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Development and validation of HPLC–ICP-MS method for the determination inorganic Cr, As and Sb speciation forms and its application for Pławniowice reservoir (Poland) water and bottom sediments variability study

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ABSTRACT

The optimization of methodology for determination and extraction of inorganic ionic As(III)/As(V), Cr(III)/Cr(VI) and Sb(III)/Sb(V) forms in water and easily-leached fractions of bottom sediments by HPLC–ICP-MS were studied. In paper total concentration of As, Cr, Sb, pH and redox potential were determined. Ions were successfully separated on Dionex IonPac AS7: As(III), As(V), Sb(III), Sb(V) and Dionex IonPac AG7: Cr(III), Cr(VI) with LOD 0.18 μg/L, 0.22 μg/L, 0.009 μg/L, 0.012 μg/L 0.11 μg/L, 0.17 μg/L, respectively. Water and bottom sediments samples were collected monthly from Pławniowice Reservoir, in three-point transects between March and December 2012. In the bottom water predominated As(III) and Cr(III) forms and the highest content of Cr(III) was in the water flowing into the Pławniowice Reservoir. Concentration of Cr(VI) increased in the bottom water in the spring and summer (April–July), while decreasing of the Cr(III) content was associated with the release of Cr(VI) from sediment into the water. Studies have shown that antimony accumulates in reservoir sediments and its reduced form was predominated except May and October–November period when high concentrations of Sb(V) was present. In contrast As(V) was the predominant arsenic form in bottom sediments.

1. Introduction

The notion of *speciation analysis* was first used in the literature in 1993. Initially, it was defined as “movement and transformation of the element forms in the environment” [1]. The results of toxicological tests demonstrate that specific element forms, rather than the total element content, often have a profound impact on living organisms. For that reason, understanding different forms of the element occurrence is more important than knowing total element content in the sample. Generally, it is believed that elements in ionic forms demonstrate biological activity and toxicity to living organisms [2–6]. Speciation analysis concerns elements that occur at different oxidation states. It helps to identify them and determine their concentrations. It is particularly useful for elements whose toxicological properties largely depend on the oxidation states (e.g. Cr(III)/Cr(VI), As(III)/As(V), Sb(III)/Sb(V)). Toxicologists and analysts find As, Sb and Cr extremely interesting. Their qualities vary as they depend on the oxidation state at which these elements occur.

Toxicological tests require limits of analyte detection to be lower and lower. Consequently, the research methods available so far have not always met the necessary requirements. To support analyses, various methods of detection and separation are combined as the so-called hyphenated methods. The HPLC–ICP-MS method seems the most promising [7].

Antimony is widespread in the natural environment. It comes from both natural processes and human activity. It occurs in the forms of Sb(III) and Sb(V). Its content in rivers is typically lower than 1 μg/L and does not usually exceed 0.5 μg/L in drinking water. Sb concentration has considerably increased in water systems as a result of human activity over the last decades. It is mainly related to copper ore processing industry and coal and municipal waste combustion. The industry of the Upper Silesian Industrial Region mainly rests upon black coal mining and metallurgy. Consequently, Sb concentration levels in the Upper Silesian drinking water deserve careful attention. The biological role of Sb has not been conclusively established yet. The element is toxic, like As, even at low concentration levels. Sb(III) is very interesting for speciation analysis as it is 10 times as toxic as Sb(V) [8–13].

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Arsenic can occur in four forms in the environment, i.e. As^{+5}, As^{+3}, As^0, As^{-3}, which depend on the redox conditions. Thus, the natural As content can range between decimal values and tens of μg/L. The anthropogenic sources of As are: coal combustion, mining of mineral resources, battery production, soil fertilization and metallurgical industry. The results of As determinations can be found in many studies [14–18]. Many cases of chronic As poisoning result from drinking water whose As concentration is high [19–23].

Chromium is an element whose speciation forms differ significantly in terms of chemical and toxicological properties. It is thought that Cr(III) compounds positively influence living organisms. They are responsible for correct glucose metabolism in mammals. Additionally, they easily undergo complexation processes with various substances present in environmental samples. On the other hand, Cr(VI) compounds are highly toxic. Their inhalation causes lung inflammation and asthma. Their contact with skin results in allergies and dermatoses [24]. The properties of Cr and its compounds and the methods of their determination were discussed in the work [25]. The literature examples of Cr(III) and Cr(VI) determinations with hyphenated methods were described in [26–29].

The aim of the following research was to observe space and time relations in the changes of concentrations of selected As, Sb and Cr inorganic forms in water and bottom sediments of the limnic ecosystem. The dissimilarities resulted from the variations in the environmental conditions such as the oxygen content, temperature, pH or redox potential. The migration of As, Sb and Cr ions from bottom sediments to water, or, conversely, from water to bottom sediments is a complex process. Understanding transformations in water reservoir ecosystems depends on recognizing proportions of particular ionic forms. There was the possibility that highly toxic As(III), Cr(VI) and Sb(III) ionic forms could be released into the pelagic zone. Consequently, the analyses were performed to check whether the bottom sediments deposited in the reservoir could pose an environmental threat.

The following study concerns the optimization of the methodology for determination and extraction of inorganic ionic forms of arsenic, antimony and chromium in water and easily-leached fractions of bottom sediments with the hyphenated method of HPLC–ICP-MS. The use of an anion exchange column Dionex IonPac AS7 for the simultaneous separation of inorganic forms of speciation antimony and arsenic (As(III)/As(V), Sb(III)/Sb(V)) was not yet applied. The analyses were carried out in order to define threats related to the toxic forms of the discussed metals and metalloids. Consequently, possessing such information should support assessing various risks connected with the Pławniowice reservoir water usage. Such research had not been conducted at Pławniowice Reservoir before.

2. Material and methods

2.1. Sampling

Samples of bottom water and sediments were collected monthly between March and December 2012 at three sampling points forming a transect (Fig. 1). Bottom sediment samples were collected in the core form with a Birge–Eckmann sampler. The layers with thickness of 0–5 cm and 15–20 cm were sampled from the sediment core. Bottom water was sampled with a Ruttner water sampler.

2.2. Sample preparation and research methodology

Bottom water samples were placed in 1 L high-density polyethylene (HDPE) containers so as to avoid the unnecessary aeration. Samples were divided into two parts, directly after their arrival at the laboratory. The first part was acidified with spectral pure nitric acid (Merck, Germany). Afterwards, it was filtered through a 0.22 μm PES syringe filter and used to determine total As, Sb and Cr contents with ICP-MS. The other part of the laboratory bottom water sample was placed into an HDPE container and kept at the temperature of −22 °C until the analysis was performed (no longer than a month).

Stability of As, Cr and Sb speciation forms during storage was verified in various time intervals i.e. 8 h, 24 h, 48 h and after 30 days. For this purpose a mixture of standards containing 10 μg/L each of the analyte was prepared and measured using HPLC–ICP-MS on the content of inorganic ionic forms of As, Sb and Cr.

Similarly the real bottom water sample collected from the Pławniowice Reservoir with the addition of a mixture of standards containing 5 μg/L each of the analytes was performed. It was found that the storage of frozen samples for 30 days at a temperature of −22 °C does not affect the changes in the concentration of oxo-species of As, Cr, Sb.

After transportation into the laboratory and determining elementary physicochemical parameters (pH, redox potential), bottom sediments were kept at the temperature of −22 °C until further analyses were carried out. Bottom sediment analyses were performed simultaneously from the layers of 0–5 cm and 15–20 cm. Each sediment sample was centrifuged at 25 000 rpm for 10 min. Afterwards, samples were extracted in order to leach easily-leached As, Sb and Cr fractions from the sample. From the biological viewpoint, they have minor significance.

Two certified reference materials for bottom sediments, i.e. NCS DC 73309 and NCS DC 73310 (China National Analysis Center for Iron and Steel), were chosen to determine and optimize possibly the best method for the extraction of easily-leached As, Sb and Cr forms. In the CRM′s total content of As, Cr, Sb was certified, however, their use allows for an estimation of extraction degree of the investigated metal/metalloid.

Two types of extraction were used, i.e. extraction with a buffer in an ultrasonic cleaner (5 mM Na_2HPO_4 and 50 mM KH_2PO_4 $pH=6.0 \pm 0.2$) [41], and extraction with deionized water at 6 h shaking precipitation at 40 °C. Inorganic Cr speciation forms were determined in bottom sediments that had undergone extraction with a buffer in an ultrasonic cleaner. Extraction with a phosphate buffer was the most optimal for As. On the other hand, high Sb background from the same extractant was also obtained for this extraction type. Additionally, it was observed that Sb(III) oxidized to Sb(V) under the phosphate buffer influence and excessively drastic conditions. Such effects were not observed in the extraction with deionized water. Such conditions enabled both extraction and simultaneous determination of inorganic As and Sb speciation forms.

Physicochemical analyses (determining pH, redox potential) preceded quantitative analyses of As, Sb and Cr speciation forms in water and bottom sediments with HPLC–ICP-MS. The preliminary activities included quantitative analyses of total As, Sb and Cr in water samples and bottom sediment extracts with ICP-MS spectrometer. Then performed mass balances (sum of species compared to total element concentration) to check more reliability of quantitative results.

2.3. Apparatus and chromatographic conditions

The Elan 6100 DRC-e ICP-MS spectrometer (PerkinElmer) was used for quantitative analyses of total As, Sb and Cr in water samples and bottom sediment extracts. The apparatus was equipped with a standard ICP quartz torch, cross-flow nebulizer and nickel cones. Samples and standards were delivered with a peristaltic pump. The spectrometer was optimized daily with

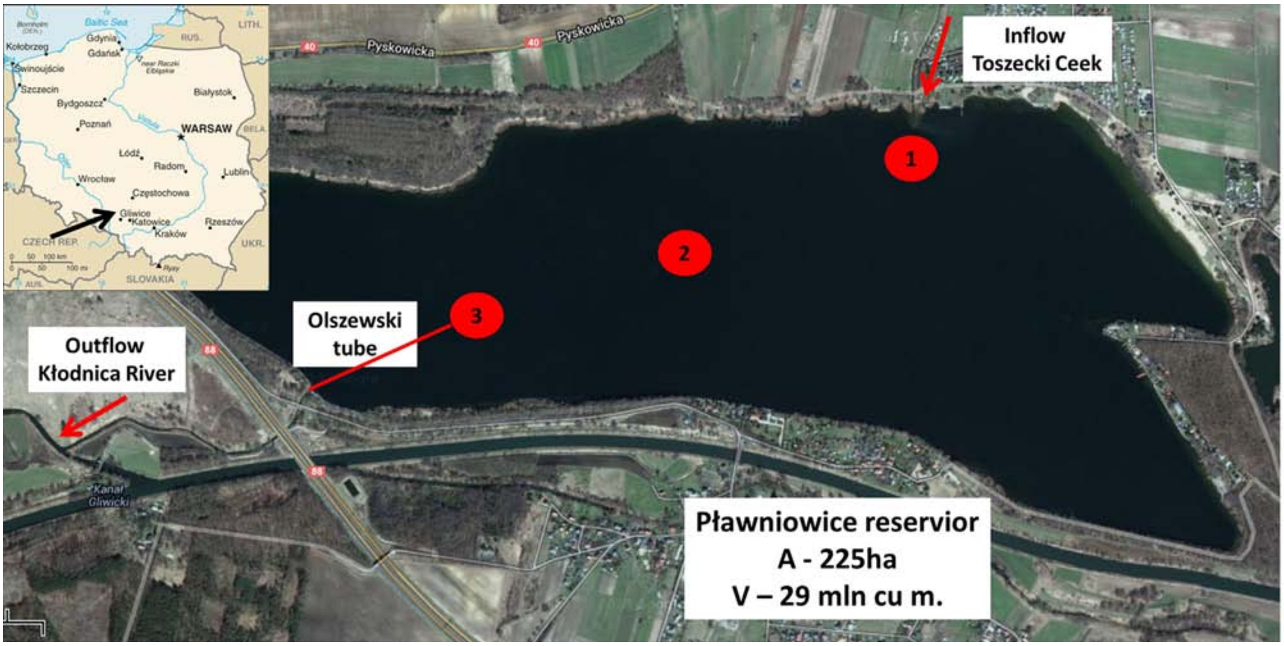

Fig. 1. Pławniowice Reservoir with marked sampling points of bottom water and sediments: 1—inflow of the Toszecki Creek, 2—the reservoir center, 3—outflow into the Gliwice Canal.

Table 1
Operating parameters of the ICP-MS spectrometer.

Parameter	Value
RF power [W]	1125
Plasma gas flow [L/min]	15
Nebulizer gas flow [L/min]	0.76–0.82
Auxiliary gas flow [L/min]	1.15–1.16
Nebulizer	Cross flow
Plasma torch	Quartz
Scanning mode	Peak hopping
Dwell time [ms]	250
Sweeps/reading	1
Number of replicates	830

a 10 μg/L solution (Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U) in 1% HNO_3 Elan 6100 Setup/Stab./Masscal. Solution (PerkinElmer). Concentrations of ^{53}Cr, ^{75}As and ^{123}Sb were measured with the internal ^{103}Rh standard. The measurements of As, Sb and Cr speciation forms in water and bottom sediment samples were performed with the HPLC–ICP-MS system. The operating parameters of the ICP-MS spectrometer are given in Table 1.

To separate analytes, a speciation apparatus set was applied. It consisted of an HPLC chromatograph (PerkinElmer) equipped with Series 200LC Peltier oven, Series 200LC autosampler and Series 200LC gradient pump. Cr(III)/Cr(VI) ions were separated with the Dionex IonPac AG-7 column (50 mm × 4 mm, particle size 10 μm). As(III)/As(V) and Sb(III)/Sb(V) ions were separated with the Dionex IonPac AS7 column (200 mm × 4 mm, particle size 10 μm). Selected separation parameters are presented in Table 2.

2.4. Chemicals and reagents

The following substances were used for analyses: ultrapure ammonium nitrate (Merck), ultrapure potassium dichromate (Merck), 1000 mg/L Cr(III) standard solution (Merck), dihydro sodium arsenate heptahydrate (Sigma-Aldrich), sodium arsenite (Sigma-Aldrich). To extract speciation forms of As and Cr from bottom sediments the following substances were used: disodium ethylenediaminetetraacetate (Na_2EDTA) (Sigma-Aldrich), ultrapure nitric acid (65%, Merck), analytically pure dihydrogen potassium phosphate (POCH) and ultrapure ammonium nitrate (Merck). The calibration solutions were prepared each time through diluting suitable standard solutions on an analytical balance. Multi-elemental standards no. XXI and VI (Merck) were used during determinations of total As, Sb and Cr with ICP-MS. Solutions made from salt were employed for calibration during quantitative determinations of As, Sb and Cr speciation forms. All solutions and standards were prepared with Milli-Q-Gradient ultrapure deionized water (Millipore, Merck), whose electrolytic conductivity was < 0.05 μS/cm. The method validation was performed with certified reference materials (NIST 1643e, NCSDC 73309 and NCSDC 73310).

2.5. Calibration

Calibration curves were obtained with measurements of 0.5 μg/L, 1 μg/L, 5 μg/L and 10 μg/L standard solutions for As(III), As(V), Sb(III) and Sb(V), respectively. 1 μg/L, 5 μg/L, 10 μg/L and 25 μg/L standard solutions were used for Cr(VI) and Cr(III). A linear model of the dependence of concentration of the total number of analyte counts was selected. The coefficient of determination of calibration curves R^2 was between 0.9991 and 0.9999. Fig. 2 presents superimposed chromatograms obtained after analyzing As and Sb standard solutions.

3. Results and discussion

3.1. Validation methodology

The method of simultaneous separation and quantitative determination of inorganic As, Sb and Cr speciation forms was validated with certified reference materials of water and bottom sediments (NCSDC 73309, NCSDC 73310 and NIST 1643-e) and standard addition method. Sediment standards underwent extraction. Then, the contents of the discussed ions were determined. The results of these procedures are given in Table 3. The method validation parameters are shown in Table 4. The LOD of As, Sb and Cr speciation forms and the method repeatability were calculated on the basis of multiple calibration curves. The LOD calculation

Table 2
Conditions of chromatographic separation.

Parameter	Value
Chromium	
Separation column	Ion Pac AG-7 50 mm × 4 mm, 10 μm
Temperature	35 °C
Mobile phase	A: 0.1 M NH_4NO_3 pH=4 B: 0.8 M HNO_3
Elution program	0–0.5 min 100% A, 1.5–3.5 min 100% B Rinsing 3.5–5.0 min. 100% A
Flow rate during the analysis [mL/min]	1.7
Flow rate during the rinsing [mL/min]	2.0
Volume of sample [μL]	170
Arsenic and antimony	
Separation column	Ion Pac AS-7 200 mm × 4 mm, 10 μm
Temperature	35 °C
Mobile phase	1 mM Phtalic acid, 10mM $EDTANa_2$ pH=4.5
Elution time	3 min
Flow rate during the analysis [mL/min]	1.2
Volume of sample [μL]	80

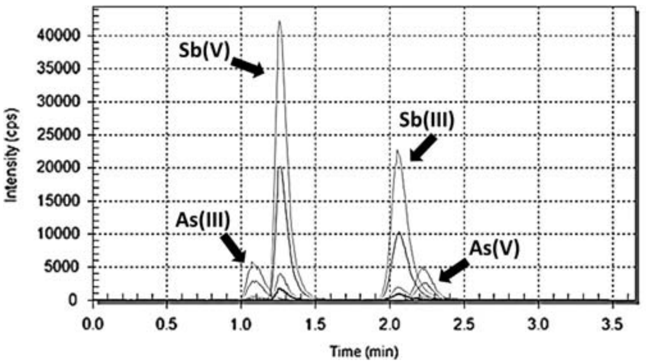

Fig. 2. Superimposed chromatograms obtained after analyzing standard solutions of As(III), As(V), Sb(III), Sb(V) with concentrations of 0.5 μg/dm^3, 1 μg/dm^3, 5 μg/dm^3, 10 μg/dm^3, respectively.

was based on the following dependence:

$$GW = \frac{3 \times s}{b} \quad (1)$$

where s—standard deviation value, b—linear coefficient of calibration line.

The standard deviation value can be determined as a standard deviation for a free factor of the obtained calibration curve. The measurement uncertainty, understood as Type A uncertainty, was determined with multiple measurements of diversified real samples ($n > 30$). The method recovery was established with the measurement of the real samples to which the known amount of the specific analyte was added (Table 5).

3.2. Bottom water

There are no natural lakes in the Silesian Voivodship. All Upper Silesian water reservoirs are anthropogenic. They constitute valuable elements of the environment and they have important economic, environmental and landscape meaning. Therefore, they need protection against degradation and devastation [30]. Pławniowice Reservoir is a part of the Kłodnica river hydrotechnical system [31–36]. Its water quality is mainly influenced by nutrients, organic compounds, heavy metals and suspensions introduced into the reservoir. In order to change this situation, water and wastewater management in the Toszecki Creek (stream supplying the reservoir) drainage area ought to be considerably improved [37]. Gradual deterioration of oxygen conditions related to the progressing reservoir eutrophication has been observed since the reservoir establishment in 1975 [38].

The total content of As, Sb and Cr in the Pławniowice Reservoir water was low and close to the natural geochemical background. Table 5 presents maximum, minimum and average results of concentrations of inorganic As, Sb and Cr speciation forms. It also offers the results of pH and redox potential measurements. The As, Sb and Cr concentrations were within the ranges imposed by the regulation on drinking water [39]. Similar results were obtained by Niedzielski et al. in the research of Lake Lednica [40]. Subtle differences were observed for As and Sb in their total contents at the points along the transect (Fig. 1). The total concentration of As and Sb decreased between spring and summer. The minimum values were observed at the vegetation period peak. It is probably related to the absorption of the metalloids by macrophytes and phytoplankton. The As absorption by phytoplankton is a well-known phenomenon. On the other hand, the mechanisms and intensity of absorbing other elements, such as Sb, are not fully understood [15]. Noticeable differences were observed for the total Cr content along the transect. The biggest Cr amounts were found at the sampling point no. 2, i.e. at the reservoir center. The Cr concentration increased at all the sampling points until the vegetation period peak (June). Cr was leached from the soil surrounding the reservoir (Cr is also a component of fertilizers), which probably caused such a situation.

As(III) and As(V) concentrations also increased in the bottom water along the transect (0.1–1.91 μg/L and 0.46–1.49 μg/L, respectively) (Fig. 3). Analyses of As(III) and As(V) indicated a clear correlation between their concentrations and oxygen conditions. The As(V) concentration values increased between March and August and were accompanied by low As(III) concentrations. The As(V) decreased dramatically under anoxic conditions (September), whereas As(III) increased substantially at the same time. The authors [42] claimed that As(III) concentration had been prevalent in summer and winter seasons in Lake Jarosławieckie (National Park of Wielkopolska). Similar results were obtained by Niedzielski et al. [40], who found over 70% predominance of As(III) over As(V) in Lake Lednica. Researchers believed that it was a complex problem which depended not only on oxygen conditions but also on pH and redox potential.

The Sb(III) and Sb(V) concentrations increased in bottom water along the transect (Fig. 4). The lowest concentration was observed at the reservoir inlet, while the highest one was found at the reservoir outlet. There was a strong correlation between Sb(III) concentration in bottom water and pH level at the sampling point no. 1 ($R_1^2 = 0.5695$). The correlation between redox potential and Sb (V) concentration was fairly strong at three sampling points of bottom water ($R_1^2 = 0.4119$; $R_2^2 = 0.4719$; $R_3^2 = 0.3481$). The Sb(III) concentration tended to rise between spring and the height of

Table 3
Results of bottom sediment certified reference materials extraction.

Analyte	Certificate	Sb(III) [mg/kg]	Sb(V) [mg/kg]	Total Sb(III)/Sb(V) [mg/kg]	Certificate [mg/kg]	Efficiency[%]
Sb	NCSDC 73309	4.86	0.24	5.09	14.90	34.19
	NCSDC 73310	7.93	0.26	8.18	24.00	34.10
Analyte		As(III) [mg/kg]	As(V) [mg/kg]	Total As(III)/As(V) [mg/kg]	Certificate [mg/kg]	Efficiency[%]
As	NCSDC 73309	53.08	25.87	78.95	188.00	41.99
	NCSDC 73310	34.71	12.27	46.98	115.00	40.85
Analyte		Cr(III) [mg/kg]	Cr(VI) [mg/kg]	Total Cr(III)/Cr(VI) [mg/kg]	Certificate [mg/kg]	Efficiency[%]
Cr	NCSDC 73309	4.56	1.06	5.62	40.00	14.04
	NCSDC 73310	3.71	0.94	4.65	35.00	13.28

Table 4
Method validation parameters.

Analyte	LOD [μg/L]	Recovery (NIST 1643-e) [%]	Relative standard deviation of repeatability [%]	Uncertainty [%]
As (III)	0.18	99	1.9	15
As (V)	0.22	103	1.7	12
Sb (III)	0.009	100	1.4	8
Sb (V)	0.012	98	1.1	10
Cr (III)	0.11	102	1.6	18
Cr (VI)	0.17	96	2.1	19

Table 5
Recoveries obtained from the standard addition procedure applied in presented study.

Analyte	The water from the Pławniowice reservoir [μg/L]	The water from the Pławniowice reservoir + 5 μg/L analytes [μg/L]	Recovery [%]
As (III)	0.78	5.76	97.54
As (V)	0.91	5.88	96.27
Sb (III)	0.19	5.18	96.97
Sb (V)	0.32	5.33	103.57
Cr (III)	14.70	20.07	102.56
Cr (VI)	1.74	6.76	101.49

summer. The minimum values of Sb(V) concentrations were observed in July and between October and December, whereas the maximum ones were found for March–May and August–September periods. Similarly, Sb(III) was the highest in September and the lowest in June. Good oxygen conditions were discerned in June and July. The oxygen content ranged between 0.22 mg/L and 0.66 mg/L, even at the reservoir bottom. Nonetheless, Sb(III) was the prevalent ionic Sb form observed at that period. The calculations revealed that Sb(V) concentration was correlated with the redox potential. Out of all the discussed ions, it was the only one that demonstrated fairly strong correlations with the redox potential. The study confirmed the literature reports claiming that Sb(III) was characteristic for water with a low oxygen level whereas the level of Sb(V) depended on the redox potential [41]. The obtained results and correlations indicated the influence of processes in the bottom sediments on the bottom water condition.

The highest Cr(III) concentration was observed in the reservoir inlet zone in April 2012 (Fig. 5). The Cr(III) concentration was the lowest between July and October. The Cr(VI) concentration increased along the transect, whereas Cr(III) concentration decreased in the spring–summer period (April–July). It was probably related to the favorable oxygen conditions. The strongest correlation between pH and Cr(VI) concentration in bottom water was observed at the sampling point no. 2 ($R_2^2=0.7367$).

3.3. *Bottom sediments*

Figs. 3–5 present time variations in particular speciation forms of As, Sb and Cr in bottom water and easily-leached bottom sediment fractions. Cr(III) was dominant in both sediment layers. There was also a difference between Cr(VI) and Cr(III) concentrations at specific sampling points in November. For Cr, differences in concentration levels of its ionic forms were observed at the three sampling points. The maximum Cr(III) concentration was observed in August–September. At the same time the Cr(VI) level was low. The bottom sediment was enriched with Cr(III) at the period of dead phytoplankton deposition. At the same time, bottom water was rich with Cr(VI). Cr(VI) passed from the sediments into the water in summer months due to favorable pH and oxygen conditions.

Bottom sediments contained more As(V). The differences in the concentration of toxic As(III) in the upper sediment layer at the three sampling points were not large. The As(III) concentration increased noticeably along the transect. The research [41] conducted at Winiary and Jelonek Lakes (lakes under the urban anthropopressure impact on the environment) showed that As (III) were prevalent in the easily-leached sediment fractions. The As(V) (oxidized As form) predominance in Pławniowice Reservoir was a desirable phenomenon as it contributed to the As demobilization in the form of bottom sediments. It was possibly related to the restoration works performed at the reservoir for many years. The method of selective hypolimnion water removal improved bottom oxygen conditions over the years. The anoxic environment helped to reduce arsenates to arsenites. As passed into the bottom sediments and, depending on the redox conditions, could transform into soluble arsenites, insoluble sulfides or free As [29] as a result of crystallization, adsorption or co-precipitation. The improvement in the oxygen conditions of Pławniowice Reservoir reduced those processes. Thus, the environmental threat related to a sudden As release was diminished.

Maximum Sb(V) concentrations were observed in May and October–November. The charts presenting Sb(V) contents in the upper and lower layers of the bottom sediments were virtually identical. Sb(V) content in bottom sediments was the lowest between June and September, which was probably caused by its release into water. Its content in water increased. When comparing contents of two Sb forms in bottom sediments, Sb(III) prevailed in the deposited bottom sediments. The regulation on drinking water for humans [39] states that the permissible Sb concentration is 5 μg/L. The Pławniowice bottom water meets this requirement. The Sb concentration in the Pławniowice bottom sediments is approx. 45 mg/kg. The prevalence of Sb(III) in the sediments is disturbing. However, it is possible to release deposited toxic Sb(III) into water while changing physicochemical conditions (i.e. pH or redox potential).

Importantly, the differences in concentrations of particular ionic forms in the upper and lower layers were not large. The same applies to samples collected at different points of Pławniowice Reservoir.

3.4. Compare the contents of speciation forms of As, Sb, and Cr in the supernatant water and bottom sediment

The content of Cr(III) is the highest in the water flowing into the Pławniowice Reservoir (point 1), which is submitted to an increase in the concentration of this ion in the bottom sediment. Concentration increase of Cr(VI) in the bottom water in the spring and summer (April–July), while decreasing of the Cr(III) content, is associated with the release of Cr(VI) from sediment into the water. Quantitatively, in the supernatant water, predominates Cr(III) form. The upper layer of the bottom sediment has a lower content of Cr(III) (released into the supernatant), in the lower layer, this form is significantly more abundant, but overall bottom sediment is richer in Cr(III) rather than the Cr(VI).

Studies have shown that antimony accumulates in reservoir sediments. During the growing season peak predominates its reduced form Sb(III), which is submitted to an increase in the concentration of this form in the supernatant water along the transect. Sb(V) is present in high concentrations in the bottom sediment in May and October–November period, wherein we can

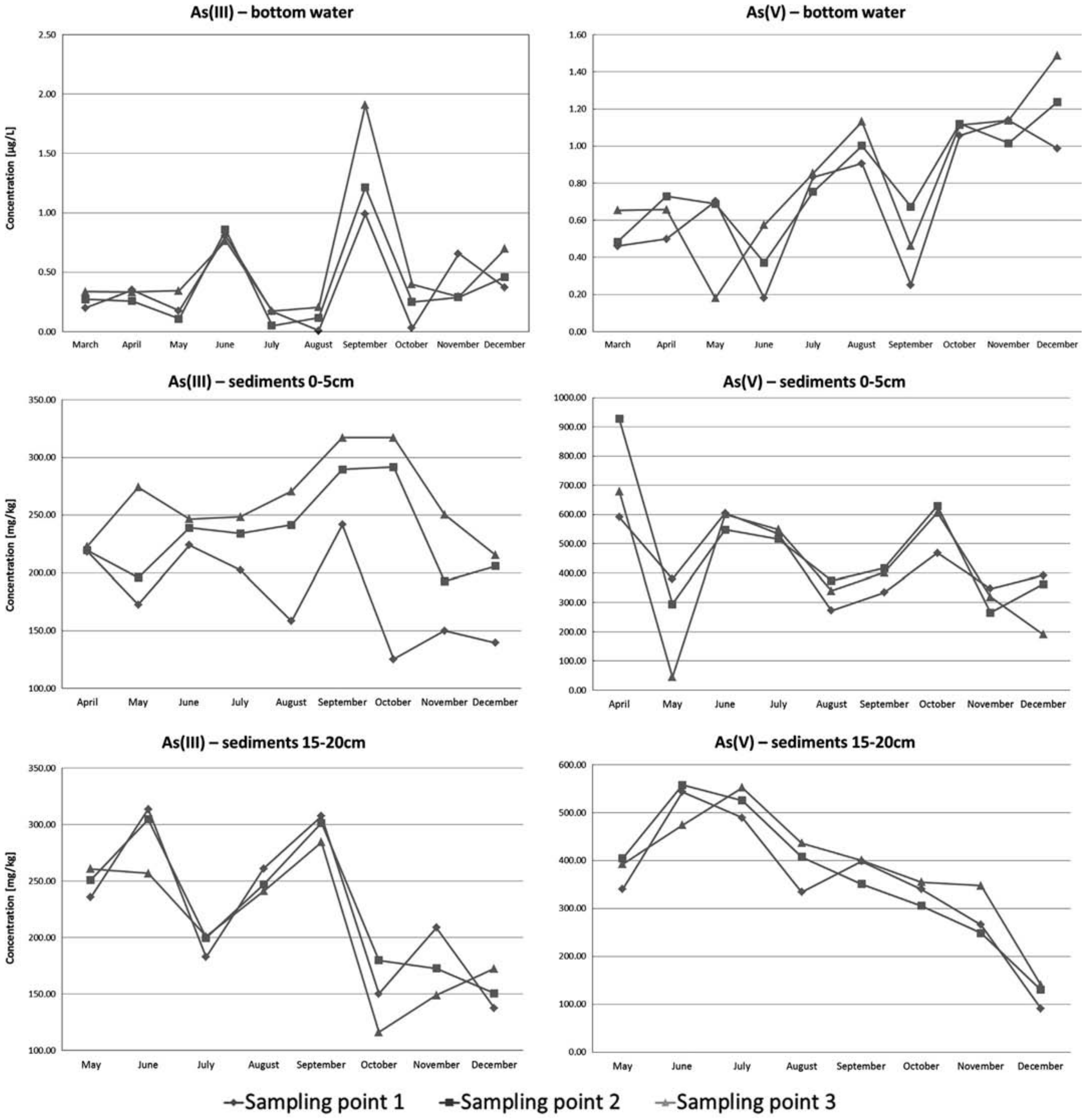

Fig. 3. Changes in concentrations of inorganic ionic As forms in bottom sediment samples from the layers of 0–5 cm and 15–20 cm.

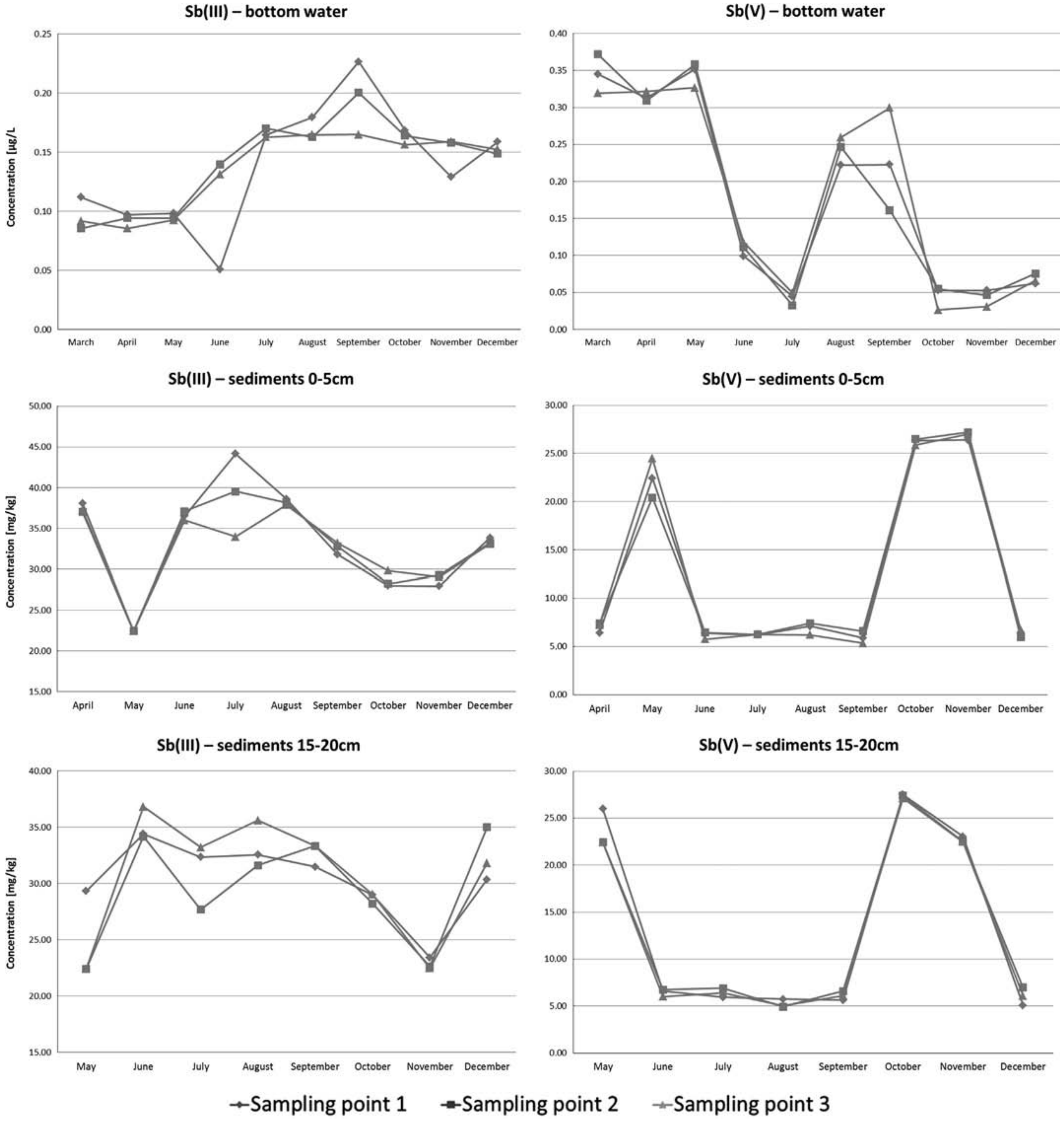

Fig. 4. Changes in concentrations of inorganic ionic Sb forms in bottom sediment samples from the layers 0–5 cm and 15–20 cm.

add that in the autumn concentration of this form is slightly lower than in May, due to unfavorable oxygen and redox condition. Of great importance is also the content of phytoplankton in water, which die in the autumn and falls to the bottom of reservoir.

In the supernatant water predominates As(III) form, except for September, when exceptionally high concentration As(V) was determined with a concomitant decrease of As(III) concentration, which is associated with anaerobic conditions. However, bottom sediment is richer in As(V). This is a desirable phenomenon from the point of view of the processes occurring in the reservoir and, therefore, most likely the supernatant water are poorer in As(V).

4. Conclusions

The examined methodology enabled obtaining reliable results despite low concentrations of As, Sb and Cr in water. The Dionex IonPac AS7 column, which had not been employed before, was used for the simultaneous determination of As and Sb speciation forms. It is known that contents of particular metal speciation forms depend on pH changes. The following study demonstrates that the increase in the pH of the reservoir water brought about increases in Sb(III) and As(V) concentrations in water. The analyses also show that there was no simple correlation between As, Sb and

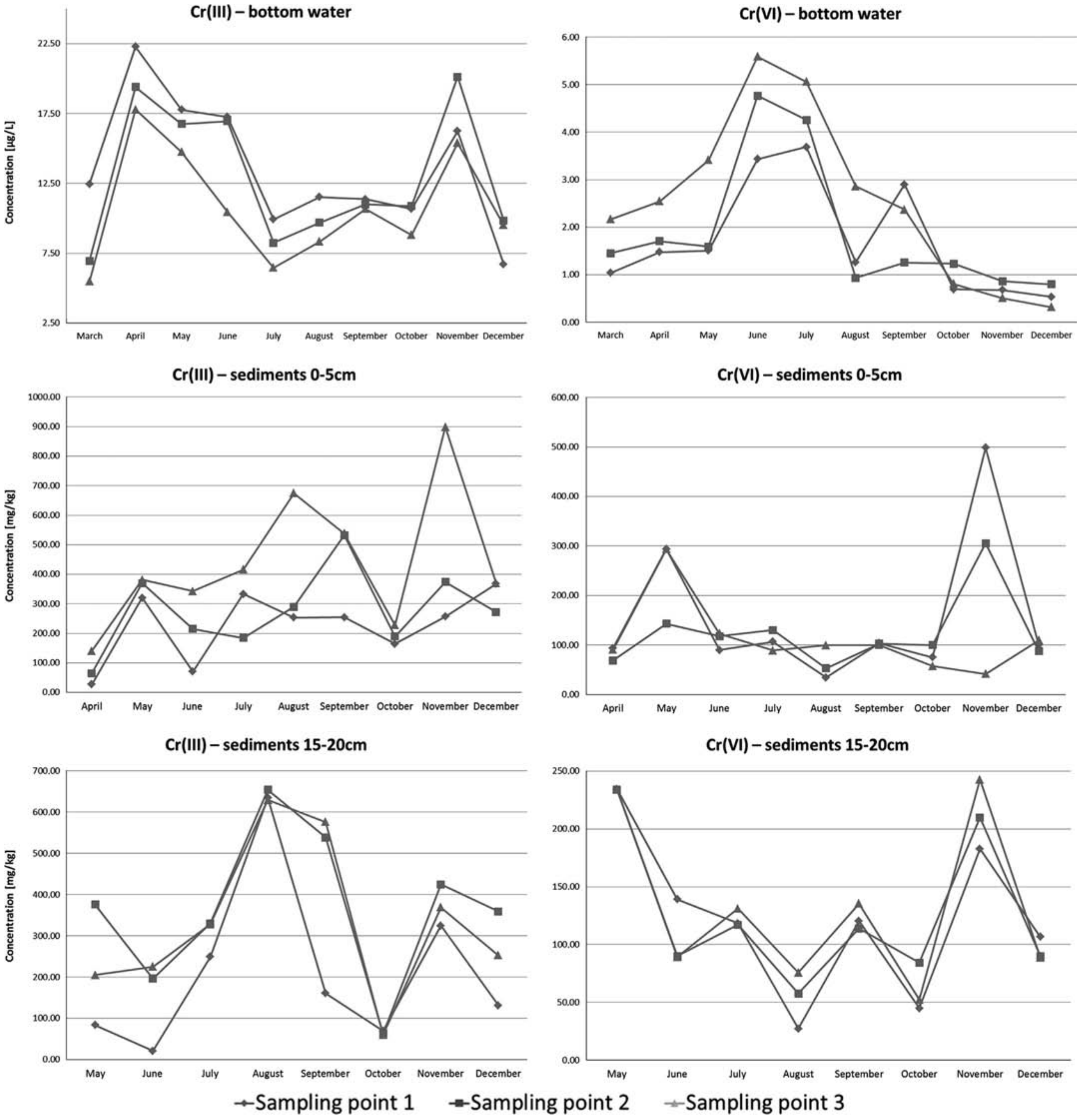

Fig. 5. Changes in concentrations of inorganic ionic Cr forms in bottom sediment samples from the layers of 0–5 cm and 15–20 cm.

Cr concentrations and pH or redox potential in bottom sediments. Increases in As and Sb concentrations along the transect indicated that those metalloids were transported in the direction of the water flow. The results also demonstrate that the transformations were similar at the lower (0–5 cm) and upper (15–20 cm) sediment layers. These concerned both the concentration values and change dynamics. Additionally, it shows that the biochemically active sediment layer made at least 20 cm. The minor differences in As, Sb and Cr concentrations in the bottom sediments among the particular sampling points proved that the location of Pławniowice Reservoir did not affect the occurring changes. The period between June and August seemed to be the most threatening as the highest concentrations of Sb(III), Cr(III) and As(V) in bottom sediments and Cr(VI) in bottom water were then observed. A considerable decrease in the Sb(V) concentration in water at the vegetation period peak (June–July) was most probably related to the fact that it was absorbed from water by living organisms.

The Pławniowice bottom sediments can pose an environmental threat due to the content of Sb(III), which can be released into the pelagic zone under favorable conditions. Even though As(V) and Cr(III) prevail in the reservoir bottom sediments, they can be transformed into As(III) and Cr(VI) as a result of drastic changes in

Table 6
Minimum, maximum and average total contents and speciation forms of Sb, As, Cr, pH and redox potential in bottom water collected at 3 sampling points of Pławniowice Reservoir: 1—inflow of the Toszecki Creek, 2—the reservoir center, 3—outflow into the Gliwice Canal.

Sampling point	1			2			3		
Analyte	**Min.**	**Max.**	**Median**	**Min.**	**Max.**	**Median**	**Min.**	**Max.**	**Median**
Sb(III) [μg/L]	0.05	0.23	0.14	0.09	0.20	0.15	0.09	0.16	0.15
Sb(V) [μg/L]	0.04	0.35	0.16	0.03	0.37	0.14	0.03	0.33	0.19
Sb total [μg/L]	0.16	0.64	0.31	0.14	0.65	0.31	0.16	0.68	0.32
As(III) [μg/L]	0.01	0.99	0.28	0.05	1.21	0.27	0.18	1.91	0.34
As(V) [μg/L]	0.18	1.14	0.77	0.37	1.24	0.74	0.18	1.49	0.76
As total [μg/L]	0.96	2.03	1.50	1.18	2.96	1.51	1.14	3.26	1.55
Cr(III) [μg/L]	6.71	22.29	11.98	6.95	20.12	10.93	5.47	17.79	9.97
Cr(VI) [μg/L]	0.53	3.69	1.37	0.79	4.77	1.35	0.32	5.59	2.46
Cr total [μg/L]	4.93	24.10	16.17	2.09	23.58	11.78	5.47	17.79	9.97
Ph	7.36	8.06	7.72	7.34	7.99	7.70	7.37	8.01	7.76
Eh [mV]	−150.7	−111.3	−129.2	−148.6	−113.1	−128.6	−147.1	−110.5	−126.5

pH or redox potential. From the viewpoint of environmental threat for the water environment, As(III) and Cr(VI) ions remain in opposition as their formation requires extreme changes in the pH conditions.

Studies on the occurrence of As, Sb, and Cr speciation forms in Pławniowice reservoir were not so far carried out, therefore at this stage of the research we are unable to compare the obtained results with other data. The results indicate the complexity of the problem and the need for continuation of research (Table 6).

References

[1] U. Forstner, Intern. J. Environ. Anal. Chem 51 (1993) 5–23.
[2] A. Kot, J. Namieśnik, Trends Anal. Chem 19 (2000) 69–79.
[3] R. Łobiński, J. Szpunar, Anal. Chim. Acta 400 (1999) 321–332.
[4] F. Cubadda, J. AOAC Int. 87 (2004) 173–204.
[5] B. Meermann, M. Sperling, Anal. Bioanal. Chem. 403 (2012) 1501–1522.
[6] B. Michalke, V. Nischwitz, Anal. Chim. Acta 682 (2010) 23–36.
[7] R. Michalski, M. Jabłońska, S. Szopa, Speciation Studies in Soil, Sediment and Environmental Samples, in: Sezgin Bakirdere (Ed.), Science Publishers/CRC Press/Taylor&Francis Group, 2013.
[8] M. Popp, S. Hann, G. Koellensperger, Anal. Chim. Acta 668 (2010) 114–129.
[9] A. Kabata-Pendias, H. Pendias, Biogeochemistry of Trace Elements, PWN, Warsaw, 1999.
[10] M. Filellal, N. Belzile, Y.W. Chen, Earth Sci. Rev 57 (2002) 125–176.
[11] S. Marcellino, H. Attar, D. Lievremont, M.C. Lett, F. Barbier, F. Lagarde, Anal. Chim. Acta 629 (2008) 73–83.
[12] A. Leonard, G.B. Gerber, Mutat. Res. Rev. Genet. Toxicol 366 (1996) 1–8.
[13] S. Garboś, E. Bulska, A. Hulanicki., Z. Fijalek, K. Sołtyk, Spectrochim. Acta B 55 (2000) 795–802.
[14] M. Jabłońska, S. Szopa, R. Skorek, Monography of the Committee of Environmental Engineering, PAS, Lublin (2009) 97–105.
[15] P. Niedzielski, M. Siepak, J. Przybyłek, J. Siepak, Arsenic, Antimony and Selenium in the Waters of the Poznan City as Micropollutants and Micronutrients, Adam Mickiewicz University, Poznan, 2002.
[16] J. Siepak, Speciation Analysis of Metals in Water and Sediments Samples, Adam Mickiewicz University, Poznan, 1998.
[17] D.Q. Hung, O. Nekrassowa, R.G. Compton, Talanta 64 (2004) 269–277.
[18] J.G. Parsons, A. Martinez-Martinez, J.R. Peralta-Videa, J.L. Gardea-Torresdey, Chemosphere 70 (2008) 2076–2083.
[19] C.H. Selene, J. Chou, C.T. De Rosa, Int. J. Hyg. Environ. Health 206 (2003) 381–386.
[20] U.K. Chowdhury, B.K. Biswas, T.R. Chowdhury, G. Samanta, B.K. Mandal, G.C. Basu, C.R. Chanda, D. Lodh, K.C. Saha, S.K. Mukherjee, S. Roy, S. Kabir, Q. Quamruzzaman, D. Chakraborti, Environ. Health Perspect 108 (2000) 393–397.
[21] M.M. Rahman, M.K. Sengupta, S. Ahamed, U.K. Chowdhury, M.A. Hossain, B. Das, D Lodh, K.C. Saha, S. Pati, I. Kaies, A.K. Barua, D. Chakraborti, Sci. Total Environ. 338 (2005) 189–200.
[22] T. Yoshida, H. Yamauchi, G.F. Sun, Toxicol. Appl. Pharm. 198 (2004) 243–252.
[23] G.F. Sun, Toxicol. Appl. Pharm. 198 (2004) 268–271.
[24] C. Watanabe, A. Kawata, N. Sudo, M. Sekiyama, T. Inaoka, M. Bae, R. Ohtsuka, Toxicol. Appl. Pharm. 198 (2004) 272–282.
[25] IARC, Monographs on the Evaluation of the Carcinogenic Risk to Human. 40, WHO, Geneva 1990.
[26] J.O. Nriagu, E. Nioboer, Chromium in Natural and Human Environments, Wiley Interscience, New York, 1988.
[27] M. Jabłońska, M. Kostecki, S. Szopa, A. Łyko, R. Michalski, Ochr. Sr 34 (2012) 25–32.
[28] R. Michalski, M. Jabłońska, S. Szopa, A. Łyko, Crit. Rev. Anal. Chem. 41 (2011) 133–150.
[29] L. Orero Iserte, A.F. Roig-Navarro, F. Hernandez, Anal. Chim. Acta 527 (2004) 97–104.
[30] Y. Morita, T. Kobayashi, T. Kuroiwa, T. Narukawa, Talanta 73 (2007) 81–86.
[31] R. Michalski, J. Liq. Chromatogr. R.T. 28 (2005) 2849–2862.
[32] M. Kostecki, Monography of the Committee of Environmental Engineering PAS, Lublin (2009) 113–126.
[33] M. Kostecki, in: Sixth Scientific and Technical Conference, Protection and restoration of lakes, Toruń, 2007, pp. 99–115.
[34] M. Kostecki, Arch. Environ. Prot. 1 (1978) 23–32.
[35] M. Kostecki, J. Kozłowski, A. Domurad, B. Zych, Arch. Environ. Prot. 27 (2001) 125–140.
[36] M. Kostecki, Work & Studies 57 (2003) 1–124.
[37] M. Kostecki, Scientific Activities—Selected Issues Polish Academy of Science, 17, 2004, 114-115.
[38] W. Nocoń, M. Kostecki Ochr. Sr. 4 (2006) 25–30.
[39] Regulation of the Minister of Health on 20 April 2010, About Drinking Water Quality, No. 72 pos. 466th.
[40] P. Niedzielski, J. Siepak, Z. Kowalczuk, Arch. Environ. Prot. 26 (2000) 73–82.
[41] L. Kozak, A. Dostatni, P. Niedzielski, Yearbook of Environmental Protection 9 (2007) 313–322.
[42] M. Pełechaty, A. Pełechata, P. Niedzielski, M. Siepak, T. Sobczyński, Pol. J. Environ.Stud. 13 (2004) 185–190.