnicowanie zawartości antymonu w glebach w zależności od typu antropopresji przemysłowej. Zawartość antymonu była najwyższa na terenie wokół zakładu przetwarzania ZSEiE, co wskazuje na tego typu działalność przemysłową jako istotne źródło zanieczyszczenia gleby antymonem.