

Speciation Analysis of Arsenic, Antimony and Selenium in the Surface Waters of Poznari

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Received 3 December, 1998

Accepted 10 March, 1999

Abstract

This paper presents the results of arsenic, antimony and selenium analyses in the municipal water reservoirs of Poznan. The study concentrates on the discrimination of speciation forms of the determined elements by means of analytical procedures. A specially designed and optimized methodology of hydride generation atomic absorption spectrometry (HGAAS) was employed in the analyses. The limits of detection were established as 0.14 ng/ml for As (III), 0.16 ng/ml for total As; 0.17 ng/ml for Sb (III); 0.18 ng/ml for total Sb, and 0.15 ng/ml for selenium.

Keywords: arsenic, antimony, selenium, speciation, hydride generation, atomic absorption spectrometry

Introduction

Speciation analysis [1, 2] (i.e. the discrimination of elements or chemical compounds in various forms in the environment), gives a fuller picture of both the state of the aquatic system and the processes and tendencies it undergoes [3-5]. For many reservoirs, speciation analyses performed for the first time may serve as an introduction to further papers and discussions.

Underground waters, depending on the geological environment, may contain from a tenth of a nanogram to micrograms per millilitre [6], as is the case of surface waters. The main forms of arsenic found in the waters are arsenates (III), arsenates (V), methyl- compounds (methylarsenic acid MMAA) and dimethylarsenates (dimethylarsenic acid DMAA) [7-9]. In the As(III)/As(V) system, there is a preponderance of arsenic compounds at higher levels of oxidation. The toxicity of arsenic is reduced in the series: As (III) > As (V) > MMAA > DMAA > other arseno-organic compounds (e.g., arsenobetaine) [10].

Antimony in natural waters exists in concentrations of one tenth to one nanogram per millilitre, in the case of polluted waters (municipal sewage, waste dump site seepage) antimony content increases to several nanograms and may serve as a monitoring parameter. Its great chemical similarity to arsenic allows one to expect a similar beha-

viour in natural waters, particularly as regards distribution and speciation.

Selenium content in natural waters is usually within one tenth or one hundredth of a nanogram per millilitre. Inorganic compounds of selenium dominate in natural water (IV) and (VI). Inorganic selenium compounds undergo biochemical transformations to organic ones in the depths of the waters; these, in turn (in the depths), undergo reduction to inorganic compounds [11].

Atomic absorption spectrometry (AAS) is one of the frequent methods of determining both general arsenic, antimony and selenium contents [12] as well as their speciation analyses at the level of environmental concentrations. Particularly the hydride generation technique allows for the isolation of a determined element out from its environmental matrix, which is often quite complex and particularly interferes with graphite furnace atomic absorption (GFAAS). Volatile hydrides are created through the reduction of compounds by free hydrogen formed in an acid environment from the decomposition of a reducing agent (sodium borohydride). The remaining hydrides are transported in an inert gas stream (following separation from the aqueous phase in a separator) to a (flame or electrothermally) heated quartz cuvette located in the path of the radiation, where they undergo thermal decomposition and the remaining free atoms absorb the radiation.

This paper reports results of speciation studies of arsenic, antimony and selenium performed for the first time in samples of waters from lakes within the borders of Poznan or near the city. Preparation and optimization of the method for determination of the speciation groups according to the criterion of oxidation degree and bonding with organic matter is described as the introductory step in environmental studies. The results are meant to be a reference for later discussions of the effects of anthropopressure on natural water ecosystems.

Materials and Methods

Instruments and Reagents

A Varian SpectrAA 20 Plus spectrometer was used in analyses as well as a Varian HCL lamp. Hydride generation was performed on a VGA-77 apparatus with an ETC-60 electrothermally heated quartz cuvette with argon as the inert gas transport medium. A Merck MW 500-microwave mineralizer was used in preparing samples. Analyses of basic physical and chemical properties were performed on a Dionex DX-120 ionic chromatograph (anions) and a Perkin Elmer Analyst 300 atomic absorption spectrometer (cations).

Only analytical grade reagents and redistilled water, further purified on a Milli-Q apparatus, were used. A commercial (Promochem) AAStandard solution of 1 mg/ml was used in preparing samples for analysis. A solution of 1 µg/ml with a shelf life of 3 months was prepared by dilution and stored in a polyethylene (Nalgene) bottle. Standard solutions of lower concentrations were prepared on the day analyses were performed, using polyethylene labware. All sample solutions were stabilized by hydrochloric acid ($p = 1.19$ µg/ml) in amounts of 1 ml per litre. Solutions of sodium borohydride were prepared by dissolving sodium borohydride in a 1% (w/v) solution of sodium hydroxide. Solutions were clear and did not require filtration. Solutions were prepared on the same day analyses were performed. For generating hydrides, solutions of hydrochloric ($p = 1.19$ µg/ml) and citric acid were used, and nitric acid (V), ($p = 1.64$ µg/ml) was used in mineralization. A standard certified materials (Promochem) SRM 1643d (after described below dilution) and SLRS-3 was used.

Study Area and Sampling

From among 12 Poznan lakes and water reservoirs we chose to study 5, three of which are located along the water track of the Bogdanka River: Strzeszyńskie Lake, Rusalka Lake, Solacki Pond (inner city reservoirs), and two along the track of the Cybina River: Malta Lake (an artificial reservoir used as a regatta racing-track), and the Swarzedzkie Lake lying outside the city borders. The lakes are characterized by an enhanced level of anthropopressure. Water samples were collected in anaerobic conditions in spring 1998 into Nalgene polyethylene bottles. All determinations were performed immediately after sample collection. The parameters determined were pH, electrolytic conductivity and concentrations of macroanions and macrocations.

Speciation Analysis Methodology

For arsenic and antimony, in a weak organic acid or a buffer solution of sufficiently high pH [13], hydrides are created almost exclusively from compounds containing elements at level III oxidation; compounds containing elements at level V oxidation, however, do not react or undergo reduction. In a strong reducing acid (HCl), however, at a pH of 1, hydrides are also formed from organic compounds (MMAA and DMAA) as well as inorganic ones containing elements at level III and level V oxidation, although the latter react more slowly and to a lesser degree. For the purpose of determining the entire element contained in the sample, an initial reduction of the element compounds present in the sample (from level V to level III oxidation) is required. This is also being done in both off- and on-line systems by means of various reducing reagents (hydrochloric acid [14], potassium iodide [15, 16], ascorbic acid, L-cysteine [17, 18] as well as their mixtures [19]). The content of elements at level V oxidation is then calculated from the difference of the total content and that of elements at level III oxidation. The content of organic matter is determined following mineralization of the sample (e.g. nitric acid in a closed system heated by microwave) from the difference of the obtained result and the content of element at oxidation levels (III) and (V).

In the case of selenium determinations in the sample, compounds containing elements at level VI oxidation do not undergo reduction in a reactive environment while forming hydrides. In a strong reducing acid (HCl) at a pH of 1, hydrides are created almost exclusively from inorganic compounds, containing elements at level IV oxidation. For the purpose of determining total element content in a sample, an initial reduction of compounds present in the sample from level VI to level IV oxidation is first required. This can be done in both off- and on-line systems by means of hydrochloric acid [20, 21]. The content of compounds at level VI oxidation is then calculated from the difference of the overall content. The content of the element combined with organic matter is determined, following mineralization of the sample (e.g. with nitric acid in a closed system heated with microwaves), from the difference of the obtained result and the element content at level (IV) and (VI) oxidation.

Speciation determinations of As (III) and Sb (III) were performed with citric acid, while hydrochloric acid was used for speciation of all other determinations. The application of hydrochloric acid for reduction of As (V), Sb (V) and Se (VI) allowed the use of the same sample for determinations of these three elements. Determinations were carried out for two samples in parallel ($n = 2$) with 6 times repetition of the HGAAS analysis.

Results and Discussion

Basic Hydrochemical Analysis

Samples, having the following pH, electrolytic conductivity and macro-content were taken from the waters of Poznan's lakes (Table 1).

The results show that the waters in Malta and Swarzedzkie Lakes are substantially polluted with municipal sewage as indicated by an elevated level of chlorides and

Table 1. Physico-chemical parameters of Poznań's lake waters.

Sample	pH	cond. μS/cm	NO ₃	Cl	PO ₄	SO ₄	Na	K	Ca	Mg	Fe	Mn
			μg/ml									
L. Strzeszyńskie	8.44	618	0.04	47	bd	42	16	3.7	83	18.7	bd	bd
L. Rusalka	8.15	756	bd	57	bd	171	21	4.3	106	20.1	0.09	0.02
Sołacki Pond	7.60	737	0.03	53	bd	145	23	4.4	103	18.2	0.14	0.05
L. Malta	8.03	822	0.39	79	bd	129	29.5	5.4	102	25.9	bd	0.05
L. Swarzędzkie	8.10	821	1.54	68	bd	148	25.5	4.1	110	25.3	bd	bd

bd – below detection limit

nitrate relative to those in the other reservoirs. The established decreasing concentration of nitrate along the Cybina River (from Swarzędzkie Lake to Malta Lake) may be indicative of successful natural water purification in the cascade of the Cybina river [22].

Analyses were performed by means of ion-exchange chromatography (anions) and flame absorption/emission spectrometry (cations).

Speciation Analysis of Arsenic, Antimony and Selenium

Speciation analyses of arsenic, antimony and selenium were performed by the hydride generated atomic absorption spectrometry method (HGAAS), with an operational discrimination of speciation forms [23]. The analytical methodology was designed and optimized for speciation analyses of environmental samples at low element concentrations. A characterization of the analytical method [24] and determinations of certified internal reference materials were performed.

Analyses were conducted according to the following procedure:

A. Analysis immediately following sampling, during the generation of hydrides, using a citric acid environment for analysis of As (III) and Sb (III) and a hydrochloric acid environment for analysis of Se (IV).

B. Analysis of (As (III) + As (V)), {Sb (III) + Sb (V)}, {Se (IV) + Se (VI)} from a common sample reduced by hydrochloric acid (1% v/v) in a microwave mineralizer (530 W, 5 min).

Table 2. Detection limits (DL) of analytical method.

	As (III)	As	Sb (III)	Sb	Se
	ng/ml				
qualitative DL (2σ)	0.09	0.11	0.11	0.12	0.10
quantitative DL (3σ)	0.14	0.16	0.17	0.18	0.15

Table 3. Analysis of reference materials - percent of recovery.

	As	Sb	Se
spiked tap water	91.4 ± 7.3	108.0 ± 10.0	103.1 ± 8.1
diluted SRM 1643d	101.0 ± 9.7	95.0 ± 9.8	96.0 ± 9.0
SLRS-3	99.5 ± 6.9	83.3* ± 15.9	not certified

* on DL level

C. General content analysis of As, Sb, and Se from a common sample with a mixture of nitric (0,1% v/v) and hydrochloric acid (1% v/v) heated in a microwave mineralizer (the same conditions as in the previous step).

D. Quantitative analysis of elements at level V (VI) oxygenation from the difference of results obtained in steps B and A, as well as the content of elements in organic compounds from the results obtained in steps C and B.

The limits of detection were established both in citric acid - As(III), Sb(III) and in hydrochloric acid environments (other determinations), Table 2. The qualitative and quantitative detection limits were assumed to be equal to twice (2s) and three times (3s) standard deviation in

Table 4. Speciation of arsenic, antimony and selenium in the waters of Poznań's lakes (mean value n = 2, RSD for all results < 10 %).

Sample	AS				Sb				Se			
	III	V	org	sum	III	V	org	sum	IV	VI	org	sum
	ng/mL											
L. Strzeszyńskie	0.95	0	0.05	1.00	0.25	0.05	0	0.30	–	–	–	bel. 0.15
L. Rusalka	0.90	0.25	0.05	1.20	0.25	0.05	0	0.30	bel. 0.15	0	0.15	0.15
Sołacki Pond	0.85	0.45	0	1.30	0.25	0.35	0.10	0.70	bel. 0.15	0	0.15	0.15
L. Swarzędzkie	1.20	0	0	1.20	0.20	0.20	0	0.40	bel. 0.15	0	0.15	0.15
L. Malta	1.10	0.75	0.05	1.90	0.25	0.15	0	0.40	bel. 0.15	0.15	0	0.15

bel. 0.15 – below 0.15 ng/ml (detection limit)

determinations of the blank sample, respectively. In order to find total contents of the elements in the samples (step C of the procedure) determinations were performed for the inner and certified standards. The inner standard was made by 50.46 times dilution of the certified SRM 1643d standard, under strict control of laboratory vessels (validation). Despite a decrease in precision and accuracy (as after dilution the standard is no longer certified) we have assumed this procedure to obtain the concentrations of the three elements close to their environmental ones. Determinations without dilutions were performed for the certified standard SLRS-3 and for tap water to which standards of the elements at the lower and higher oxidation degree were added in the concentration of 0.5 ng/ml. Recovery is high (Table 3), even for the antimony in SLRS-3 determined at the limit of detection, and can be assumed as satisfactory for trace analyses being comparable to those reported in other analytical works [25, 26].

All of the above analyses were performed at a detection limit of 0.15 ng/ml at a minimal standard deviation of 0.05 ng/mL [27]. In Table 4, the confidence level was presented along with determined quantities, a zero value was given for those amounts coming from calculations. It should be noted, that values below 0.15 (3s) are only very general indicators and may be burdened by considerable error.

Determined element content is considerably lower than even values allowable for drinking water, at 50 and 10 ng/ml for As and Se, respectively, or according to WHO guidelines 10, 5 and 20 ng/ml for As, Sb and Se, respectively [28]. The authors found no previous analyses of these elements of Poznan's waters, which is why they were unable to determine whether the element content values are natural ones or caused by the changed effects of anthropopressure.

The analyzed water samples were characterized by a higher content of determined elements than were the waters from areas not subjected to the effects of anthropopressure. The overall content of arsenic in lakes from environmentally protected areas, not subjected to anthropopressure, do not usually exceed 1 ng/ml, antimony 0.5 ng/ml, selenium 0.15 ng/ml, depending on the geochemical environment.

In the water of all inner city reservoirs the concentration of selenium is close to the limits of detection - 0.15 ng/ml. The concentration of antimony is also not diversified ranging from 0.30 to 0.40; however, it considerably increases in Solacki Pond, at the end of the Bogdanka River. No changes in antimony concentration were noted along the Cybina River (Swarzedzkie and Malta Lakes). As far as arsenic is concerned, its concentration was observed to increase down the rivers, especially down the Cybina River and Malta Lake. A much higher concentration of arsenic in Malta Lake (1.90 ng/ml) may indicate an increased level of anthropopressure, which is rather obvious for this inner city reservoir.

In the waters of Poznan lakes forms As (III) and Sb (III) are prevalent, while forms at oxidation level V occur in lesser amounts. These results are consistent with the data reported by other authors for surface waters: 1.5 ng/ml As (V) and 0.5 As (III) in river water; 0.134 ng/ml As (III) and 1.02 ng/ml As (V) in the Vistula River. In very clean waters the concentrations of arsenic were much lower: 0.026 ng/ml for As (III) and 0.35 ng/ml for As (V) [13, 29]. The total content of antimony in the samples of water from the

Vistula River was 0.60 ng/ml [30], so at a level close to that in Poznan lake waters. The organic compounds of antimony were determined practically only in the samples from Solacki Pond. No significant amounts of organic compounds of arsenic were found.

In the waters studied selenium was found in organic compounds, and in Malta Lake their mineralization to inorganic ones was observed. The total content of selenium reported in different works - varying from 0.12 to 0.15 ng/ml - was similar to that established for Poznafi Lakes.

Speciation analyses of traces elements in Poznan's waters give a new view of the processes undergone by the lakes, also on the effects of anthropopressure. Continuation of analyses, of not only the overall content of heavy elements but also their speciation forms, appears warranted.

Acknowledgements

Research was financed by the Communal Fund for the Protection of the Environment in Poznan, included in grant OS-GF-3051-2/4/98.

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