# Microtrace Level Speciation of Arsenic, Antimony and Selenium in Lake Waters of the Pszczewski Landscape Park, Poland

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## Abstract

This paper reports results of determination of arsenic, antimony and selenium inorganic species in samples of surface water from the lakes of the Pszczewski Landscape Park located in western Poland. Concentrations of total arsenic, antimony and selenium, determined by atomic absorption spectrometry with generation of hydrides, were up to 0.66 ng/ml, 0.62 ng/ml and 0.76 ng/ml, respectively, at respective detectability limits of 0.04 ng/ml, 0.04 ng/ml and 0.03 ng/ml. For arsenic and antimony the concentrations of the two species determined (As(III)/As(V) and Sb(III)/Sb(V)) were similar, while for selenium the Se(IV) species was dominant.

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

## Introduction

Determination of total concentration of a given element in a water sample is insufficient for drawing conclusions about its toxicity, bioavailability, migration, accumulation or biomagnification. The properties of a given element depend on the type of the physico-chemical form in which it occurs in a given environment. Speciation analysis, helping to establish the concentrations of different species of elements or chemical compounds, provides more comprehensive information on the status of a given ecosystem. Therefore, speciation analysis, often performed for the first time for samples from certain areas, is essential for interpretation of environmental results [1].

The main arsenic species met in water samples are arsenates (III), (V), methyl- (mono methylarsenic acid MMAA) and dimethyl-arsenates (dimethylarsenate acid DMAA). The concentration of As(V) is usually higher than that of the species with As(III). The toxicity of arsenic species decreases in the sequence: As(III)> As(V)> MMAA> DMAA> other organo-arsenic compounds [2,3]. The concentration of arsenic species in surface waters can vary from a tenth of a nanogram to micrograms of a millilitre, depending on the geological surrounding. High chemical similarity between antimony and arsenic implies a supposition that their distribution and speciation in natural waters is similar. The concentration of antimony in natural waters varies from a tenth of a nanogram to one nanogram per millilitre. In polluted waters (municipal waste, dumping ground waste) this increases to a few nanograms and can be a monitoring parameter. In natural waters the dominant forms of selenium are inorganic species with (IV) and (VI). The inorganic selenium compounds in bulk water undergo conversions to organic

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compounds, which are further reduced to inorganic compounds in bottom sediments [4,5]. The concentration of selenium in natural waters can vary from hundredths to tenths of a nanogram in a millilitre.

The Pszczewski Landscape Park (Fig.1) occupies an area in the mid-eastern part of Lubuskie voivodship and western Wielkopolskie voivodship, in the middle of the triangle delineated between Gorzów Wielkopolski, Poznań and Zielona Góra in western Poland. It was founded in 1986 to preserve and protect the unique landscape, vegetation and culture of the Lubuskie and Wielkopolskie Lake Districts, which it partly includes. Total area of the Park, including the protective belt, is over 45 thousand ha, of which the park itself occupies 12,200 ha, divided into two regions. The first, of 1,970 ha covers the area of the Kamionka river valley, between Lewice and Kamionna. The second (area of research) covers an area of 10,250 ha, localised along the middle section of the Obra river and the sequence of lakes spreading from Trzciel in the south through Pszczew to Lubikowo and Rokitno in the north/west. The two complexes of the strict park are surrounded by a protective belt in an area in 33,080 ha. The area of the park and the protective belt includes 6 communes: Pszczew, Przytoczna, Międzychód, Miedzichowo, Międzyrzecz and Trzciel. The young-glacial landscape of the park is characterised by great diversity of terrain forms and richness of flora and fauna [6-8].

## Experimental

### Apparatus and Solutions

Determinations were made using atomic absorption spectrometry (AAS) in combination with the generation of hydrides, at operational discernment of species. De-

Table 1. The conditions of determination of arsenic, antimony and selenium.

|  |  | 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 | |
| Sample flow rate | ml/min | | 7.5 | |
| Reductor flow rate | ml/min | | 1 | |
| Reductor concentration | % | | 1 | |
| Acid flow rate | ml/min | | 1 | |
| HCl concentration | mol/l | | 1 | |
| Delay time | s | | 30 | |
| Time of measurement | s | | 1 | |
| Number of repetitions | - | | 6 | |

terminations were made on a fast-sequential atomic absorption spectrometer SpectrAA 220 FS made by Varian, with HCL lamps made by S&J Juniper. Hydrides were generated in continuous mode in a VGA-77 attachment with a four-channel peristaltic pump and glass u-separator of gas phase. Atomisation was performed in a quartz cell electrothermally heated by an ETC-60 controller with temperature programming in the range from room temperature to $999^0$ C , to an accuracy of $1^0$ C. Argon was a carrier gas (Table 1).

All the reagents were of analytical purity, water was redistilled and Milli-Q (Millipore) purified. Standard solutions were made by dissolving sodium m-arsenite (III), sodium arsenate (V), potassium hexahydroxyantimonate (V) and potassium antimony (III) tartrate, sodium selenite(IV), sodium selenate (VI) at a final concentration of 1 mg/ml. A solution of the concentration 1 µg/ml, made by dilution, was stable for about 3 months, and was stored in a polyethylene Nalgene vessel. Lower concentration standards were made on the day of determination using polyethylene vessels. Sodium borohydride solutions were made by dissolving sodium borohydride in a 1% solution of sodium hydroxide on the day of determination. The solutions were clear and did not need filtration. Hydrochloric acid solutions were made by dissolving the acid of ρ=1.19 g/ml. A 1 mol/l solution of thiourea was made by dissolving 15.2 g of thiourea in 200 ml of water.

### The Methods of Determining Arsenic, Antimony and Selenium

The cycle of determinations of As, Sb and Se in samples of underground waters by AAS with hydride generation can be described as follows:
1. Direct determination of As(III), Sb(III) and Se(IV) in the samples without their preliminary treatment. Fast-sequential determinations of As(III), Sb(III), Se(IV) were performed in an environment of HCl acid, which for arsenic and antimony means that the value obtained is approximate and the experimentally found correction factors have to be applied: 0.75 and 0.85 for As and Sb, respectively.
2. Determinations of total arsenic, antimony and selenium, in the samples after preliminary reduction with thiourea and hydrochloric acid.
3. Calculations of the contents of As (V), Sb (V) and Se (VI).

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 concentrations at which they occur in the natural environment. 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 and spiked samples (Table 3).

Table 2. Parameters of the analytical methods for determining arsenic, antimony and selenium by AAS with generation of hydrides (n=60).

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

Recovery is high, satisfactory for trace element analysis and comparable to the results reported by other authors, which means that the accuracy of the results is also satisfactory. Two separate determinations were performed for each sample and for each of them the spectrometric measurement was repeated 6 times.

## Sample Collection and Preparation

Studied samples were collected twice (in November 2001 and February 2002). 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 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 AAS analyses portions of 1 ml of hydrochloric acid (10 mol/l) and 1 ml of a thiourea solution (1 mol/l) were added to 20 ml of 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 using the AAS method, applying the fast sequential technique, and therefore all elements were determined in the same sample.

## Results and Discussion

### Speciation of Arsenic, Antimony and Selenium

The concentrations of As(III), Sb(III), Se(IV) and total contents of these elements were determined in 34 surface water samples from the lakes of the Pszczewski Landscape Park. The concentrations of As(V), Sb(V) and Se(VI) were corrected as indicated in the methods. The results are given in Table 4.

The concentration of arsenic is low, in the majority of the samples studied even lower than the mean value determined for the lakes of Wielkopolski National Park [9] and Drawieński National Park [10], both located in western Poland, of 0.43 ng/ml and 0.95 ng/ml, respectively. Nevertheless, in the majority of the samples a small prevalence of the species with As(III) was observed [11,12]. The content of selenium was slightly higher than in the samples from the lakes of the Wielkopolski [9] and Drawieński National Parks [10], where it was below 0.15 ng/ml. In most samples selenium occurred as Se (IV) species, and the prevalence of this form was much greater than for arsenic [13]. The concentrations of antimony are also lower than the mean ones in the samples from the lakes of the Wielkopolski (0.49 ng/ml) and Drawieński (0.53 ng/ml) National Parks. In the samples collected in autumn (November) the total concentration of antimony is greater and the Sb(V) species dominate [14], in the samples collected in February total concentration is lower and the prevalent species are those with Sb(III). These differences can be explained by seasonal changes in temperature and the partial winter freezing of the lakes. The lack of such differences in the concentrations of different species of arsenic and antimony collected in November and February indicates a stronger relation of the type of antimony species to seasonal changes in the water environment.

## Statistical Analysis of Results

The results of determinations of arsenic, selenium and antimony in samples of surface water have been subjected to statistical analysis. The ensembles for statistical analysis have been distinguished on the basis of the criterion of collection from the same region.

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, kurtosis). The arith-

Table 3. Results of determinations of arsenic, antimony and selenium in the certified reference material SLRS-3 and spiked samples (n=6).

|  | Sample | The certified concentration ng/ml | Determined concentration ng/ml | Recovery % |
|---|---|---|---|---|
| **As** | SLRS-3 | 0.72 ± 0.05 | 0.65 ± 0.02 | 90 |
| **Sb** | SLRS-3 | 0.12 ± 0.01 | 0.13 ± 0.01 | 108 |
| **Se** | SLRS-3 | Not certified | 0.11 ± 0.02 | - |
|  |  | Added ng/ml | Found ng/ml | Recovery % |
| **As** | Lake's water | 0.5 | 0.47 | 94 |
| **Sb** | Lake's water | 0.5 | 0.52 | 104 |
| **Se** | Lake's water | 0.5 | 0.49 | 98 |

metic 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. Skewness informs about the asymmetry of results, for symmetric results it is zero, for right-hand side asymmetry it takes positive values and for left-hand side asymmetry - negative. Kurtosis 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 to interpret the obtained data.

As follows from the mean values of the arsenic species As(III) and As(V) in the samples, the species with As(III) were dominant, but the difference between them relatively small (Table 5). Similar were the differences between the maximum and minimum values of the species concentrations, median, upper and lower quartile. Small values of standard deviation prove a small scatter of results. Low positive values of skewness indicate almost symmetrical distribution of results with respect to the mean value, with a small prevalence of values higher than the mean. The values of kurtosis inform about a different character of statistical distribution of the results for the two arsenic species, for As(III) the negative value indicates a broadening of the distribution curve.
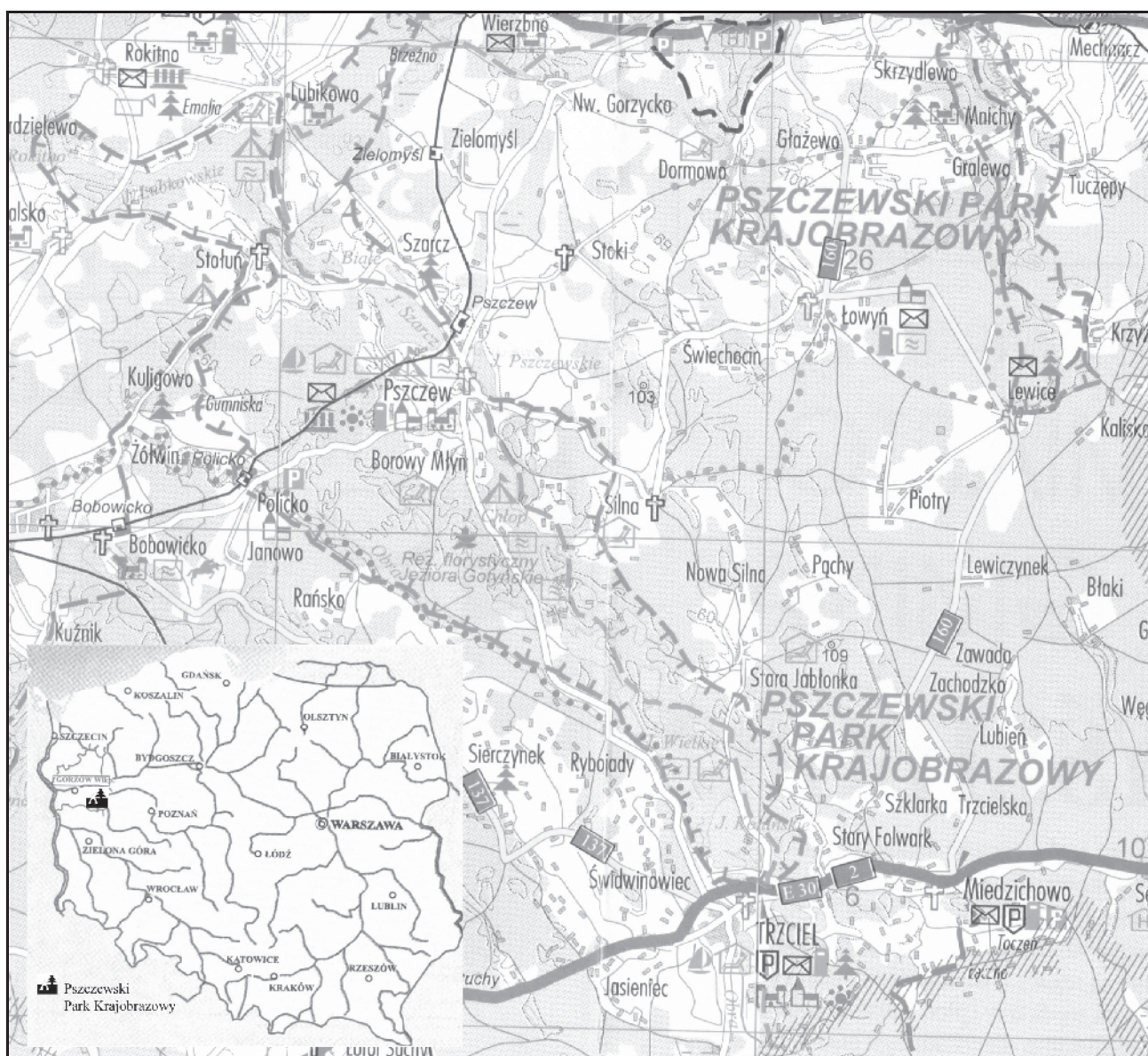


Fig. 1. The Pszczewski Landscape Park - the area of study.

Statistical analysis of the results obtained for antimony brings different conclusions (Table 6). The mean concentration of the species with Sb(III) is insignificantly lower than that of the species with Sb(V), so that these two values can be treated equally. The values of the minimum and maximum concentrations, median and quartiles are also insignificantly smaller for the species with Sb(III) than for those with Sb(V). The values of standard deviation indicate a relatively great scatter of results, and the positive values of skewness prove that the values higher than the mean one dominate. The positive value of kurtosis for the results of the species with Sb(III) indicate

Table 4. Concentrations of different species of arsenic, antimony and selenium in the water samples of the Pszczewski Landscape Park (ng/ml)

| Lake | As(III) | As(V) | As$_{total}$ | Sb(III) | Sb(V) | Sb$_{total}$ | Se(IV) | Se(VI) | Se$_{total}$ |
|---|---|---|---|---|---|---|---|---|---|
| 10.11.2001 | | | | | | | | | |
| Wielkie - south | 0.33 | 0.33 | **0.66** | 0.33 | 0.18 | **0.51** | 0.16 | 0.15 | **0.31** |
| Wielkie - island | 0.34 | 0.29 | **0.63** | 0.26 | 0.05 | **0.31** | 0.17 | 0.11 | **0.28** |
| Chłop | 0.29 | 0.15 | **0.44** | 0.14 | 0.06 | **0.30** | 0.11 | 0.08 | **0.19** |
| Czarne - south | 0.26 | 0.06 | **0.32** | < 0.04 | 0.38 | **0.38** | 0.10 | 0.16 | **0.26** |
| Białe - north | 0.29 | 0.13 | **0.42** | < 0.04 | 0.17 | **0.17** | 0.15 | 0.07 | **0.22** |
| Pszczewskie-west | 0.16 | 0.12 | **0.28** | < 0.04 | 0.23 | **0.23** | 0.10 | 0.09 | **0.19** |
| Szarcz - north | 0.31 | 0.24 | **0.55** | < 0.04 | 0.20 | **0.20** | 0.13 | 0.04 | **0.17** |
| Szarcz – south | 0.42 | 0.24 | **0.66** | < 0.04 | 0.27 | **0.27** | 0.10 | 0.05 | **0.15** |
| Stołunek – south | 0.26 | 0.18 | **0.44** | < 0.04 | 0.25 | **0.25** | 0.10 | 0.08 | **0.18** |
| Stołunek – north | 0.32 | 0.21 | **0.53** | 0.05 | 0.15 | **0.20** | 0.20 | <0.03 | **0.20** |
| Pszczewskie – south | 0.19 | 0.12 | **0.31** | 0.05 | 0.20 | **0.25** | 0.11 | <0.03 | **0.11** |
| Cegielniane | 0.11 | 0.14 | **0.25** | 0.11 | 0.10 | **0.21** | 0.20 | <0.03 | **0.20** |
| Wędromierz-west | 0.39 | 0.25 | **0.64** | 0.18 | 0.18 | **0.36** | 0.64 | 0.10 | **0.74** |
| Wędromierz – north | 0.36 | 0.21 | **0.57** | 0.17 | 0.10 | **0.27** | 0.44 | 0.32 | **0.76** |
| Młyńskie | 0.26 | 0.14 | **0.40** | 0.14 | 0.22 | **0.36** | 0.57 | 0.04 | **0.61** |
| Konin – north | 0.28 | 0.27 | **0.55** | 0.24 | 0.09 | **0.33** | 0.34 | 0.37 | **0.71** |
| Żydowske - south | 0.15 | 0.13 | **0.28** | 0.26 | 0.36 | **0.62** | 0.16 | 0.04 | **0.20** |
| Żydowskie - north | 0.17 | 0.14 | **0.31** | 0.09 | 0.30 | **0.39** | 0.21 | <0.03 | **0.21** |
| Lubikowskie – south | 0.39 | 0.22 | **0.61** | < 0.04 | 0.19 | **0.19** | 0.14 | 0.05 | **0.19** |
| Lubikowskie-west | 0.40 | 0.25 | **0.65** | < 0.04 | 0.16 | **0.16** | 0.16 | 0.07 | **0.23** |
| 17.02.2002 | | | | | | | | | |
| Młyńskie – east | 0.20 | 0.19 | **0.39** | 0.14 | < 0.04 | **0.14** | 0.26 | <0.03 | **0.26** |
| Młyńskie –beach | 0.21 | 0.15 | **0.36** | 0.15 | < 0.04 | **0.15** | 0.26 | <0.03 | **0.26** |
| Młyńskie – south | 0.22 | 0.17 | **0.39** | 0.07 | 0.05 | **0.12** | 0.24 | <0.03 | **0.24** |
| Szarcz – east | 0.35 | 0.20 | **0.55** | 0.09 | < 0.04 | **0.09** | 0.12 | 0.07 | **0.19** |
| Szarcz – north | 0.34 | 0.24 | **0.58** | 0.06 | 0.05 | **0.11** | 0.11 | 0.08 | **0.19** |
| Szarcz –beach | 0.40 | 0.19 | **0.59** | 0.07 | < 0.04 | **0.07** | 0.05 | 0.12 | **0.17** |
| Chłop – forest | 0.18 | 0.19 | **0.37** | 0.08 | < 0.04 | **0.08** | 0.11 | 0.11 | **0.22** |
| Chłop -east | 0.18 | 0.19 | **0.37** | 0.07 | < 0.04 | **0.07** | 0.12 | 0.10 | **0.22** |
| Chłop – north | 0.19 | 0.22 | **0.41** | 0.06 | 0.06 | **0.12** | 0.10 | 0.12 | **0.22** |
| Pszczewskie –south | 0.20 | 0.17 | **0.37** | 0.11 | < 0.04 | **0.11** | 0.13 | 0.05 | **0.18** |
| Pszczewskie – east | 0.20 | 0.22 | **0.42** | 0.18 | < 0.04 | **0.18** | 0.17 | <0.03 | **0.17** |
| Pszczewskie – west | 0.18 | 0.20 | **0.38** | 0.12 | 0.07 | **0.19** | 0.10 | 0.07 | **0.17** |
| Stobno – east | 0.20 | 0.17 | **0.37** | 0.10 | < 0.04 | **0.10** | 0.11 | 0.09 | **0.20** |
| Stobno - south | 0.21 | 0.12 | **0.33** | 0.06 | 0.05 | **0.11** | 0.09 | 0.11 | **0.20** |

Table 5. Statistical parameters of the results of arsenic-particular species in water of the lakes from Pszczewski Landscape Park.

|  |  | As(III) | As(V) |
|---|---|---|---|
| Number of samples | - | 34 | 34 |
| Mean concentration | ng/ml | **0.26** | **0.19** |
| Minimum concentration | ng/ml | 0.11 | 0.06 |
| Maximum concentration | ng/ml | 0.42 | 0.33 |
| Max-min range | ng/ml | 0.31 | 0.27 |
| Median | ng/ml | 0.26 | 0.19 |
| Lower quartile | ng/ml | 0.19 | 0.14 |
| Upper quartile | ng/ml | 0.34 | 0.22 |
| Quartiles range | ng/ml | 0.15 | 0.08 |
| Standard deviation | ng/ml | 0.09 | 0.06 |
| Variance | - | 0.007 | 0.003 |
| Skewness | - | 0.28 | 0.21 |
| Kurtosis | - | -1.14 | 0.22 |

Table 6. Statistical parameters of results of determination of antimony-particular species in water of the lakes from Pszczewski Landscape Park.

|  |  | Sb(III) | Sb(V) |
|---|---|---|---|
| Number of samples | - | 34 | 34 |
| Mean concentration | ng/ml | **0.09** | **0.12** |
| Minimum concentration | ng/ml | <0.04 | <0.04 |
| Maximum concentration | ng/ml | 0.33 | 0.38 |
| Min-max range | ng/ml | 0.33 | 0.38 |
| Median | ng/ml | 0.07 | 0.10 |
| Lower quartile | ng/ml | 0.04 | 0.04 |
| Upper quartile | ng/ml | 0.14 | 0.20 |
| Quartiles range | ng/ml | 0.10 | 0.20 |
| Standard deviation | ng/ml | 0.08 | 0.11 |
| Variance | - | 0.007 | 0.01 |
| Skewness | - | 1.05 | 0.66 |
| Kurtosis | - | 0.69 | -0.48 |

Table 7. Statistical parameters of results of determination of selenium-particular species in water of the lakes from Pszczewski Landscape Park.

|  |  | Se(IV) | Se(VI) |
|---|---|---|---|
| Number of samples | - | 34 | 34 |
| Mean concentration | ng/ml | **0.18** | **0.08** |
| Minimum concentration | ng/ml | 0.05 | <0.03 |
| Maximum concentration | ng/ml | 0.64 | 0.37 |
| Min-max range | ng/ml | 0.59 | 0.37 |
| Median | ng/ml | 0.14 | 0.07 |
| Lower quartile | ng/ml | 0.10 | <0.03 |
| Upper quartile | ng/ml | 0.19 | 0.11 |
| Quartiles range | ng/ml | 0.09 | 0.10 |
| Standard deviation | ng/ml | 0.13 | 0.08 |
| Variance | - | 0.02 | 0.007 |
| Skewness | - | 2.35 | 2.02 |
| Kurtosis | - | 5.46 | 5.38 |

a high and narrow curve of their distribution, while the negative value of kurtosis for the results of determinations of Sb(V) species points to a broadening of the distribution curve.

Analysis of the results of selenium concentration shows a clear dominance of the species with Se(IV) as the mean concentration of these species is over twice higher than that of the species with Se(VI) (Table 7). The values of the minimum, maximum concentrations, median, upper and lower quartiles take higher values for the Se(IV) species. The values of standard deviation testify to a significant scatter of result both of Se(IV) and Se(VI) species concentrations. The positive values of skewness obtained for the data for both species indicate that the values greater than the mean value dominate. The positive and relatively high values of kurtosis show that the distribution curve is not broadened.

## Conclusion

Concentrations of total arsenic, antimony and selenium determined in the water of the lakes studied are low, characteristic of samples from areas of limited human impact. For arsenic and antimony the concentrations of the two species determined As(III)/As(V) and Sb(III)/Sb(V) were very similar. For selenium the species with Se(IV) was dominant. Moreover, for antimony changes in the concentration and species contribution were noted between the samples collected in November and February. The low concentrations of the elements studied testify to limited anthropopressure in the area studied.

## Acknowledgements

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