

Original Research

# Determination of Inorganic Speciation Forms of Arsenic, Antimony and Selenium in Water from a Grate Ashes Dumping Ground as an Element of Hydrogeochemical Monitoring of Pollution Spread

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## Abstract

This paper presents results of the determination of the total concentration of arsenic, antimony and selenium and their inorganic speciation forms in water samples from grate ashes dumping grounds. Determined concentrations of elements were up to 128.8 ng/mL for arsenic, 153.7 ng/mL for antimony and 52.9 ng/mL for selenium, at the detection limits of 0.16 ng/mL for As, 0.18 ng/mL for Sb and 0.15 ng/mL for Se. Water from some study sites was characterized by very high concentrations of determined elements, which were used to follow their migration. Leakage of dangerous micro-pollutants to ground water was stated. Based on results of speciation analysis the vertical migration of pollutants through unsaturated zone was found.

**Keywords:** arsenic, antimony, selenium, speciation, ground water, migration

## Introduction

The still growing emission of pollutants to hydrogeological environments creates threats to ground water resources. Degradation of ground water quality is caused not only by geochemical factors but also by anthropogenic factors, which are getting stronger every day. Increase of concentrations of chemical substances in hydrogeological environments is a reason to follow pollutants' expansion in the area of their emission. Following pollutants migration in ground water and observing concentration of microelements (at the level of  $\mu\text{g/mL}$ ) or even concentration of heavy metals is often very difficult to interpret obtained results. So it seems intentional to follow migration of pol-

lutants to ground water and interpret results of analysis using trace elements occurring in natural environment at the level of ng/mL i.e. arsenic, antimony and selenium.

In a geological environment arsenic usually appears as arsenate (i.e. scorodite,  $\text{Fe}^{3+}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$ ). Other mineral forms are: sulphurs (i.e. commonly met arsenopyrite,  $\text{FeAsS}$ ) and arsenide (for example trippkeite,  $\text{CuAs}_2\text{O}_4$ ). All compounds and minerals of arsenic are easily soluble in water but argillaceous mineral: iron and alumina hydroxides and organic substances can limit their migration. Besides, some minerals like mica or goethite show inclinations to bind arsenic and may influence its placing in hydrogeological environment. In ground water it usually occurs in the form of different anions:  $\text{AsO}_4^{3-}$ ,  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{AsO}_2^-$  or as inert particles of  $\text{H}_2\text{AsO}_3$ . These forms remain in proper conditions of pH and Eh

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in state of thermodynamical balance. The concentration of selenium in ground water is usually connected with areas of mineral ledges or local accumulations of minerals containing arsenic as well as areas of pollutant inflow. Depending on geological surroundings, ground water can contain from one-tenth of nanograms up to micrograms per milliliter, which is similar to surface water. The main arsenic species met in water samples are arsenates (III) and (V), methyl (monomethylarsenic acid MMAA) and dimethyloarsenate (dimethylarsenic acid DMAA). A small amount of arsenic can have a stimulating influence on humans and animals and higher amounts are toxic. The toxicity of arsenic depends on the element's form in which it occurs and on property of particular organism. Toxicity of arsenic decreases in the sequence: As(III)>As(V)>MMAA>DMAA>other arsenic organic compounds (i.e. arsenobetaine) [1-5].

Antimony is one of the very mobile elements and is widespread in the environment. The concentration of antimony is low and does not overcome  $1\mu\text{g/g}$ , except for argillaceous deposits, where its content ranges up to  $2\mu\text{g/g}$ . Antimony occurs also within sulfur bed, mostly in the form of antimonite ( $\text{Sb}_2\text{S}_3$ ). The great chemical similarity of antimony to arsenic allows us to think of similar behavior in natural water, especially when distribution and speciation are discussed. Antimony migrates to ground water with humic acids as complexes. Depending on the geological environment and its potential contamination, water can contain up to some  $\text{ng/mL}$  of antimony. Some mineral water and especially hot fountains can contain up to a few  $\mu\text{g/mL}$  of antimony. In the case of water contamination (communal sludge), the concentration of antimony is increasing to a few nanograms and can be a monitoring parameter like arsenic and selenium. Surface water contains usually less than  $1\text{ ng/mL}$ , the same in the case of rainwater (in the built-up area up to some  $\text{ng/mL}$ ). In the environment antimony is present in forms of antimonite (III) and (V), methyl derivate: monomethyloantimonic acid (MMSbA) and dimethyloantimonic acid (DMSbA). Antimony and its compounds, especially at third oxidation degree are toxic. Toxicity of Sb (III) is ten times higher than of Sb (V) – toxicity increases with decrease of oxidation state [1].

Because of multioxidation states of selenium and its complex geochemical properties it behaves variably in environment. It forms different mobile species which are adsorbed by iron oxides, argillaceous mineral and organic compounds. Selenium concentration in magmatic rocks and in sedimentary rocks is very seldom higher than  $0.5\mu\text{g/g}$ . It is a part of 50 minerals, which are often bounded, with beds of metal sulphides (i.e.  $\text{CuSe}$ -klockmannite,  $\text{FeSe}_2$ -ferroselit,  $\text{PbSe}$ -clausthalite). Higher concentrations of selenium can be met in deposits rich in iron and organic compounds. Depending on the geological environment and eventual contamination, water can contain from hundreds to thousands of  $\text{ng/mL}$  of selenium. Selenium (also arsenic and antimony) can get to ground water by waste leaching, especially from ashes dumped on the ground or from

industrial areas. In the environment selenium occurs as: selenites, seleniate (IV) and (VI), derivatives di- (volatile dimethylo selenium - DMSe and dimethylo diselenium - DMDSe) and trimethyl (trimethylo selenium - TMSe), selenoamino acids (selenocystein - SeC and selenometionin - SeM), and in many organic compounds. Selenium excess as well as its deficit is harmful (selenium compounds are necessary for metabolism). A small range between desirable and toxic concentrations is really important from an environmental monitoring point of view[1-3].

This paper shows results of determination of total concentration and results of speciation analysis of arsenic, antimony and selenium in samples of ground water and surface water from the area of the coal power-plant ashes dumping ground. The aim of this research was to follow migration of pollutants to ground water on a base of determination of metalloids. Not only determinations of total concentrations were done, but also their speciation forms were determined because determination of total concentration of microelements does not show processes in which elements take part in the environment. It does not inform about real toxicity, bioavailability, biomagnification, accumulation or the place in which ground water is supplied. Owing to separation of speciation forms we obtain more detailed information about role and behavior of elements in environment and it is easier to interpret obtained results.

## Materials and Methods

### Equipment and Reagents

To determine water microelements (As, Sb and Se) a double beam spectrometer SpectrAA 20 Plus manufactured by Varian was used. HCL lamps manufactured by Varian were used during analysis. During preparation of samples a Merck MW 500 microwave oven was used. The conditions applied for determinations and parameters of the analytical method are shown in Table 1. Hydride generation was performed in the unit VGA-77 combined with electro thermally heated quartz cuvette ETC-60. Argon was used as a carrier gas.

Precision of results was checked by exterminating reference material for determinations made by using atomic absorption spectrometry (AAS) combined with the hydride generation and electro-thermally heated atomizer – Table 2.

During analysis only reagents of analytical purity (*analytical grade*) were used, water was redistilled and purified by Milli-Q (Millipore). The basic solution of the standards at a concentration of  $1\text{ mg/mL}$  was made from a trade standard to AAS analysis (Promochem). The solutions of  $1\mu\text{g/mL}$  concentration, persistent for three months were prepared by dissolving and stored in polyethylene flasks (Nalgene). Lower concentrations of standards were made on the day of determination. All standard solutions were stabilized by hydrochloric acid ( $\rho=1.19\text{ g/mL}$ ) at  $1\text{ mL}$  per liter. Sodium borohydride solutions were prepared by dissolving sodium borohydride in 1% solution of sodium hydroxide. All solutions were

Table 1. The conditions of determination and parameters of the analytical method for determination of arsenic, antimony and selenium by atomic absorption spectrometry with hydride generation.

		As	Sb	Se
Wavelength / Slit	nm	193.7 / 0.5	217.6 / 0.2	196.0 / 1
Lamp current	mA	10	10	10
Detection limit ( $3\sigma$ )	ng/mL	(0.14*) 0.16	(0.17*) 0.18	0.15
Sensitivity	ng/mL	0.08	0.11	0.08
Repeatability (for 10 ng/mL)	%	1.1	0.9	1.2

\*for determination As (III) or Sb(III)

Table 2. Determination results for arsenic, antimony and selenium in reference material SLRS-3.

		Certificated value ng/mL	Determined value ng/mL	Recovery %
As	SLRS-3	$0.72 \pm 0.05$	$0.70 \pm 0.07$	$97.2 \pm 9.7$
Sb	SLRS-3	$0.12 \pm 0.01$	$0.14 \pm 0.02$	$116.6^* \pm 16.7$
Se	SLRS-3	Non certificated	< 0.15	-

\*on detection limit

lucid and did not need to be filtered. They were made on the day of determination. In hydrides generation solutions of the hydrochloric acid ( $\rho=1.19$  g/mL) citric acid were used.

### Application of Speciation Analysis

Determination was made using atomic absorption spectrometry (AAS) combined with the generation of hydrides (HGAAS). An application of analysis was prepared and optimization for determinations of environmental speciation samples was made [6].

Determination was performed due to the above scheme:

1. Direct determination was performed with hydride generation in the environment of citric acid for As (III) and Sb (III) and for Se (IV) in the environment of HCl acid.
2. Determination of {As (III) + As (V)}, {Sb (III) + Sb (V)}, {Se (IV) + Se (VI)} from one sample reduced by hydrochloric acid (1% v/v) in microwave mineralizer (530 W, 5 min time).
3. Calculations of elements content at V and VI oxidation state from a result of subtraction of results from points 1 and 2.

### Samples

Samples to be determine were collected from piezometers (piezometers A-F) located around an ash dump and a river flowing near the dump ground (sample number 1). Moreover, samples obtained from water protecting ashes from expansion were collected (sample number 2). Samples intended for research were collected during four years. In the fourth year of research,

apart from the determination of total concentrations of microelements, determination of inorganic speciation forms of arsenic, antimony and selenium was carried out.

### Results and Discussion

The aim of the research was to observe pollutants migration from ash dump ground to groundwater. Results of determination of concentrations of arsenic, antimony and selenium are shown in Table 3.

Water directly adjoined to the warehoused ashes contains the highest concentrations of examined elements (sample number 2). This water is placed there to avoid distribution of flying ashes outside of the dump ground. High concentrations of arsenic, antimony and selenium determined in piezometer E indicate pollutants' migration from

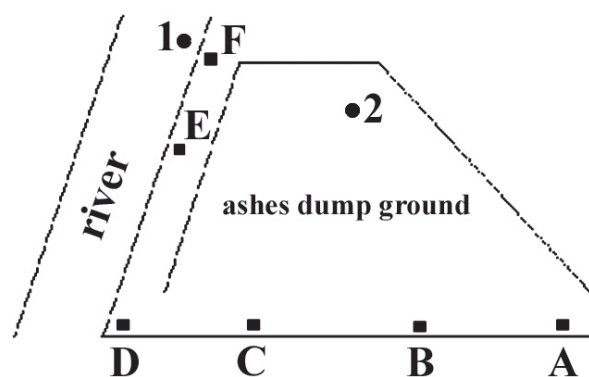


Fig. 1. Schematic plan of ashes dump ground with sampling sites (A-F –piezometers' localization; 1 and 2 –sites of surface water sampling).

Table 3. Total concentrations of As, Sb and Se in water from ash dump ground area (ng/mL).

Sample	As				Sb				Se			
	1 year	2 year	3 year	4 year	1 year	2 year	3 year	4 year	1 year	2 year	3 year	4 year
	ng/mL											
1	3.10	4.25	2.05	1.50	1.05	1.10	0.60	0.60	<0.15	0.20	0.25	<0.15
2	128.8	86.7	127.1	94.9	4.70	5.55	5.35	5.60	18.5	39.1	53.7	52.9
A	0.95	0.85	1.05	0.75	0.60	0.65	0.60	0.55	<0.15	0.25	0.45	0.40
B	0.85	1.60	0.80	0.50	0.95	0.75	0.45	0.40	<0.15	0.15	0.25	0.20
C	1.65	4.60	1.00	0.60	1.15	0.80	0.45	0.50	<0.15	0.15	0.25	0.20
D	1.10	2.15	1.15	1.00	0.55	0.75	0.45	0.50	0.20	0.45	0.85	0.65
E	32.0	52.5	49.1	39.3	1.50	2.65	2.95	2.60	1.75	3.80	6.25	6.00
F	0.85	0.80	1.05	1.00	0.45	1.65	0.55	0.60	<0.15	<0.15	0.35	0.25

the ashes dump ground. The level of concentration of arsenic and antimony in water from this piezometer increased in second and third year of research and then went down to the similar level like at the beginning of research period. The concentration of selenium in water from piezometer E was increasing during the research. It was correlated with the increase of Se concentration in water covering flying ashes (sample number 2). In other piezometers concentration of arsenic stayed at the same level during four years long research when concentration of antimony showed downward tendency after reaching maximum in the second year of research. In the case of selenium the highest concentration was found in the third year of research. Substantial element of research is statement of high level of determined elements in one of a control piezometers (piezometer E), which indicates leakage of pollutants from the ash dump to ground water and their migration in the ground water flow towards the river.

In the last year of research additional speciation determination of arsenic, antimony and selenium was performed. Inorganic species concentrations ratios: As(V)/As(III), Sb(V)/Sb(III) and Se(IV)/Se(VI) were taken into consideration (Table 4).

In water examined dominating inorganic form for selenium was an element at the lower oxidation level (Se(IV)). This tendency is independent from the level of total concentration of elements determined in the sample. In the case of speciation determination of arsenic, antimony and selenium the prevailing form was an element at the higher oxidation state (As(V) i Sb(V)). On the other hand in the case of water sample from piezometer E majority of arsenic and antimony speciation forms was stated: concentration of As(V) was 64.5 times higher than As(III), concentration of Sb(V) was 12 times higher than Sb(III). Similar interdependence was found for speciation determination of sample obtained from water covering ashes (sample number 2). This similarity can testify to higher concentration of determined metalloids in water from piezometer E, which can be caused by migration of pollut-

ants from the ash dump to groundwater and it indicates penetration of these pollutants from the dump to groundwaters and migration of pollutants in groundwater flow in the river direction. In that case it is possible to state not only the presence of pollutants in water but also to indicate the migration direction: vertical migration through unsaturated zone [7].

It is possible to find in literature results of determination of arsenic, antimony and selenium in groundwater. Concentration of arsenic in groundwater on the territory of Poland oscillates from 0.1 ng/mL to tens ng/mL [1], whereas in ground water of Warta river valley in Poznań was determined to 2.31 ng/mL As [7]. In ground water of east and north Wielkopolska voivodship determined concentrations of As were up to 3.00 ng/mL [8]. India ground water and some mineral water contain 58-164 ng/mL As (III) and 181-275 ng/mL As (V) [9, 10]. High concentrations of arsenic in ground water (up to 50 ng/mL) are found in desert [11]. The mean concentration of antimony in the ground water of Poland is up to 0.13 ng/mL [1].

Table 4. Concentration ratios of different inorganic forms of As, Sb and Se at various oxidation levels.

Sample	As(V)/As(III)	Sb(V)/Sb(III)	Se(IV)/Se(VI)
1	3.3	2.0	-*
2	51.7	6.0	7.7
A	2.0	1.8	1.7
B	2.7	1.7	-*
C	1.0	1.0	-*
D	1.0	1.5	2.2
E	64.5	12.0	1.5
F	2.3	1.0	-*

\*concentration of one of speciation forms bellow detection limit.

Groundwater of the Warta river valley in Poznań contains 0.46 ng/mL Sb [7]. In groundwater of south and east Wielkopolska voivodship Sb concentration of 1.25 ng/mL was determined [8]. Natural water contains 0.13-0.19 ng/mL Sb (III) [12] and 0.39 ng/mL Sb (V) [13]. Ground water from deserts can contain up to 0.1-0.2 ng/mL of antimony [11]. Selenium, according to the geochemical surroundings and potential pollution occurs in concentrations at the level of hundreds to even few thousands of ng/mL. Selenium in the ground water of Poland is found at concentration levels from 0.10 ng/mL and is increasing together with the pollutants inflow [1]. On the other hand in ground water of Poznań the concentration of Se was up to 0.50 ng/mL [7]. In Niedzielski works concentration of selenium was found at the level of <0.15 ng/mL [8]. In the ground water of Slovenia selenium concentration was up to 0.2 ng/mL [10], while in the ground water of deserts ranges from 0.9 to 2.8 ng/mL [11].

### Conclusions

This work presents results of determination of total concentration and speciation forms of metalloids: arsenic, antimony and selenium at the level of micro trace concentrations (ng/mL). The results were used to state probable direction of pollutant migration.

The high concentrations of metalloids determined in E piezometer show strong influence of the dump on groundwater.

Results of determination of macro compounds and total concentrations of trace elements in water do not allow us to determine unequivocally the way of pollutants migration to examined water: if it is vertical or horizontal migration. Scarce speciation determination let state (for arsenic and antimony) similarity of examined water (sample number 2 and water from E control point) that is visible on example of interdependence of inorganic species' ratio (Table 4). Moreover, only presence of As(V) and Sb(V) testifies to direction of pollutants' migration: vertical migration through unsaturated zone.

The research shows a new approach to the problem of pollutant migration in groundwater. Proposed calculations of interdependence of inorganic species' ratio As(V)/As(III), Sb(V)/Sb(III) and Se(IV)/Se(VI),

which are characteristic values for each sample let us to obtain information about the environment studied as well as about processes occurring there. This information is often impossible to gain by means of different determinations.

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