

Occurrence of Arsenic, Antimony and Selenium in Surface Waters of Drawieński National Park

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Abstract

This paper reports the results of determinations of total amounts of arsenic, antimony, selenium and macrocomponents in water samples from lakes in Drawieński National Park. The total content of arsenic was up to 0.95 ng/mL, antimony up to 0.53 ng/mL, while selenium was below 0.15 ng/mL, at the limits of detectability of 0.16 ng/mL 0.18 ng/mL and 0.15 ng/mL, respectively. The water samples studied had a relatively low content of the elements determined in comparison to their content in water samples from other regions of Poland. Taking into regard that the samples were collected from an area under special protection, the contents of arsenic, antimony and selenium determined in them can be interpreted as representing the natural level of these elements.

Keywords: arsenic, antimony, selenium, surface waters, hydride generation atomic absorption spectrometry

Introduction

In the natural environment arsenic, antimony and selenium occur in trace amounts. Recently, interest in these elements has increased considerably as evidenced by a large number of scientific reports devoted to them [1]. On the other hand recent progress in the development of analytical methods in biochemistry, toxicology and chemistry of the environment has enabled a new and deeper approach to the role of trace elements and the processes taking place in the environment.

Arsenic is commonly found in natural waters and its concentration depends on the type of geological environment and degree of pollution in a given area. Hence, the natural concentration of arsenic can vary from decimal

fractions of ng/ml to tens of µg/ml (in some water reservoirs in California, Chile and India it can reach hundreds of ng/ml). The contribution of compounds with As (III) and As (V) is similar [2]). In a stratified lake arsenic is exchanged between the thermal layers and between water and bottom sediment. Arsenic prevalently occurs at two degrees of oxidation As (III) and As(V) forming a number of inorganic [arsenates (III) and arsenates (V) showing a tendency of interchange depending on environmental conditions] and organic compounds [3]. The admissible level of arsenic concentration in surface waters in Poland is 50 ng/ml for the 1st and 2nd class of water and 200 ng/ml for 3rd class of water, while in the USA less than 100 ng/ml.

Antimony migrates to ground waters in the form of stable complexes with humid acids. Depending on the geological environment and pollution, the ground waters

can contain up to a few ng of antimony/mL. The surface waters usually contain less than 1 ng/ml, similarly as the precipitation which in urban areas can have up to a few ng of antimony per millilitre). In the natural environment antimony is found in the form of inorganic antimonates (III) and (V), as methyl derivatives such as monomethyloantimonic acid (MMSbA) and dimethyloantimonic acid (DMSbA), detected in natural waters [3, 4].

The content of selenium in surface waters can vary from 10^{-2} even to thousands of ng/ml, and is generally higher in fresh water. The mean content of selenium in water reservoirs in Poland is ~ 0.05 ng/ml. Since little or practically no differences were found between the selenium contents in pure non-polluted wastewaters and in water reservoirs subjected to significant anthropopressure, (apart from some specific instances), the neighbourhood of industrial plants and/or urban areas seems to have no effect of the level of this element in surface waters [5, 6]. In the natural environment selenium occurs in the form of selenides, selenates (IV) and selenates (VI), derivatives of di- (lotne dimetyloselen – DMSe and dimetylidwuselen – DMDSe) and trimethyl (trimetyloselen – TMSe), seleno-amino acids (selenocysteina – SeC and selenometionina – SeM), and in many organic compounds [3]. The admissible concentration of selenium in surface waters ranges from 1 ng/ml in Russia, 8 ng/mL in Germany, 10 ng/ml in Egypt, USA, Australia, to 50 ng/ml in the Czech Republic [6].

Experimental

Apparatus and Reagents

Spectral analyses were performed on a double-beam spectrometer SpectraAA 20 Plus made by Varian, using HCl lamps made by Varian. Generation of hydrides was carried out in the instrument VGA-77 in electrothermal contact with a heated quartz tube ETC-60. Argon was used as a carrier gas. The samples were mineralised in a Merck MW 500 microwave mineraliser. The conditions of analytical determination for the three elements studied are described in Table 1.

Basic physical and chemical parameters were determined on a Dionex DX-120 ionic chromatograph (anions) and a Perkin Elmer Analyst 300 atomic absorption spectrometer (cations). All the reagents used were of analytical grade and water was redistilled and purified in Mili-Q. The standards were made of the commercial standard for AAS analysis (Promochem). The standard solutions were stabilised by HCl ($\rho = 1.19$ g/mL) at 1 mL/L. The sodium borohydride solutions were made by dissolving sodium borohydride in a 1% (w/v) solution of sodium hydroxide. The solutions were clear and did not require filtration. The solutions were made on the day they were used. Generation of hydrides was performed with the use of HCl solutions $\rho = 1.19$ g/mL, while mineralisation with nitric (V) acid, $\rho = 1.64$ g/mL. The analytical methods are described in detail in [7, 9].

Table 1. The parameters of AAS spectrometer used for determinations of arsenic, antimony and selenium with hydride generation.

		As	Sb	Se
Wavelength	nm	193.7	217.6	196.0
Slit	nm	0.5	0.2	1
Lamp current	mA	10	10	10
Quartz tube temperature	°C	950	850	900
Sample flow rate	mL/min		5	
Reducing agent flow rate	mL/min		1	
Reducing agent concentration	%	3.0	0.3	0.3
Acid flow rate	mL/min		1	
HCl concentration	M	10	0.1–1	1
Delay time	s		20	
Time of measurement	s		6 x 1	

Table 2. Parameters of the analytical method for determination of arsenic, antimony and selenium by AAS with generation of hydrides.

		As	Sb	Se
Limit of detectability (3σ)	ng/mL	0.16	0.18	0.15
Sensitivity	ng/mL	0.08	0.11	0.08
Repeatability (for 10 ng/mL)	%	1.1	0.9	1.2

Table 3. Results of determinations of arsenic, antimony and selenium in the certified reference material SLRS-3.

	The certified concentration ng/mL	Determined concentration ng/mL	Recovery %
As SLRS-3	0.72 ± 0.05	0.70 ± 0.07	97.2 ± 9.7
Sb SLRS-3	0.12 ± 0.01	0.14 ± 0.02	$116.6^* \pm 16.7$
Se SLRS-3	Not certified	–	–

* at the limit of detectability

Samples

The samples to be studied were collected from surface waters in an area of limited anthropopressure in Drawieński National Park in western Poland. The samples were taken from bulk water or from the stratified layers. The sample collection procedure was consistent with the technique routinely used for determination of environmental samples. The samples were transported in polyethylene bottles for trace element analysis (Nalgene). Determinations were made immediately after bringing the samples to the lab. When necessary, the

Table 4. Statistical parameters describing determinations of the basic physical and chemical parameters of the water of Drawieński National Park lakes.

		p*	NO ₃	Cl	PO ₄	SO ₄	Na	K	Ca	Mg	Fe	Mn
Number of samples	–	29	38	38	38	38	38	38	38	38	38	38
Mean concentration		226	0.32	13	0.46	9	5.3	1.2	41.3	3.9	0.26	0.12
Lowest conc.		22	nw	3	0.10	nw	1.0	0.6	1.4	0.4	0.02	0.01
Highest conc.		373	4.00	23	3.10	25	12.2	2.3	69.9	9.5	0.91	1.97
Median	µg/mL	289	nw	13	0.30	9	5.0	1.1	47.1	3.9	0.20	0.06
Lower quartile		99	nw	7	0.30	6	2.4	0.9	29.6	1.9	0.12	0.02
Upper quartile		324	0.42	18	0.60	12	8.9	1.5	56.4	5.6	0.31	0.08
Standard deviation		124	0.68	6	0.46	5	3.3	0.4	19.2	2.2	0.21	0.31

* – conductivity [µS/cm]; nw – not detected

samples were frozen and stored at temperatures below 0°C with an addition of HCl and HNO₃ (V) acids were heated in a microwave and stored at about 4°C. No loss in the amount of the elements studied was detected even after a few days of storage. Other physical and chemical parameters of the water (conductivity, concentrations of NO₃, Cl, PO₄, SO₄, Na, K, Ca, Mg, Fe, Mn) were determined according to the international standards (ISO) and Standard Methods [8].

Prior to the determination of the total contents of arsenic, antimony and selenium, the samples had to be subjected to the following procedures [9]:

1. mineralisation of the organic compounds in a given sample,

2. reduction to As(III), Sb(III) and Se(IV).

The above procedures were carried out in a microwave mineraliser in closed Teflon containers. The sample was mineralised by nitric (V) acid and reduced with hydrochloric acid. The analytical procedures were the same as described earlier in [10-13].

Results and Discussion

The parameters of the analytical method determined in the process of its validation are given in Table 2.

The limits of detectability of the method permit determination of the three elements at the concentrations at which they occur in the natural environment. Although the detectability limit obtained for selenium of 0.15 ng/mL seems too high to apply the method for determination of the natural concentrations of this element, it can be a threshold value for further determinations with preliminary concentration of the analyte [14, 15].

For determinations by atomic absorption spectrometry with generation of hydrides in an electrothermally heated atomiser, the method's accuracy was verified in determinations of the certified reference material.

Recovery is high (even for antimony determined at the limit of detectability), satisfactory for trace elements analysis and comparable to the results reported by other authors [9], which means that the accuracy of the results also is satisfactory.

Two separate determinations were performed for each sample and for each of them the spectrometric measurement was repeated 6 or 10 times. Statistical analysis of the results was performed for the samples grouped according to the place of collection. The results of the statistical analysis are shown in the Tables below. For arsenic, antimony and selenium the detectability was assumed to be 0.15 ng/ml at the minimum standard deviation of 0.05 ng/ml and all the results are given with this accuracy.

On the basis of the mean values of the basic physical and chemical parameters the waters studied can be classified under first class purity except for phosphate content, which would classify them under second class purity. The maximum values of the parameters determined also point to the same classification. Only on the basis of the maximum contents of manganese and phosphates (high content suggesting eutrophy) should the waters be described as beyond classification. High values of skewness and kurtosis for nitrates and phosphates (high positive values) point to differences in the eutrophy of the lakes – the lakes with water containing the elements studied at concentrations higher than the mean value dominate.

Table 5. Statistical parameters for determinations of arsenic, antimony and selenium in the water of the lakes in Drawieński National Park.

		As	Sb	Se
Number of samples	–	38	38	38
Mean content		0.95	0.50	< 0.15
Lowest content		< 0.15	0.20	–
Highest content		3.45	2.60	–
Median	ng/mL	0.90	0.45	–
Lower quartile		0.65	0.40	–
Upper quartile		1.15	0.60	–
Standard deviation		0.55	0.35	–

Table 6. Results of the determinations of arsenic, antimony and selenium in particular lakes and rivers in Drawieński National Park (ng/ml).

Lake or river	Number of samples	As			Sb			Se
		mean	min	max	mean	min	max	
Kocie lake	1	0.40	–	–	0.40	–	–	< 0.15
Czarne lake	3	0.55	0.50	0.65	0.40	0.35	0.40	< 0.15
Ostrowiec lake	4	0.65	0.55	0.90	0.65	0.45	0.95	< 0.15
Jamno lake	2	0.15	< 0.15	0.25	0.30	0.25	0.35	< 0.15
Płociczno lake	4	0.85	0.65	1.15	0.35	0.25	0.45	< 0.15
Płociowe lake	3	1.10	1.00	1.25	0.40	0.25	0.55	< 0.15
Sitno lake	4	1.15	1.10	1.25	0.40	0.20	0.60	< 0.15
Głodne lake	4	1.75	0.90	3.45	1.05	0.35	2.60	< 0.15
Perkoz lake	2	1.40	1.35	1.45	0.55	0.40	0.75	< 0.15
Pustelnia lake	2	1.20	1.05	1.35	0.55	0.45	0.65	< 0.15
Piaseczno Małe lake	2	1.50	1.15	1.90	0.40	0.40	0.45	< 0.15
Piaseczno Duże lake	4	0.90	0.80	1.00	0.65	0.40	0.95	< 0.15
Drawa river	2	0.95	0.80	1.15	0.40	0.40	0.40	< 0.15
Płociczna river	1	0.65	–	–	0.25	–	–	< 0.15

In samples from all the lakes studied the content of selenium was below the limit of detectability. The mean content of arsenic and antimony were higher than in the samples from lakes in Wielkopolski National Park [16]. In one sample from lake Głodne the contents of the elements studied were 4 or 5-times higher than the mean values which had increased the range between the minimum and the maximum contents of these elements in this particular group of results. The difference between the quartiles is small for arsenic and antimony, which means that the majority of the results of determinations are concentrated in the vicinity of the mean value. This is confirmed by the fact that the standard deviation is half of the mean value. The values of skewness and kurtosis indicate that the results are grouped to the right of the mean value, so the results higher than the mean dominate. Although the contents of arsenic and antimony in the waters of the lakes in Drawieński National Park than in the lakes in Wielkopolski National Park [16], these differences are due to natural processes and different geochemical environments rather than anthropopressure. However, this supposition should be verified on the basis of long-term monitoring of the lakes in the two areas and investigation of other elements of natural environment. Table 5 gives the mean, minimum and maximum contents of the elements determined in particular lakes and rivers from the area studied. The mean contents varied between 0.40 ng/ml and 1.75 ng/ml, and did not differ much from the contents determined for the other regions [16].

From 10 lakes samples of water were collected at different depths, that is at different strata: epilimnion, metalimnion and hypolimnion, the results of determinations of arsenic, antimony and selenium are given as mean values for particular strata of different lakes (Table 7). For arsenic no statistically significant differences in

concentration at different strata were found. For antimony the greatest concentration was determined in the hypolimnion; however, because of the small number of samples collected from this stratum this result is not reliable.

Table 7. A comparison of the mean contents of arsenic and antimony in different stratigraphic zones of the lakes (ng/ml).

	Number of samples	As	Sb
Epilimnion	10	0.90	0.40
Metalimnion	10	1.05	0.45
Hypolimnion	3	0.95	0.65

In the samples of waters from Drawieński National Park lakes and rivers 38 determinations of the total contents of arsenic, antimony and selenium were made. Moreover, the fundamental macrocomponents of the sample matrix were identified and their contributions determined. The determined contents of arsenic, antimony and selenium are lower than the current standards than those proposed for the future, and do not exceed the values recommended by WHO. Different authors have reported results of determinations of these elements in natural waters. For instance the contents of arsenic in river water were 1.5 ng/mL As (V) and 0.5 ng/mL As (III) [17], in the Vistula river 0.134 ng/mL As (III) and 1.02 ng/mL As (V), in very pure rivers the contents of arsenic were much lower 0.006 ng/mL – 0.026 ng/mL for As (III) and 0.007 ng/mL – 0.35 ng/mL [18, 19] for As (V). The water from the river Vistula contained 0.60 ng/mL of antimony [20], the lake waters 5-8 ng/mL Sb (III) and from 12 to a few hundred ng/mL Sb (V) [21]. As to the

contents of selenium, in surface waters it has been reported at a similar level 0.12 ng/mL [22] – 0.15 ng/mL [23]. With regard to the specific character of each biotope determined by geochemical environment hydro-geochemical conditions and anthropopressure, any direct comparison of our data with those of other authors seems pointless. Such a comparison of results obtained for water samples from different geochemical environments determining different natural levels of the elements studied, could lead to erroneous conclusions about the natural concentrations of the elements studied and the effect of anthropopressure. The results presented in this work are the first contents of arsenic, antimony and selenium in water samples from the lakes in the area of Drawieński National Park and can be used as comparative material in studies on the effects of anthropopressure in the area.

References

1. NIEDZIELSKI P., SIEPAK M., SIEPAK J., *Rocznik Ochrona Środowiska*, (in Polish) **2**, 317, **2000**.
2. CHATTERJEE A., DAS D., MANDAL B.K., CHOWDHURY T.R., SAMANTA G., CHAKRABORTI D., *Analyst*, **120**, 3, **1995**.
3. ŁOBIŃSKI R., ADAMS F.C., *Spectrochim. Acta Part B* **52**, 1865, **1997**.
4. YUSUF M., SARKI A.C., IDRIS S.B., AYOKO G.A., SINGH K., *Talanta*, **35**, 496, **1988**.
5. Guidelines for drinking-water quality, WHO, Geneva **1984**.
6. DOJLIDO J.R., BEST G.A., *Chemistry of water and water pollution*, Ellis Horwood **1993**.
7. NIEDZIELSKI P., Ph.D. Thesis, Adam Mickiewicz University, Faculty of Chemistry, (in Polish) Poznań **1999**.
8. GREENBERG A.E., CLESCERI L.S., EATON A.D., *Standard methods for the examination of water and wastewater*, **1992**.
9. SIEPAK J., *Speciation analysis of metals*, (in Polish) Wyd. UAM, Poznań **1998**.
10. NIEDZIELSKI P., SIEPAK J., *Chem. Anal. (Warsaw)*, **46**, 51, **2001**.
11. NIEDZIELSKI P., SIEPAK J., SIEPAK M., *Polish J. Environ. Stud.*, **10(5)**, 347, **2001**.
12. NIEDZIELSKI P., SIEPAK J., KOWALCZUK Z., *Polish J. Environ. Stud.*, **8(3)**, 183, **1999**.
13. NIEDZIELSKI P., SIEPAK J., KOWALCZUK Z., *Arch. Environ. Protect.*, **1**, 73, **2000**.
14. MATUSIEWICZ H., STURGEON R. E., *Spectrochimica Acta B*, 1283, **1996**.
15. SIEPAK M., M.Sc. Thesis, Adam Mickiewicz University, Faculty of Chemistry, (in Polish) Poznań **2000**.
16. NIEDZIELSKI P., SIEPAK J., PEŁECHATY M., BURCHARDT L., *Morena*, (in Polish) **7**, 69, **2000**.
17. DRIEHAUS W., JEKEL M., *Fresenius J. Anal. Chem.*, **343**, 343, **1992**.
18. KANKE M., KUMAMARU T., SAKAI K., YAMAMOTO, *Anal. Chim. Acta*, **247**, 13 **1991**.
19. CHAKRABORTI D., DE JONGHE W., ADAMS F., *Anal. Chim. Acta*, **120**, 121 **1980**.
20. POSTUPOLSKI A., GOLIMOWSKI J., *Electroanalysis*, **3**, 793, **1991**.
21. SUN Y.C., YANG J.Y., LIN Y.F., YANG M.H., *Anal. Chim. Acta*, **276**, 33, **1993**.
22. CARRERO P.E., TYSON J.F., *Analyst*, **122**, 915, **1997**.
23. ORNEMARK U., PETTERSSON J., OLIN A., *Talanta*, **39**, 1089, **1992**.