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Microtrace Contents of Arsenic, Antimony and Selenium in Surface Waters of Pszczewski Landscape Park as a Region Potentially Free from Anthropogenic Pressure

P. Niedzielski, M. Siepak*, K. Grabowski

Department of Water and Soil Analysis, Adam Mickiewicz University, Drzymały Street 24, 60-613 Poznań, Poland, e-mail: zawig@amu.edu.pl
* Department of Hydrogeology and Water Protection, Adam Mickiewicz University, Maków Polnych 16, 61-686 Poznań, Poland, e-mail: siep@amu.edu.pl

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Abstract

This paper presents results of determination of the total content of arsenic, antimony and selenium in samples of surface water from selected lakes of Pszczewski Landscape Park. The concentrations of arsenic, antimony and selenium determined by the absorption atomic spectrometry method were up to 0.66 ng/ml, 0.62 ng/ml and 0.76 ng/ml, respectively, at the detection limits of 0.04 ng/ml for As, 0.04 ng/ml for Sb and 0.03 ng/ml for Se. The water samples studied revealed low concentrations of the elements of interest relative to the values obtained for the samples from other regions. The determined concentrations of arsenic, antimony and selenium can be interpreted as natural.

Keywords: arsenic, antimony, selenium, surface waters, absorption atomic spectrometry with generation of hydrides

Introduction

Arsenic is commonly found in surface waters and its content is determined by the geological environment and the presence of possible sources of pollution. Therefore, the natural concentration of arsenic can vary from tenths of ng/ml to tenths of μg/ml (in ground waters in California, Chile, and India it may reach even a few hundred ng/ml). The content of As (III) and As (V) compounds is at a similar level [1]. In a stratified lake arsenic circulates among the thermal layers and is exchanged with bottom sediments. In general arsenic there occurs two levels of oxidation: (III) and (V). Arsenic forms a number of inorganic compounds (arsenate (III) and arsenate (V), which tend to interconvert depending on environmental conditions) and organic compounds [2]. Of great importance are methyl derivatives of arsenic monomethlyarsenic acid (MMAA) and dimethylarsenic acid (DMAA), which are direct products of microbiological conversions of inorganic arsenic compounds. According to toxicity the arsenic compounds are ordered as arsenates (III) then 60 times less toxic arsenates (V) and 100 less toxic methylated forms mono- and dimethylatedarsenic acids and arsenic organic compounds [1].

Antimony penetrates into ground waters in the form of complexes with humic acids. Depending on the geological environment and possible pollution ground waters can contain up to a few ng/ml of antimony. Some mineral waters and hot springs in particular can contain even up to a few μg/ml of antimony. Surface waters usually con-

Correspondence to: Dr. P. Niedzielski, e-mail: pnied@amu.edu.pl

tain less than 1 ng/ml, similarly precipitation (in urban areas up to a few ng/ml). In the natural environment antimony occurs in the form of inorganic antimonates (III) and (V), and methyl derivatives: monomethylantimonic acid (MMSbA) and dimethylantimonic acid (DMSbA) [2, 3].

The concentration of selenium in water can vary from hundredths to thousands ng/ml and it is greater in inland waters. The mean content of selenium in surface waters in Poland is - 0.05 ng/ml. Selenium can be washed into the ground waters (along with arsenic and antimony) from dumping grounds, especially coal combustion ashes. No significant differences were found between the content of selenium in natural waters and in waters subjected to strong anthropopressure. This finding proves that urban and industrial development has little effect on the content of selenium in water [4, 5]. In natural environment selenium occurs in the form of selenate (IV) and selenate (VI), dimethyl (dimethyloselenium - DMSe i dimethylodiselenium - DMDSe) and trimethyl (trimethyloselenium - TMSe) derivatives, selenium amino acids (selenocysteine - SeC and selenometionine - SeM), and in a number of organic compounds [2].

The admissible concentrations of arsenic in surface waters in Poland are 50 ng/ml for the 1st and 2nd class, 200 ng/ml for the 3rd class, in the USA less than 100 ng/ml. In drinking water the admissible level of arsenic is 10 ng/ml in Poland; 50 ng/ml in Japan, Russia, Austria, Czech Republic and Hungary; 40 ng/ml in Germany; ard 10 ng/ml in the USA. As different species of arsenic have different toxicities usually the contents of particular species are given. In Poland the admissible concentration of antimony in drinking water has been accepted as 5 µg/l since the year 2000. No admissible concentration of antimony in surface waters has been proposed. The admissible concentration of antimony in drinking water in EU countries is 10 µg/l, but has recently been suggested being reduced to 3 µg/l. The admissible concentration of selenium in surface waters varies from 1 ng/ml in Russia, 8 ng/ml in Germany, 10 ng/ml in Egypt, USA, Australia up to 50 ng/ml in Czech. In EU countries the maximum concentration of selenium in drinking water is 10 ng/ml, and this admissible level will probably not be changed. The standards in Poland are the same as in EU countries.

Experimental

Equipment and Solutions

The concentrations of the elements studied were determined by absorption atomic spectrometry (AAS) with generation of hydrides, on a fast-sequence spectrometer SpectrAA 220 FS made by Varian. For analysis HCL lamps made by S&J Juniper were used. Generation of hydrides was performed in the continuous mode in the attachment VGA-77 with a multichannel peristaltic pump and glass u-separator of the gas phase. Atomisation was performed in a quartz cuvette electrothermally heated by a ETC-60 controller with programmable temperature conditions in the range from rt to 999°C, to an accuracy of 1°C. Argon was used as carrier gas.

Table 1. The conditions used for determinations of arsenic, antimony and selenium concentrations by the AAS method with generation of hydrides (fast sequence).

		As	Sb	Se
Wavelength	nm	193.7	217.6	196.0
Slit	nm	0.5	0.2	1
Lamp current	mA	7	7	5
Cell temperature	°C	900		
Rate of sample flow	ml/min	7		
Rate of reductor flow	ml/min	1		
Reductor concentration	%	1		
Rate of acid flow	ml/min	1		
Concentration of HCl	mol/l	1		
Delay time	s	30		
Measurement time	s	1		
Number of repetitions	–	6		

Table 2. Parameters of analytical method use for determination of arsenic, antimony and selenium by AAS with generation of hydride (n=60).

		As	Sb	Se
Detection limit (3σ)	ng/ml	0.04	0.04	0.03
Determinability limit (6σ)	ng/ml	0.08	0.08	0.06
Sensitivity	ng/ml	0.09	0.06	0.09
Repeatability for 2 ng/ml	%	1.7	1.9	1.5

Analytical method parameters are given in Table 2.

All reagents were analytically pure and water was redistilled in a Milli-Q (Millipore). Standard solutions were made of commercial standards for AAS analysis of a concentration of 1 mg/ml. They were dissolved to the concentration of 1 µg/ml, stable for about 3 months, and stored in a a polyethylene vessel (Nalgene). Standards of lower concentrations were made on the day of use in polyethylene vessels. The solutions of sodium hydroboride were made by dissolving sodium hydroboride in a 1% solution of sodium hydrochloride on the day of use. The solution was clear and did not have to be filtered off. The solution of thiourea of the concentration of 1 mol/1 was made by dissolving 15.2 g of thiourea in 250 ml water.

Samples

Characterisation of the Study Area

Pszczewski Landscape Park is localised in the mid-eastern part of Lubuskie voivodship and in the western part of Wielkopolskie voivodship, in the middle of the triangle delimited by the cities of Poznan, Gorzow

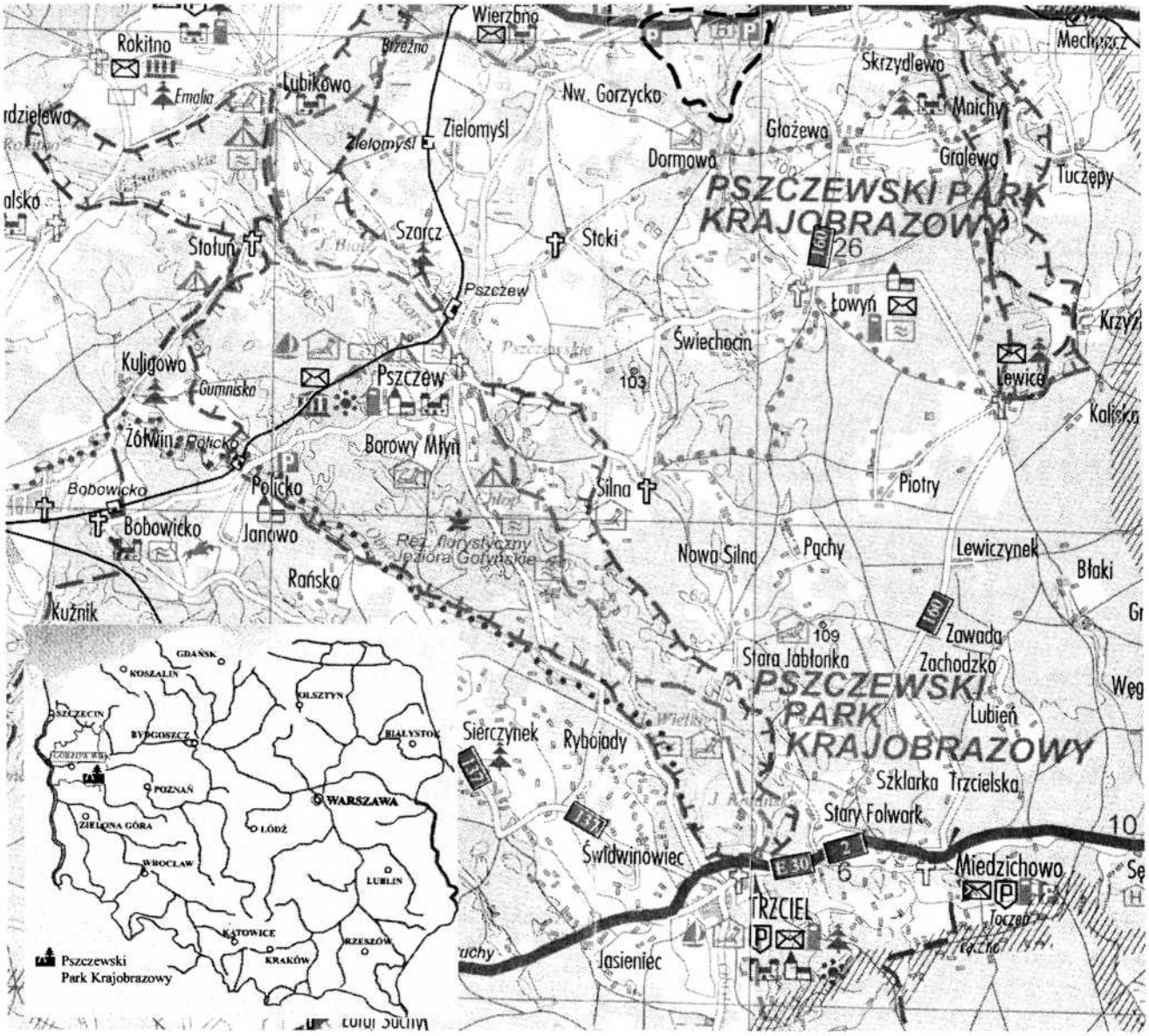

Fig. 1. Pszczewski Landscape Park.

and Zielona Gora. It was founded in 1986 in order to preserve and protect unique landscape sculpture, vegetation and culture of the region.

Total area of the park with the protective belt is over 45,000 ha, of which the park itself occupies 12,200 ha and is divided into two separate regions.

- The first of 1,970 ha in area covers the Kamionka Valley, situated between Lewice and Kamionna, through which flows the small Kamionna river.
- The second covers an area of 10,250 ha, localised along the middle section of the Obra river and the se quence of lakes spreading from Trzciel in the south through Pszczew to Lubikowo and Rokitno in the north-west.

The two complexes of the park are surrounded by a protective belt of an area of 33,080 ha. The area of the park and the protective belt include 6 areas: Pszczew, Przytoczna, Miedzychod, Miedzichowo, Miedzyrzecz and Trzciel. The young-glacial landscape of the park is characterised by great diversity of terrain forms and richness of flora and fauna [6].

Lubikowskie Lake is the largest (314.6 ha) and the deepest (35.5 m) lake in the park. It is localised a few kilometres north-west of Pszczew. It has a well-developed shoreline, a few bays, peninsulas and an island of an area of 5.9 ha. The lake is a catchment reservoir of a few streams of which the greatest are the inflows from the lakes Czarne, Biale and Stolun. Near Lubikowo, on the east bank there are a few resorts and camping grounds.

Czarne Lake is situated between Stolun lake and the south bay of Lubikowskie lake, and covers an area of 24 ha. Czarne lake is characterised by a narrow coastal zone

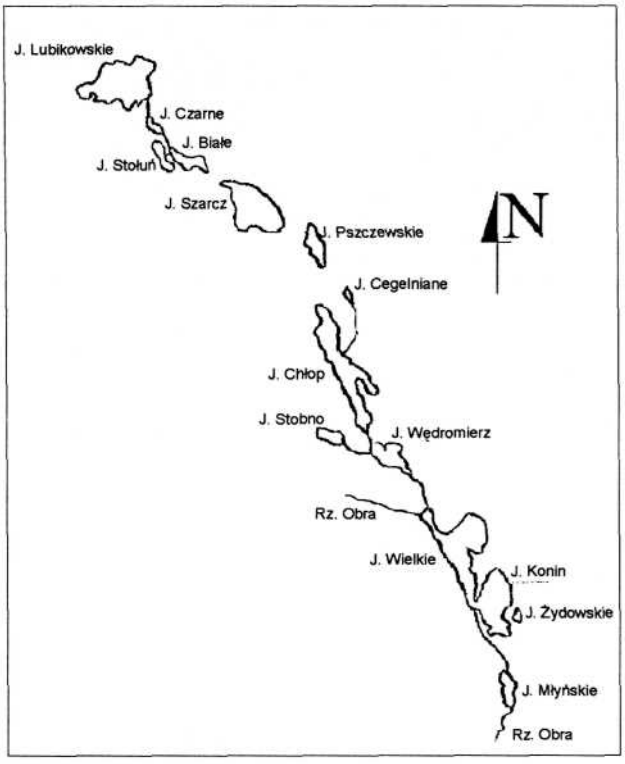

Fig.2 The lakes of the Pszczewski Landscape Park studied

and slopes gently declining towards the deep water (11 m) in the middle of the lake.

Stolun Lake is to the north-west of Pszczew, near the Biale and Czarne lakes, covers the area of 21.3 ha and is a typical tunnel-valley lake. It is characterised by a poorly developed shoreline, narrow coastal littoral zone and slopes sharply falling towards the deepest water (17.9 m). Stolun lake is supplied by two streams and a drainage ditch and has one outflow to Biale lake.

Biate Lake covers an area of 55.6 ha and is localised between Lubikowskie lake from the north and Szarcz lake from the south. It is not much elongated and has a poorly developed shoreline. The southern bank has a narrow coastal zone, while the northern one has a wide littoral belt and there is a shallow part in the eastern fragment of the lake. The maximum depth of this lake is 11.5 m. It is supplied with water from Szarcz lake and a few drainage ditches from nearby fields, and has outflow to Czarne lake connected with Lubikowskie lake. For many years the water of the lake was polluted by wastes from the grounds cultivated by a nearby state farm in Szarcz. Recently, a significant improvement of water quality has been observed.

Szarcz Lake lies to the north-west of Pszczew along the water division Obra-Warta (along the division of the catchments of the rivers Obra and Warta) and occupies an area of 169.9 ha. The banks are flat and of the same size. The lake has two depths - one in the northern part of 14.5 m and one in the southern part of 13.8 m. The lake is supplied by ground waters and precipitations and water from the lake supplies Lubikowskie lake through a small ditch.

Pszczewskie Lake of an area of 68.7 ha, is situated at 1.2 km to the north of the Chlop lake in the same glacial valley and in the catchment of the Obra river. The city of Pszczew lies along the eastern bank of the lake. The lake has a poorly developed shoreline and a narrow coastal zone. The maximum depth of the lake is 17.8 m. It is supplied by short streams and drainage ditches from the nearby fields and meadows.

Cegielniane Lake of 7.9 ha is localised to the north-east of Chlop lake, which it supplies with water.

Chtop Lake lies south of Pszczew, between lakes Wedromierz and Pszczewskie and is the longest in the park at 4,150 m and covers an area of 227.8 ha. The shoreline is rich in bays and peninsulas. Along the eastern steep banks there are ozowe hills reaching a height of 100 m asl. The banks of the lake are elevated to 52.7 m asl. The lake has three deep parts (northern, middle and southern), of which the deepest is the middle one reaching 23.0 m deep. The catchment of the lake is over 50% forested.

Stobno Lake has no outlet and is and supplied by a stream. It lies to the west of Chlop lake, occupies an area of 29.1 ha, and has a maximum depth of 12.0 m. It is surrounded with forests and its northern bank has been used for recreational purposes by local people.

Wedromierz Lake belongs to the catchment of the Obra river, occupies an area of 73.8 ha and its maximum depth is 11.8 m. It is surrounded by forests. The shoreline is well-developed and grown with a belt of rushes. In the south there is an outlet to the Rybojady lake.

Wielkie Lake occupies an area of 217.3 ha, its maximum depth is 3.7 m and mean depth 2.1 m. It has a well-developed shoreline, many shallow bays and three islands. The coastal zone is poor and the flat bottom is covered with a thick layer of sediments. The lake is supplied from a few streams of well-developed hydrological network. In the north-western part it is connected with Rybojady lake.

Konin Lake occupies an area of 77.2 ha and its maximum depth is 4.3 m, so it is shallow with a poorly developed shoreline. The bottom is covered with a thick layer of sediments. The lake is connected with the Obra river. The east bank is taken by a resort, camping ground and a large beech.

Zydowskie Lake is located 270 m south-east of Konin lake, it is closed with no inlets or outlets, and occupies an area of 9.2 ha.

Mtynskie Lake occupies an area of 43.5 ha, is bordering on eastern city limits of Trzciel (Nowe Miasto). It has an almost parallel poorly developed shoreline, flat bottom covered with a thick layer of bottom sediments [6-8].

Sampling and Sample Preparation

Samples to be studied were collected twice a year in November and February. The samples were taken from a site at about 8 m from the shore by a sampler on an arm. The samples were immediately transported to a laboratory and stored in polyethylene vessels for trace analyses (Nalgene). The samples were stored for no longer than a few days frozen at about -20°C. Directly prior to ASA analyses portions of lml of hydrochloric acid

(10 mol/1) and 1 ml of a thiourea solution (1 mol/1) were added to the samples in order to reduce the compounds of arsenic, antimony and selenium to As(III), Sb(III) and Se(IV). The determinations were performed by the AAS method applying the fast sequence technique, and therefore all elements were determined in the same sample.

Results and Discussion

Analytical determinations of the total contents of arsenic, antimony and selenium at the level of ng/ml were performed for 34 samples of water from 14 lakes in the area of Pszczewski Landscape Park and the surrounding protective belt. The results are given in Table 3.

The concentration of arsenic in the samples studied varies from 0.25 ng/ml to 0.66 ng/ml, antimony - from 0.07 ng/ml to 0.62 ng/ml, and selenium - from 0.15 ng/ml to 0.76 ng/ml. The concentrations of arsenic and antimony are at the limits of values commonly met in natural waters [9]. The concentration of arsenic in surface waters is at the ng/ml level; in the river waters in Germany 1.5 ng/ml As (V) and 0.5 ng/ml As (III), reported by Driehaus [10], in the Vistula river 0.134 ng/ml As (III) and 1.02 ng/ml As (V). In the waters of very clean rivers the concentrations of arsenic were lower from (Kanke) 0.006 ng/ml [11] to (Chakraboti) 0.026 ng/ml [12] for As (III) and 0.007 ng/ml (Japan) [11] to 0.35 ng/ml (Belgium) [12] for As (V). In the waters from the stratified lakes in New Zealand, Aggett found a decrease of As (V) concentration and an increase of that of As (III) with increasing depth [13]. Siepak et al. reported the mean value of arsenic concentration in the lakes from Wielkopolski National Park as 0.40 ng/ml, and the particular values varied from 0.15 to 1.5 ng/ml. In the waters from lakes in Drawienski National Park the mean value was 0.95 ng/ml and the values varied from 0.15 to 3.45 ng/ml. In the waters from Wielkopolskie Lake District, including the lakes from within the borders of the cities Poznari and Gniezno, the mean concentration of arsenic was significantly higher (1.3 ng/ml) and the values varied from 0,65 to 2.65 ng/ml [14-19].

The lake waters in China contained 58 ng/ml Sb (III) and from 12 to a few hundreds ng/ml Sb (V), after Sun [20]. In the precipitation in India the concentration of antimony was reported as 10-20 ng/ml, by Tripathi [21], in marine waters in Spain the concentration of a few ng Sb/ml was determined, with dominant contribution of Sb(V), by de la Calle Guntinas [22]. Siepak et al. reported the mean concentration of antimony in lakes from Wielkopolski National Park at a level of 0.35 ng/ml, the values varied from below 0.15 to 2.15 ng/ml. In the lake waters of Drawienski National Park the mean concentration of antimony was 0.50 ng/ml and the values varied from 0.20 to 2.60 ng/ml. In lake waters from Wielkopolski Lake District, including the lakes from Poznan and Gniezno, the mean concentration of antimony was 0.50 ng/ml and the values varied from 0.20 to 1.0 ng/ml [14-19].

The concentration of selenium in surface waters is at the level of decimal points of ng/ml: 0.12 ng/ml after Carrero [23], 0.15 ng/ml after Ornemarka for Sweden [24]. Marine waters contain from 0.19 ng Se/ml (Kubota) [25] to a few ng Se/ml in Spain (Larray) [26], and the concentration of Se (IV) compounds is greater: 1.8 ng/ml Se (IV) and 0.98 ng/ml Se (VI). In the lake waters from the Wielkopolski and Drawienski National Parks, Siepak et al. reported selenium concentrations below 0.15 ng/ml. In lakes from Wielkopolski Lake District the selenium concentration varied from below 0.15 to 0.35 ng/ml [14-19].

Table 3. Total concentration of arsenic, antimony and selenium in the lakes of Pszczewski Landscape Park.

Lake	Number of samples	As			Sb			Se		
		mean	min	max	mean	min	max	mean	min	max
Wielkie	2	0.65	0.63	0.66	0.41	0.31	0.51	0.30	0.28	0.31
Chłop	4	0.41	0.37	0.44	0.14	0.07	0.30	0.21	0.19	0.22
Szarcz	5	0.59	0.55	0.66	0.15	0.07	0.27	0.17	0.15	0.19
Pszczewskie	5	0.35	0.28	0.42	0.18	0.11	0.23	0.18	0.17	0.19
Młyńskie	4	0.39	0.36	0.40	0.19	0.11	0.36	0.34	0.24	0.60
Czarne	1	0.32	–	–	0.38	–	–	0.26	–	–
Białe	1	0.42	–	–	0.17	–	–	0.22	–	–
Stołuń	2	0.48	0.44	0.53	0.26	0.25	0.27	0.19	0.18	0.20
Cegielniane	1	0.25	–	–	0.21	–	–	0.20	–	–
Wędromierz	2	0.60	0.57	0.64	0.32	0.27	0.36	0.75	0.74	0.76
Konin	1	0.55	–	–	0.33	–	–	0.74	–	–
Żydowskie	2	0.30	0.28	0.31	0.51	0.39	0.62	0.20	0.19	0.21
Lubikowskie	2	0.63	0.61	0.65	0.18	0.16	0.19	0.22	0.19	0.23
Stobno	2	0.35	0.33	0.37	0.10	0.10	0.10	0.20	0.20	0.20

Significantly higher were the selenium concentrations in the four lakes Wielkie, Młynskie, Wedromierz and Konin. All these lakes have some kind of connection to the river Obra, either directly or through the drainage system, which can be responsible for the differences. At present it is difficult to establish if these elevated values are a result of anthropogenic pressure or geochemical factors.

Statistical Analysis of Results

The results of determinations of the concentrations of arsenic, antimony and selenium in the samples from the lakes within the area of the Pszczewski Landscape Park, were subjected to statistical analysis. The criterion of the samples grouping was their origin from the same area.

The statistical parameters analysed included (descriptive statistics): mean value for a given group of samples (the initial value for interpretation), parameters of position (median, minimum and maximum values, upper and lower quartile) and scatter parameters (standard deviation, variance, the range between the maximum and minimum values, the range between the quartiles, skewness, curtosis). The arithmetic mean was assumed as the mean value. The median is the middle value obtained after ordering all the results from the maximum to the minimum value, so it divides the results of measurements into two groups. The partial median calculated for the lower group is defined as the lower quartile, and the upper quartile is defined analogously. The skewness informs about the asymmetry of results, for symmetric results it is zero, for right-hand side asymmetry it takes positive values and for the left-hand side asymmetry - negative. Curtosis describes the shape of the distribution curve (for the normal Gaussian distribution). It takes positive values for a narrow and high curve, and negative values for a broad and low curve. The above parameters characterise groups of results of determinations of environmental samples and are usually used in interpretation of the obtained data.

Table 4. Statistical parameters describing the results of determinations of the total concentrations of arsenic, antimony and selenium in water samples from lakes in Pszczewski Landscape Park.

		As	Sb	Se
Number of samples	–	34	34	34
Mean concentration	ng/ml	0.45	0.22	0.26
Minimum concentration		0.25	0.07	0.11
Maximum concentration		0.66	0.62	0.76
Range		0.41	0.55	0.65
Median		0.42	0.20	0.20
Lower quartile		0.37	0.11	0.19
Upper quartile		0.57	0.30	0.26
Quartiles range		0.20	0.19	0.07
Standard deviation		0.13	0.13	0.17
Variance	–	0.02	0.02	0.03
Skewness	–	0.30	1.20	2.31
Curtosis	–	–1.27	1.58	4.20

In the samples from the lakes of Pszczewski Landscape Park the mean values of the concentrations of selenium and antimony were similar, while the concentration of arsenic was somewhat higher. The concentration of selenium was similar for the majority of samples, except for the determinations for lakes Wielkie, Mlyriskie, Wedromierz and Konin. The intervals between the quartiles for selenium concentrations are small, which means that the results are concentrated near the mean value. A high value of curtosis also confirms that the results are close. For the concentrations of arsenic and antimony the values of curtosis are lower, and for arsenic even negative, with a greater scatter of results than for selenium, which is also confirmed by a greater interval between the quartiles for the concentrations of arsenic and antimony. The positive values of skewness for all these three elements indicate that among the results concentrated near the mean, the values higher than the mean dominate. The mean values of arsenic and antimony are lower than those determined in the lakes of Drawienski and Wielkopolski National Parks - the areas under special protection [18, 19]. The mean values of arsenic concentration in the samples from Wielkopolski National Park was 0.43 ng/ml, Drawienski National Park 0.95 ng/ml, and Pszczewski Landscape Park 0.45 ng/ml, while the concentration of antimony was 0.49, 0.53 ng/ml and 0.22 ng/ml, respectively. The mean concentrations of arsenic and antimony in the lakes from the area of Pszczewski Landscape Park can indicate the absence of anthropopressure.

The mean concentration of selenium in water samples from the lakes of the Pszczewski Landscape Park was at the level of 0.26 ng/ml. In the samples from Wielkopolski and Drawienski National Parks, it was below the detection limit of 0.15 ng/ml [18, 19]. A higher level of selenium in the lakes from Pszczewski Landscape Park is a consequence of the elevated values of its concentration in the four lakes Wielkie, Mfynskie, Wedromierz and Konin. Since the results reported are the first in the area we are not able to discern whether the higher concentrations of selenium in these lakes follow from geochemical reasons or are a result of anthropopressure.

Summary

The values of microtrace concentrations of arsenic, antimony and selenium determined in the water samples from the lakes in the Pszczewski Landscape Park are similar or even lower than those reported for the lakes from the areas under special protection in the Wielkopolski and Drawienski National Parks. The low values (except those of selenium concentrations in four lakes) might indicate the absence of anthropopressure in the area, which would qualify Pszczewski Landscape Park as a reference area in which the concentrations of different elements corresponding to the geochemical background level could be determined. Knowledge of the background levels of different elements is essential for analysis of different tendencies accompanying environmental changes in a given area.

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Reference

1. CHATTERJEE A, DAS D., MANDAL B.K., CHOWDHURY T.R., SAMANTA G., CHAKRABORTI D., Arsenic in ground water in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part I. arsenic species in drinking water and urine of the affected people, Analyst, **120,** 3, **1995.**
2. LOBINSKI R., ADAMS F.C., Speciation analysis by gas chromatography with plasma source spectrometric detection, Spectrochim. Acta Part B **52,** 1865 **1997.**
3. YUSUF M., SARKI A.C, IDRIS S.B., AYOKO G.A., SINGH K., Separation and determination of selenium (IV) and molybdenum(VI) in mixtures by selective precypitation with potassium thiocarbonate, Talanta, **35,** 496 **1988.**
4. Guidelines for drinking-water quality, WHO, Geneva **1984.**
5. DOJLIDO J.R., BEST G.A., Chemistry of water and water pollution, Ellis Horwood **1993.**
6. KRAJNIAK J.J., The Pszczewski Landscape Park Lakes, (in Polish) Bydgoszcz-Miedzyrzecz **1998.**
7. KAMINSKA K. ed., The Gorzowskie department environment. The live of lakes, (in Polish) Gorzow Wielkopolski **1996.**
8. CHOINSKI A, Directory of Polish Lakes, (in Polish) Wyd. UAM, Poznan **1995.**
9. KABATA-PENDIAS A., PENDIAS H., Biogeochemistry of trace elements, (in Polish) PWN, **1999.**
10. DRIEHAUS W., JEKEL M, Determination of As(III) and total inorganic arsenic by on-line pretreatment in hydride generation atomic absorption spectrometry, "Fresenius" J. Anal. Chem. **343,** 343, **1992.**
11. KANKE M., KUMAMARU T., SAKAI K., YAMAMOTO, Determination of arsenic by graphite furnace atomic absorption spectrometry combined with liquid-liqwid extraktion of arsenomolibdic acid, Anal. Chim. Acta, **247,** 13, **1991.**
12. CHAKRABORTI D., DE JONGHE W, ADAMS F., The determination of arsenic by electrothermal atomic absorption spectrometry with a graphite furnace, Anal. Chim. Acta, **120,** 121, **1980.**
13. AGGETT J., KRIEGMAN M.R., The extent of formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in lake Ohakuri, Water Res., **22,** 407, **1988.**
14. NIEDZIELSKI P., SIEPAK J., Speciation analysis of metals, (in Polish) Wyd. UAM Poznan 47-66, **1998.**
15. NIEDZIELSKI P., SIEPAK J., KOWALCZUK Z., Speciation Analysis of Arsenic, Antimony and Selenium in the Surface Waters of Poznan, Pol. J. Environ. Stud., **8(3),** 183, **1999.**
16. NIEDZIELSKI P., SIEPAK J., KOWALCZUK Z., Speciation Analysis of Arsenic, Antimony and Selenium in the Waters of Lakes Subjected to Various Levels of Anthropopressure, (in Polish) Chemia i inzynieria ekologiczna, **4,** 1, **1999.**
17. NIEDZIELSKI P., SIEPAK J, KOWALCZUK Z., Antimony and Selenium in Waters of the Lednickie Lake, Arch. Environ. Prot., 1, 73, **2000.**
18. NIEDZIELSKI P, SIEPAK J., SIEPAK M, KRASKA M, Occurence of Arsenic, Antimony and Selenium in Surface Waters of Drawiefiski National Park, Pol. J. Environ. Stud., **11(1),** 41, **2002.**
19. NIEDZIELSKI P., SIEPAK J., PELECHATY M., BURCHARDT L., Occurence of Arsenic, Antimony and Selenium in Waters of Wielkopolski National Park Lakes, (in Polish) Morena 7, 69, **2000.**
20. SUN Y.C., YANG J.Y, LIN Y.F., YANG M.H., Determination of antimony(III,V) in natural waters by coprecipitation and neutron activation analysis, Anal. Chim. Acta, **276,** 33, **1993,**
21. TRIPATHI A.N., PATEL K.S.,, Determination of antimony in rain water at the nanogram level with surfactant and brilliant green, Fresenius J. Anal. Chem. **360,** 270, **1998.**
22. DE LA CALLE GUNTINAS M.B, MADRID Y, CAMARA C, Flow-injection and continuous-flow systems to determine antimony(III) and antimony(V) by hydride generation atomic absorption spectrometry, Anal. Chim. Acta, **252,** 161, **1991.**
23. CARRERO P.E., TYSON J.F., Determination of selenium by atomic absorption spectrometry with simultaneous retention of selenium(IV) and tetrahydroborate(III) on an anion-exchange resin followed by flow injection hydride generation from the solid phase, Analyst, **122(9),** 915, **1997.**
24. ORNEMARK U, PETTERSSON J., OLIN A, Determination of total selenium in water by atomic-absorption spectrometry after hydride generation and preconcentration in a cold trap system, Talanta **39,** 1089, **1992.**
25. KUBOTA T, SUZUKI K., OKUTANI T, Determination of total selenium content in sediments and natural water by graphite furnace-atomic absorption spectroscopy after collection as a selenium (IV) complex on activated carbon, Talanta **42,** 949, **1995.**
26. LARRAYA A., COBO-FERNANDEZ M.G., PALACIOS M.A., CAMARA C, Preconcentration of inorganic selenium species (Se (IV) and Se (VI)) in an alumina filled microcolumn and on-line determination by hydride generation atomic absorption spectrometry, Fresenius J. Anal. Chem. **330,** 667, **1994.**