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Analysis of the Spatial and Seasonal Variability of Inorganic Species of Arsenic, Antimony and Selenium in a Shallow Lake Subjected to Moderate Anthropopressure

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Abstract

This study was aimed at recognizing the levels of arsenic, antimony and selenium concentrations in different zones of the lake ecosystem. Total content as well as inorganic species of the studied metalloids were considered. Shallow Lake Jarosławieckie (Wielkopolski National Park) was chosen for the study reported. Water samples were collected in different macrophyte communities of the phytolittoral and in the middle of the lake in early spring and mid-summer 2002. Total concentrations of all studied metalloids in samples collected in summer were lower than in those collected in spring but not all studied mineral species of As, Sb and Se followed the same pattern of changes. Despite seasonal changeability the lack of significant spatial differentiation in the concentrations of the elements studied at the peak of the vegetation season, in particular no differences in their concentrations between the sites in the bulk water in the middle of the lake and the sites in the plant communities was stated. This finding might testify to the fact that the effect of vegetation on the concentration of the elements studied is limited.

Keywords: arsenic, antimony, selenium, speciation, shallow lake, macrophytes

Introduction

Determination of the content of trace elements in a large number of lake ecosystems provides not only a possibility of a general assessment of micropollution but also gives information on the geohydrochemical background of these micropollutants, their sources and migration pathways. Taking into regard the spatial structure of the lake ecosystem and seasonal changes in its biotic and abiotic elements, it seems a natural consequence to study the spatial and seasonal changes in the content of trace elements. The seasonal changes are accompanied by alternations of water mixing and stagnation, increase and decrease in the effect of water organisms, in particular hydromacrophytes, significantly affecting the physico-chemical features of lake ecosystems and development of other organisms [1, 2].

Determination of the total content of a given element in a water sample is not enough to draw conclusions about element migration, bioavailability, toxicity, accumulation and biomagnification. As the properties and behaviour of a given element depend on its physico-chemical species, only speciation analysis can bring more complete information on the water ecosystem and the changes taking place in it [3].

The main species of arsenic met in water ecosystems are arsenates (III), arsenates (V), methylarsenates

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(monomethylarsenic acid MMAA) and dimethylarsenates (dimethylarsenic acid DMAA). The toxicity of arsenic decreases in the sequence: As(III)> As(V)> MMAA> DMAA> other organic arsenic species [4, 5]. Depending on the geological background, the surface waters can contain arsenic in the amount of from one tenth of a nanogram to a few nanograms in a millilitre.

A high affinity of antimony to arsenic suggests a similarity in its behaviour in water ecosystems, especially its distribution and speciation. In natural waters antimony occurs in the concentrations from a few tenth to one nanogram in a millilitre, in highly polluted water its content increases to a few nanograms and can be a parameter in monitoring environmental changes.

In natural waters inorganic species of selenium (IV) and (VI) dominate, undergoing biochemical transformations to organic compounds in bulk water, which undergo further reduction to inorganic species in bottom sediments [6, 7]. In natural waters the content of selenium usually ranges from a few tenths to a few hundredths of a nanogram in a millilitre.

The aim of this study was to estimate the concentration of arsenic, antimony and selenium in the lake ecosystem localized in the protected area of the National Park and simultaneously subjected to the anthropopressure related to the recreational use of the lake. Particular attention was focused on the seasonal changes of these concentrations (samples were collected in early spring, and at the peak of the vegetation season) and the spatial distribution of the elements studied (samples were collected at the middle of the lake and at different plant communities of the phytolittoral). On the basis of the data collected an attempt was made to find out whether the seasonal development and type of vegetation affects the concentration of the trace elements studied, taken up in different amounts by plants with the use of various physiological mechanisms [8].

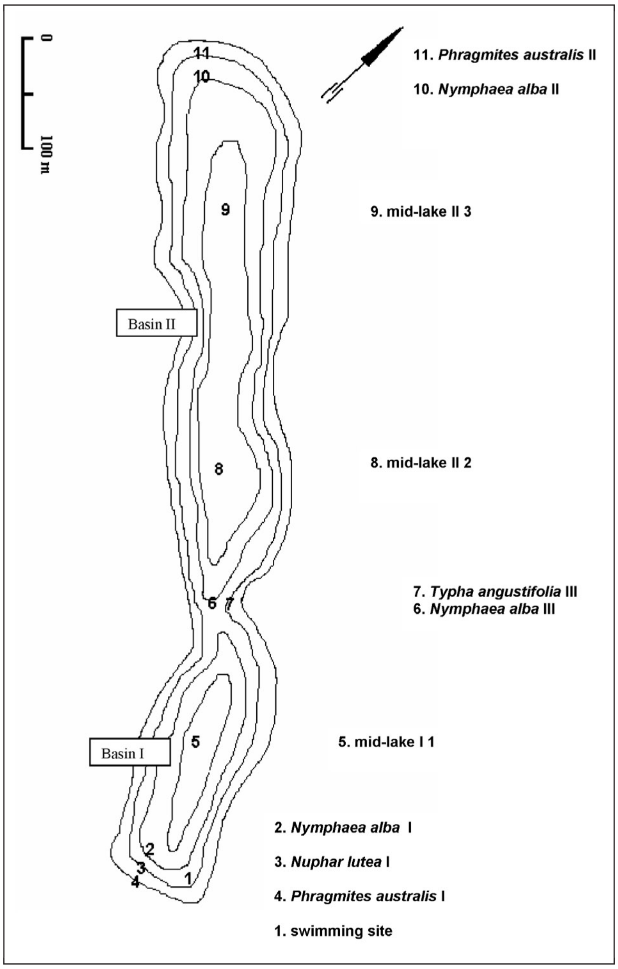

Fig. 1. Map of Lake Jarosławieckie with the distribution of the studied sites.

Study Sites and Methods

Lake Jarosławieckie is localized in the area of the Wielkopolski National Park. It is a post-glacial formation, with no flows, of maximum depth 6.56 m and area of 11.2 ha [9]. It is composed of two basins separated by a wide band of vegetation (Fig. 1). Basin I is smaller but deeper and more intensely used for swimming, while basin II is larger, shallower, less used for swimming but very popular among anglers [10]. The lake shows incomplete stratification with epilimnion and metalimnion developing in summer [9,11].

Sample Collection

Water samples were collected in March 2002 after ice cover disappearance and in July 2002. The sites of sample collection were chosen by taking into account the elongated shape of the lake as well as different types of macrophyte communities in the lake (Fig. 1).

Eight sample collection sites were distributed along the transect coinciding with the longer axis of the lake traversing macrophyte communities as well as open water sites in the middle of the lake (called mid-lake). The sites in vegetation are denoted by the name of the plant predominating a particular community. The site names are accompanied by two numbers, the first referring to the basin and the second to the subsequent points in the lake: *Phragmites australis* (Cav.) Trin ex Steud. I - *Nuphar lutea* (L.) Sibth. et Sm. I - *Nymphaea alba* L. I – mid-lake I 1 – mid-lake II 2 – mid-lake II 3 - *Nymphaea alba* II - *Phragmites australis* II.

In the narrowest place a transversal transect was drawn with two sites: one in the community of *Typha angustifolia* L. III and another one in the community of *Nymphaea alba* III (number III was added to differ the sites in this transect from the remaining sites). Additionally, samples were collected from the central point of the swimming site.

The samples were collected from the surface layer and at the sites in plant communities - from among the plants.

Table 1. The conditions of determination of arsenic, antimony and selenium and parameters of the analytical methods.

		As	Sb	Se
Wavelength / Slit	nm / nm	193.7 / 0.5	217.6 / 0.2	196.0 / 1
Lamp current	mA	7	7	5
Cell temperature	^{O}C	900		
Sample flow rate	ml/min	7.5		
Reductor flow rate (concentration)	ml/min (%)	1 (1)		
Acid flow rate (concentration)	ml/min (mol/l)	1 (1)		
Detection limit (3σ)	ng/ml	0.04	0.04	0.03
Sensitivity	ng/ml	0.09	0.06	0.09
Reproducibility (for 2 ng/ml)	%	1.7	1.9	1.5

Methods of Determinations

The elements studied were determined by the method of atomic absorption spectrometry (AAS) combined with the hydride generation method, at the operational differentiation of the species. The analyses were performed on a fast-sequence spectrometer SpectrAA 220 FS made by Varian, using HCl lamps made by S&J Juniper. Generation of hydrides was conducted in the continuous mode using a VGA-77 attachment with a four-channel peristaltic pump and glass u-separator of the gas phase. Atomisation was performed in an electrothermally heated quartz cell. The heating was controlled by an ETC-60 controller, ensuring temperature programming in the range from room temperature to 999°C to an accuracy of 1°C. The carrier gas was argon. The conditions of determination and the parameters of the analytical method are specified in Table 1. The cycle of determinations of As, Sb and Se in samples of natural water using the AAS method with hydride generation can be described by the following scheme [12]:

1. Direct determination of the content of As (III), Sb (III) and Se (IV) in the samples collected without preliminary processing. The determination was performed by the method of fast sequence in HCl environment, which for arsenic and antimony gives approximate concentrations of their species.
2. Determinations of the total contents of arsenic, antimony and selenium in samples preliminarily reduced by thiourea and HCl.
3. Calculation of the concentrations of the species As (V), Sb (V) and Se (VI).

Statistical Analysis

The empirical distributions of abundances of each metalloid were asymmetrical (W Shapiro-Wilk test, $p<0,05$), however, the asymmetry was not much and permitted the use of the arithmetic mean as the central measure and the standard deviation to characterize the sample. Statistical analysis included clustering based on Ward's method and Euclidean distance generated for the two inorganic species of all elements studied (the missing data for spring collection at one site were replaced by mean values). The diagrams of scatter were also made. The statistical significance of the differentiation in contents of the elements studied was checked by the nonparametric U Mann-Whitney test.

Results

The concentrations of the metalloids studied at particular sites and in two seasons are given in Table 2. As far as arsenic is concerned, in both seasons the concentration of As(III) was visibly higher than that of As(V) species. In summer season the concentration of Se(IV) species was higher than that of Se(VI). In the case of Sb in both seasons and Se in spring the differences in concentrations were rather insignificant. Total contents of all studied metalloids were lower in samples collected at the peak of the vegetation season. However, not all studied species of As, Sb and Se followed the same pattern of changes. In general, the scatter diagrams (Figs 2-4) allow concluding differentiation in the concentration of As, Sb and Se in Lake Jarosławieckie between spring and summer groups of samples, which is particularly to be seen in the case of antimony (Fig. 3). Table 3 provides evidence for the statistical significance of the above-stated seasonal differentiation. It applies to both mineral species of the studied metalloids and their total concentrations with the exception of As(V) and Se(IV) (the differences were not statistically significant).

As it emerges from the scatter diagrams (Figs 2-4) neither in spring nor in summer clear grouping of sites in particular macrophyte communities and in the middle of the lake can be stated, although such differences might have been expected at the peak of vegetation season. Especially in the case of antimony (Fig. 3) the summer concentrations among studied sites were visibly similar.

The clustering based on mineral species of all the metalloids (Fig. 5) generated two groups of samples more

Table 2. Spring and summer concentrations of As, Sb and Se in different sites of Lake Jarosławieckie (see numbers of sites given in Fig. 1).

Site	As(III)	As(V)	As(tot.)	Sb(III)	Sb(V)	Sb(tot.)	Se(IV)	Se(VI)	Se(tot.)
	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}
March 2002									
1	0.42	0.15	0.57	0.30	0.98	0.78	0.11	0.21	0.32
2	0.46	0.10	0.56	0.36	0.26	0.62	0.10	0.16	0.26
3	0.58	0.23	0.81	0.34	0.14	0.48	0.13	0.26	0.39
4	0.54	0.20	0.74	0.38	0.11	0.49	0.19	0.11	0.30
5	0.56	0.05	0.61	0.28	0.25	0.53	0.12	0.20	0.32
6	0.55	0.15	0.70	0.32	0.23	0.55	0.17	0.12	0.29
7	0.52	0.18	0.70	0.38	0.38	0.76	0.19	0.10	0.29
8	0.43	0.07	0.50	0.32	0.30	0.62	0.27	0.05	0.33
9	0.43	0.21	0.64	0.35	0.13	0.48	0.09	0.17	0.26
10	0.44	0.08	0.52	0.38	0.38	0.76	0.09	0.22	0.31
11	-	-	-	0.30	0.17	0.47	0.14	0.07	0.21
Mean	0.49	0.14	0.64	0.34	0.30	0.60	0.14	0.15	0.30
SD	0.06	0.06	0.10	0.04	0.24	0.12	0.06	0.07	0.05
July 2002									
1	0.31	0.21	0.52	0.07	0.04	0.11	0.14	0.08	0.22
2	0.33	0.21	0.54	0.08	0.03	0.11	0.17	0.06	0.23
3	0.32	0.25	0.57	0.06	0.05	0.11	0.15	0.09	0.24
4	0.35	0.17	0.52	0.07	0.05	0.12	0.17	0.05	0.22
5	0.34	0.2	0.54	0.06	0.07	0.13	0.19	0.05	0.24
6	0.38	0.16	0.54	0.06	0.06	0.12	0.19	0.04	0.23
7	0.36	0.18	0.54	0.05	0.07	0.12	0.17	0.07	0.24
8	0.36	0.23	0.59	0.06	0.04	0.10	0.17	0.07	0.24
9	0.33	0.19	0.52	0.07	0.03	0.10	0.18	0.06	0.24
10	0.39	0.14	0.53	0.05	0.06	0.11	0.18	0.08	0.26
11	0.33	0.16	0.49	0.05	0.06	0.11	0.17	0.06	0.23
Mean	0.34	0.19	0.54	0.06	0.05	0.11	0.17	0.06	0.24
SD	0.03	0.03	0.03	0.01	0.01	0.01	0.02	0.02	0.01

related to the sampling season than to the location of sites. In other words, it rather evidences seasonal changeability of As, Sb and Se concentrations in Lake Jarosławieckie than the spatial one. However, the difference in linkage distance within the groups of spring and summer samples suggests greater site-to-site variability and thus environmental heterogeneity in the studied lake during the spring season. Additionally, the swimming site was separated from the rest of spring samples. This might have resulted from the concentrations of Sb determined at this site in spring (Fig. 3). In the summer season closely clustered were some samples taken at the helophyte sites as well as at the nymphaeid ones. Although not all samples followed the same pattern of clustering.

Discussion

As follows from earlier determinations of the contents of As, Sb and Se in natural waters from the area of Wielkopolski National Park, the total content of these elements is in general low [13], corresponding to the level implied by the natural geochemical environment. The results reported in this work support this finding, despite the intense recreational use of the lake [9, 13, 14]. Even in the case of samples collected from the swimming site the metalloids concentrations (with the exception of Sb) did not differ clearly from the remaining sampling sites. However, it should be emphasized that irrespective of the season the concentrations of As(III) species (more toxic) were higher than those of As(V), although for natural waters the reverse was reported [13 and references therein].

The lack of significant spatial differentiation in the concentrations of the elements studied in the peak of the vegetation season and in particular no differences in their concentrations between the sites in the bulk water in the middle of the lake and the sites in the plant communities testify to the fact that the effect of vegetation on the concentration of the elements studied is limited. Hence, in other words, the effect of intake of As, Sb and Se by macrophytes might be assumed to be rather insignificant. This conclusion is supported by insignificant differences in the concentration of these elements among the sites in plant communities and between them and the middle of the lake (this being shown by small linkage distances, Fig. 5), much lower than seasonal differences. It should be added that the mechanism of As intake by plants has been recognised; however, the mechanisms and intensity of intake of the other elements are only partly known

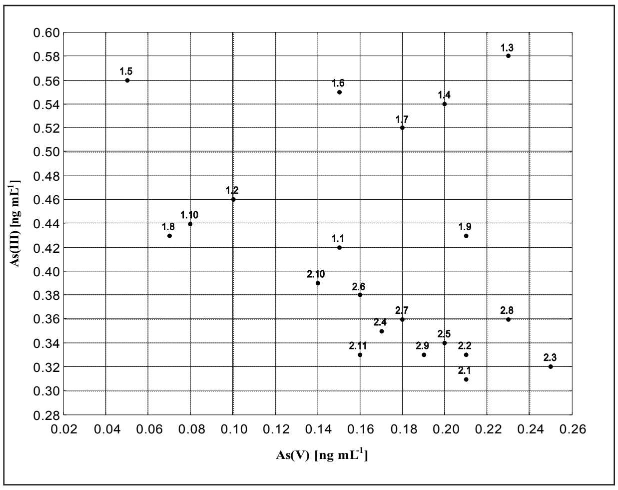

Fig. 2. Spring and summer concentrations of As(III) and As(V) in different sites of Lake Jarosławieckie (1.1-1.11 – samples collected in March 2002; 2.1-2.11 – samples collected in July 2002; 1-11 – sites numbers, for details see Fig. 1).

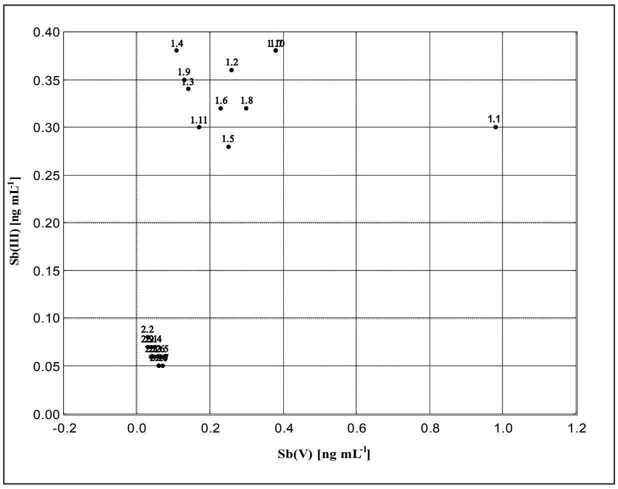

Fig. 3. Spring and summer concentrations of Sb(III) and Sb(V) in different sites of Lake Jarosławieckie (1.1-1.11 – samples collected in March 2002; 2.1-2.11 – samples collected in July 2002; 1-11 – sites numbers, for details see Fig. 1).

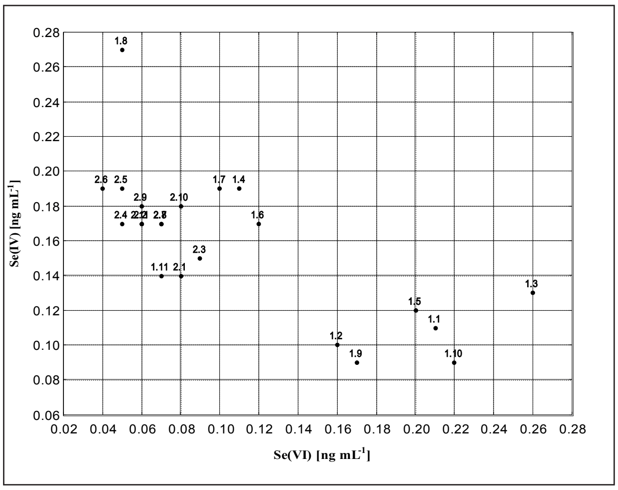

Fig. 4. Spring and summer concentrations of Se(IV) and Se(VI) in different sites of Lake Jarosławieckie (1.1-1.11 – samples collected in March 2002; 2.1-2.11 – samples collected in July 2002; 1-11 – sites numbers, for details see Fig. 1).

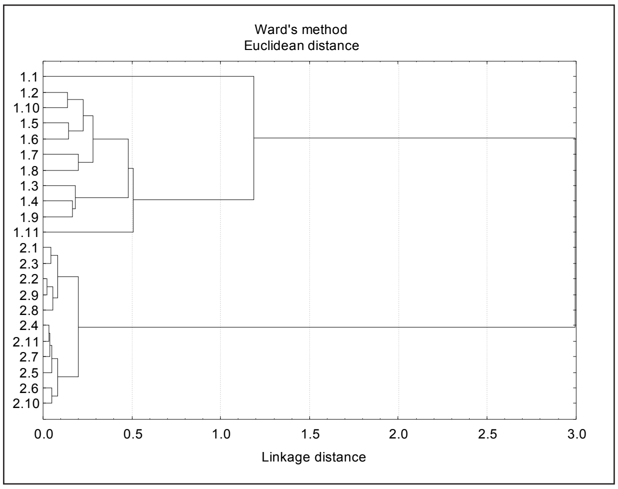

Fig. 5. Results of cluster analysis generated on the basis of mineral speciation forms of As, Sb and Se studied in Lake Jarosławieckie in spring and summer 2002 (1.1-1.11 – samples collected in March 2002; 2.1-2.11 – samples collected in July 2002; 1-11 – sites numbers, for details see Fig. 1).

Table 3. Statistically significant differences between spring and summer concentrations of As, Sb and Se studied in Lake Jarosławieckie (2002).

Variable	Sum.rank spring	Sum.rank summer	N spring	N summer	U	Z	p
As(III)	165.0000	66.0000	10	11	0.00000	3.88055	0.000006
As(tot)	143.0000	88.0000	10	11	22.00000	2.34057	0.019665
Sb(III)	187.0000	66.0000	11	11	0.00000	3.99993	0.000003
Sb(V)	187.0000	66.0000	11	11	0.00000	3.98287	0.000003
Sb(tot)	187.0000	66.0000	11	11	0.00000	4.00452	0.000003
Se(VI)	174.0000	79.0000	11	11	13.00000	3.13060	0.001040
Se(tot)	175.0000	78.0000	11	11	12.00000	3.21300	0.000765

[8]. In general, it seems that the decrease in the total concentrations of the elements studied in the period from spring to summer might be related to physical and chemical interactions such as pH value [15], hardness, and the presence of dissolved organic compounds [16]. The effect of plankton is also possible, although there are data indicating the lack of relation between the concentration of As and planktonic algae [17].

There is one more factor worth analyzing, that is the mictic type of the lake studied. In Lake Jaroslawieckie complete thermal stratification of water can develop only in a short period [11]. Usually in summer the epilimnion develops and the beginning of the thermocline is observed. These properties of the lake waters can definitely affect water circulation. Frequent mixing of water masses can mask the effect of macrovegetation and, in the case of elements less important for plants than, e.g., nutrients, lead to spatial homogeneity of water.

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