

ARSENIC SPECIATION IN RYBNIK RESERVOIR

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Abstract

This study was aimed at determining the speciation of arsenic in water, bottom sediments, and interstitial water of Rybnik Reservoir. The speciation analysis of inorganic forms of arsenic in the water and interstitial water samples was conducted by means of column technique using Dowex 1X8 anion exchanger. Arsenic speciation in the bottom sediment was carried out by means of the procedure suggested by Tessier. The concentration of arsenic was determined by HG-AAS using a Varian SpectrAA 880 spectrophotometer coupled with a VGA-77 system for hydride generation and an ETC-60 electrothermal furnace that enabled accurate temperature settings. In the surface and bottom waters of the reservoir, arsenic occurred primarily as As(V). Arsenic(V) concentration in water ranged from 0.49 $\mu\text{g}/\text{dm}^3$ to 2.42 $\mu\text{g}/\text{dm}^3$, and As(III) – from 0.19 $\mu\text{g}/\text{dm}^3$ to 0.93 $\mu\text{g}/\text{dm}^3$. Arsenic was strongly bound to the bottom sediment, predominant arsenic forms in the reservoir were sulfides and organically bound fraction. Arsenic concentration in the interstitial water was almost twice as high as that in the water of Rybnik Reservoir. The average As(III) concentration in the interstitial water was 0.52 $\mu\text{g}/\text{dm}^3$, As(V) – 3.00 $\mu\text{g}/\text{dm}^3$.

Streszczenie

Celem pracy było określenie specjacji arsenu w wodzie, osadach dennych i wodzie interstycjalnej Zbiornika Rybnickiego. Analizę specjacyjną nieorganicznych form arsenu w próbkach wody przeprowadzono metodą kolumnową z zastosowaniem anionitu Dowex 1X8. Specjację arsenu w osadzie dennym przeprowadzono metodą Tessiera. Zawartość arsenu oznaczano metodą HG-AAS wykorzystując spektrofotometr SpectrAA 880 firmy Varian, rozbudowany o układ do generacji wodorków VGA-77 oraz elektrotermiczny piec ETC-60 z możliwością precyzyjnego ustawienia temperatury. Zawartość As(V) stanowiła dominującą formę występowania arsenu w wodzie na obszarze całego zbiornika. Zawartość arsenu(V) w wodzie wahała się od 0.49 $\mu\text{g}/\text{dm}^3$ do 2.42 $\mu\text{g}/\text{dm}^3$, podczas gdy As(III) od 0.19 $\mu\text{g}/\text{dm}^3$ do 0.93 $\mu\text{g}/\text{dm}^3$. Arsen należał do pierwiastków silnie związanych z osadem dennym, dominującymi formami występowania arsenu w osadzie dennym Zbiornika Rybnickiego były połączenia organiczne i siarczki. Zawartość arsenu w wodzie interstycjalnej była prawie dwukrotnie większa od zawartości arsenu w wodzie Zbiornika Rybnickiego. Średnia zawartość As(III) w wodzie interstycjalnej wynosiła 0.52 $\mu\text{g}/\text{dm}^3$, średnia zawartość As(V) – 3.00 $\mu\text{g}/\text{dm}^3$.

Keywords: Arsenic; Speciation; Rybnik Reservoir; Water; Bottom sediment; Interstitial water.

1. INTRODUCTION

Arsenic is a natural component of waters and its levels in uncontaminated reservoirs do not exceed 5 $\mu\text{g}/\text{dm}^3$ [12]. Its natural concentrations in water are associated with the processes of rock washing and are dependent

on prevailing local geological and hydrological conditions and geochemical characteristics of an aquifer [3]. Its natural, high concentrations can also occur in desert reservoirs and closed lakes as a result of evaporation and/or geothermal effects [4].

The increase in arsenic concentration in water may also be the effect of contamination by industrial or municipal wastewater [2, 28].

In most aquatic environments, arsenic does not remain long in the dissolved phase but it is precipitated and sorbed by organic matter as well as aluminium and iron hydroxides present in bottom sediments. The reservoirs located in highly industrial areas can contain arsenic whose concentrations in bottom sediments may reach 2000 µg/g [1].

The use of speciation analysis in arsenic assays is absolutely essential since its particular compounds differ greatly in toxicity. The inorganic compounds of arsenic are 25-100 times as toxic as the organic ones [11]. Furthermore, degree of oxidation also affects arsenic toxicity – As(III) is 60 times as toxic as As(V). The speciation of arsenic in the aquatic environment also provides data on its mobility, bioavailability and possible entrance into the food chain.

Speciation analysis is of particular significance in reservoirs located in industrial areas contaminated with anthropogenic arsenic. Rybnik Reservoir, a dammed reservoir constructed on Ruda river for Rybnik Power Station and constantly affected by emission from Rybnik Mining Region and Upper Silesian Industrial Region, is one of them. Previous research revealed considerable contamination of the reservoir with metals, including arsenic [15, 16]. This study was aimed at determining the speciation of arsenic in the bottom sediments and water of Rybnik Reservoir.

2. STUDY AREA, MATERIALS AND METHODS

Rybnik Reservoir was constructed in the 1970s of 20th century. Its primary function covers the supply of water to condensers where water vapour which leaves the turbine condenses, but the water is also used to top up the closed cycle. At present, it acts as a flood-control reservoir and recreation centre as well.

Total capacity and area of Rybnik Reservoir are 24 million m³ and 5.55 km² respectively [14]. There are several zones in the reservoir which differ in depth:

- 1) dam zone – maximum depth of 12 m,
- 2) middle zone – depth of 4-7 m,
- 3) shallow water zone – depth of 4 m.

Water and sediment samples were collected at 9 sampling sites located along the main axis of the reservoir – Fig 1.



Figure 1.
Location of sampling stations in the area of the Rybnik Reservoir

Water samples were taken from the surface and bottom layers at the depths of 2 m, 4 m, 6 m and 8 m with a Mera-Błonie Toń-2 instrument.

Bottom sediment samples were collected with an Eckman-Birge sampler up to the depth of 8 cm and subsequently divided into 2 cm units.

Interstitial water was recovered from the bottom sediment samples by pressure driven filtration using Amicon system.

Arsenic concentration in bottom sediments was assayed after microwave digestion of bottom sediment samples with a mixture of 0.5 cm³ HNO₃ and 1.5 cm³ HCl [17]. Parallel digestion of the JMS-2 (Marine sediment) and JMS-1 (Marine sediment) reference material was carried out.

Concentration of arsenic was determined by HG-AAS using a Varian SpectrAA 880 spectrophotometer coupled with a VGA-77 system for hydride generation and an ETC-60 electrothermal furnace that enabled accurate temperature settings.

Formation of arsenic hydride during the assays was described by the following reaction:



Generation of arsenic hydride needed an additional step which caused the prereduction of arsenic(V) to arsenic(III). It involved the use of KI whose final concentration in the sample was 1%.

Control of arsenic determination methodology was based on JMS-2 (Marine sediment) and JMS-1 (Marine sediment) certified materials manufactured by GSJ (Table 1).

The speciation analysis of inorganic forms of arsenic

Table 1.
Analysis of JMS-2 (Marine sediment) and JMS-1 (Marine sediment) certified materials [$\mu\text{g/g}$]

Reference material	As certified	As measured (n=6)	Recover [%]	Accuracy [%]
JMS-1 (Marine sediment)	18	16.3	90.6	-9.4
JMS-2 (Marine sediment)	35	31.9	91.1	-8.9

Table 2.
Schematic of sequential extraction procedure by Tessier [29]

Fraction	Extractant
Exchangeable	1 M MgCl_2 ; pH 7,0
Arsenic sorbed on carbonates	1 M $\text{CH}_3\text{COONH}_4\text{-CH}_3\text{COOH}$; pH 5, 5h
Arsenic bound to Fe-Mn oxides	20% CH_3COOH in 0.04 M, $\text{NH}_2\text{OH}\cdot\text{HCl}$, temp. 96°C , 6h
Organically bound and sulfides	30% H_2O_2 , pH 2, (85% HNO_3), 3.2 M NH_4OAc in 20% HNO_3
Residue	$\text{HF} + \text{HClO}_4$

Table 3.
As(III) and As(V) concentrations in particular layers of water in Rybnik Reservoir [$\mu\text{g/dm}^3$]

Layer	As(III)		As(V)	
	Range	Mean \pm SD	Range	Mean \pm SD
upper	0.19-0.72	0.36 \pm 0.11	0.49-1.94	0.93 \pm 0.24
2 m	0.19-0.59	0.33 \pm 0.08	0.53-1.38	0.88 \pm 0.18
4 m	0.24-0.57	0.34 \pm 0.09	0.49-1.14	0.82 \pm 0.19
6 m	0.20-0.82	0.37 \pm 0.14	0.51-2.38	0.99 \pm 0.38
8 m	0.29-0.41	0.35 \pm 0.14	0.71-1.15	0.96 \pm 0.16
bottom	0.19-0.93	0.43 \pm 0.17	0.55-2.42	1.14 \pm 0.44

in the water samples was conducted by the column technique using Dowex 1X8 anion exchanger.

Arsenic speciation in the bottom sediment was carried out by the procedure suggested by Tessier [29] (Table 2).

Statistical analysis of the results was made by employing Microsoft Excel and Stastica for Windows 6.1pl.

3. RESULTS AND DISCUSSION

The content of organic forms, DMAA and MMAA, in Rybnik Reservoir was found to be below the determination limit. Arsenic(III) concentration in water ranged from $0.19 \mu\text{g/dm}^3$ to $0.93 \mu\text{g/dm}^3$, $0.39 \mu\text{g/dm}^3$ on average (Table 3). The differences in As(III) concentrations in the water in individual layers were statistically significant ($p < 0.01$), the highest As(III) concentration being found in the bottom layer.

The average As(III) concentration was similar in the entire area of the reservoir. No significant differences in As(III) concentrations were found at individual sites, both in the surface and bottom waters as well as water collected at particular depths.

The differences in arsenic concentrations in the cross-section of the water in the reservoir were not statistically significant. Slightly higher As(III) concentrations were found in the bottom water than surface one.

As(V) concentrations in the water ranged from $0.49 \mu\text{g/dm}^3$ to $2.42 \mu\text{g/dm}^3$ (Table 3). It was significantly higher in the deeper layers, below 6 m ($p < 0.0001$). Like As(III), no significant differences were observed for As(V) in water from individual zones.

As(V) was the predominant form in the entire reservoir. In the surface water, its share in the total arsenic concentration was 70%, leaving the remaining 30% for As(III). The percentage of As(V) in the bottom water was similar to that assayed in the surface water and ranged from 69.4% at site 4 to 75.7% at site 9 (Fig. 2). Slightly higher concentrations of As(V) were characteristic of the surface and bottom waters in the backwater area of the reservoir and the dam zone.

Analysis of the literature shows that, depending on different conditions, both As(III) and As(V) may be predominant forms of arsenic in aquatic environments [9, 10, 13, 19, 20, 23]. As(III) dominated the ground waters of Americas and Asia [13]. There are also

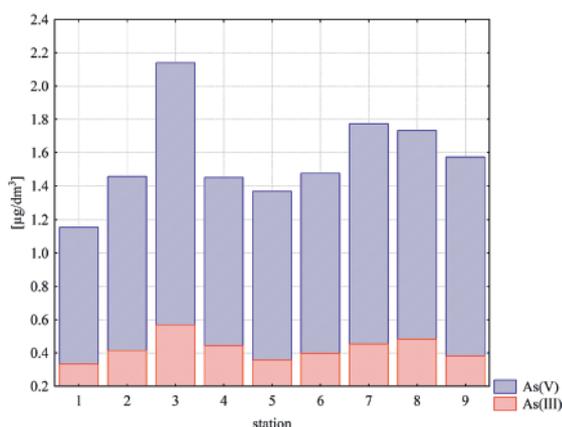


Figure 2. Comparison of average As(III) and As(V) concentrations in the bottom water of the Rybnik Reservoir at individual stations [$\mu\text{g}/\text{dm}^3$]

reports that indicate similar proportions of As(III) and As(V) in reservoirs [10, 20] and wide diversity in concentrations and As(V)/As(III) proportions [18, 19, 23]. As(III)/As(V) ratio, similar to that found in the water of Rybnik reservoir, was characteristic of water reservoirs investigated by Chen et al., [5].

The differences in the reports on As(III) and As(V) proportions are primarily the effect of a large number of factors affecting their concentrations in waters [24]. Arsenic sources, redox conditions, pH and biological activity in a reservoir are of special importance. For instance, arsenic that originates from rock and sediment dissolution occurs mainly in the form of As(III). High concentrations of As(III) can also be found in geothermal waters and water reservoirs located in the areas characterized by high total arsenic content caused by industrial contamination. The presence of As(III) in waters may also be the effect of biological reduction of As(V) [22].

As(III)/As(V) proportion may also be affected by the presence of iron and manganese oxides and hydroxides [13, 24]. Particularly strong links occur between iron and manganese compounds and As(V) ones. This correlation was found in the water of Rybnik Reservoir as well – Fig. 3.

Arsenic was one of the metals which were strongly bound to the bottom sediment. Speciation analysis revealed that 1-3% of the bottom sediment in the backwater area constituted the exchangeable arsenic forms (Fig. 4). The predominant forms of arsenic in the bottom sediment of Rybnik Reservoir turned out to be organically bound fraction and sulfides – they accounted for 56-60% in the surface area of the sed-

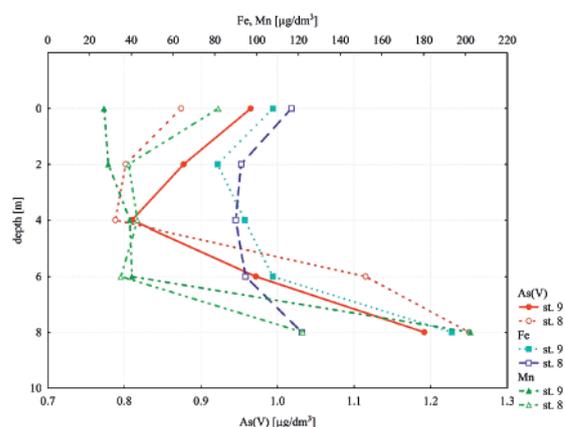


Figure 3. Relationship between As(V) and iron and manganese contents in water of the Rybnik Reservoir

iment and 45-49% in the 6-8 cm layer. The residue constituted 8-15% in the bottom sediment collected from 0-2-cm layer and approximately 35% in the 6-8 cm layer. Arsenic bound to Fe-Mn oxides accounted for 25% in the surface layer of the bottom sediment and 15% in the 6-8 cm layer.

As far as the bottom sediment in the deep water zone is concerned, the organically bound forms and sulfides were predominant forms in the surface layer of the sediment [Fig. 5]. The 6-8 cm layer revealed a high percentage of the residual fraction of 50-60%. Like the bottom sediment in the backwater area, the dam zone also showed a small percentage of exchangeable arsenic which accounted for 2% of its total concentration in the bottom sediment.

Low concentration of mobile arsenic was also characteristic of the bottom sediment investigated by other authors [6, 7, 21, 26]. The residual fraction dominated sediment of Italian lakes [26], and in the sediment of Spanish Tinto and Odiel rivers, arsenic was bound mainly to iron and manganese oxides [6].

Low percentage of the exchangeable form in total arsenic concentration in the bottom sediment indicates that only a small part of arsenic is easily washed from the bottom sediment into the bottom water. The migration of arsenic bound to iron and manganese oxides, sulfides and organic matter is possible provided that a significant change in physical and chemical conditions in the water environment takes place. Arsenic bound to organic matter is released after the matter is decomposed and that bound to iron and manganese hydroxides is released when redox conditions change. Release of arsenic bound to

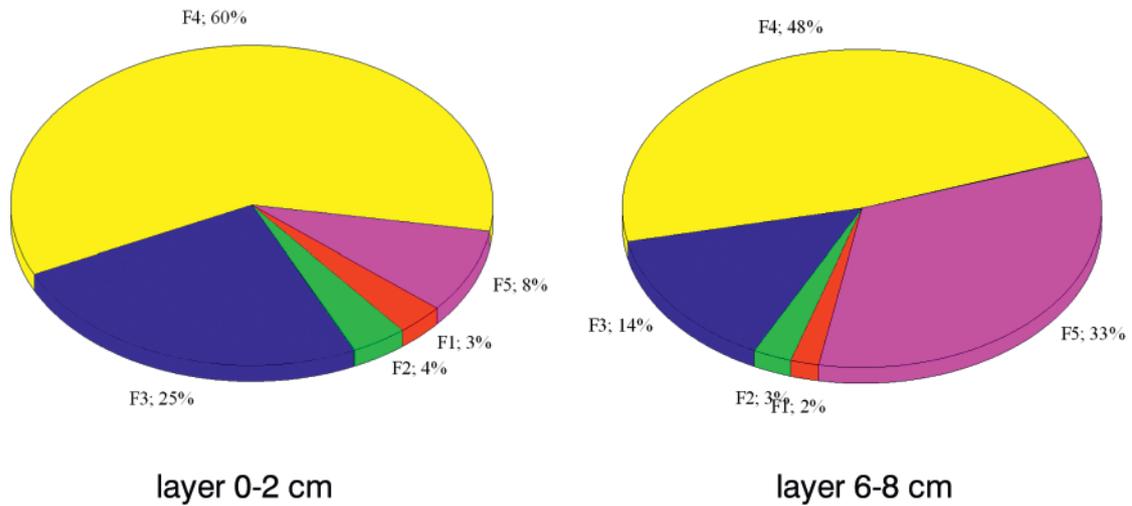


Figure 4. Arsenic speciation in the bottom sediment at station 1 in the backwater area, F1 – exchangeable form, F2 – sorbed on carbonates, F3 – sorbed on Mn-Fe oxides, F4 – organic bonds and sulfides, F5 – residue

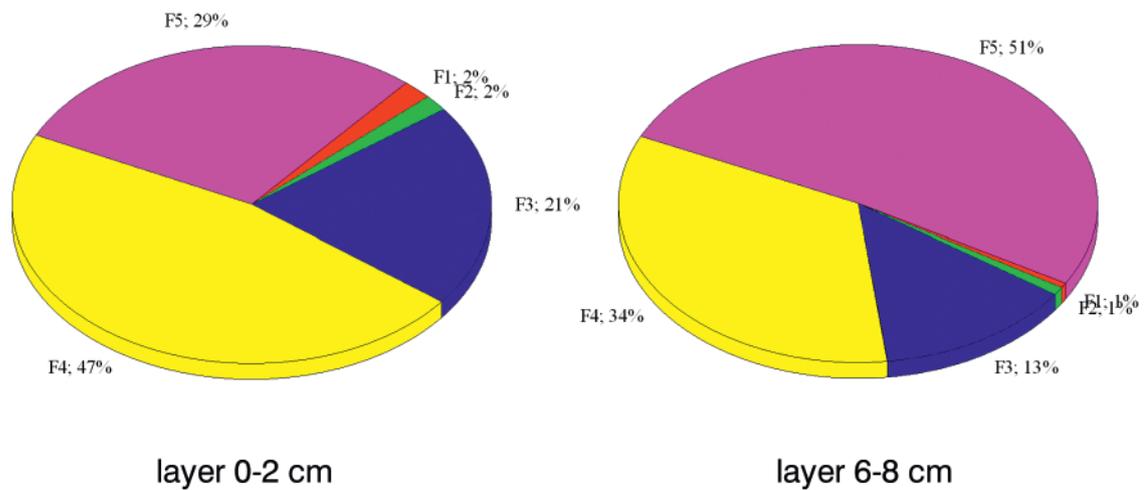


Figure 5. Arsenic speciation in the bottom sediment at station 1 in the dam area, F1 – exchangeable form, F2 – sorbed on carbonates, F3 – sorbed on Mn-Fe oxides, F4 – organic bonds and sulfides, F5 – residue

Table 4. As(III) and As(V) concentrations in the interstitial water of Rybnik Reservoir [$\mu\text{g}/\text{dm}^3$]

Layer	As(III)		As(V)	
	Range	Mean \pm SD	Range	Mean \pm SD
0-2 cm	0.34-1.09	0.62 \pm 0.24	1.51-6.03	3.48 \pm 1.47
2-4 cm	0.32-0.67	0.43 \pm 0.09	1.64-4.48	2.54 \pm 0.78
4-6 cm	0.34-0.59	0.46 \pm 0.06	1.44-5.16	2.63 \pm 0.87
6-8 cm	0.40-0.87	0.58 \pm 0.13	1.31-5.62	3.34 \pm 1.13

carbonates is feasible under the conditions of low pH [8, 30]. Lowest mobility is typical of sulfides which release arsenic in oxygen abundant environments [27] and residue that comprises elements bound in the crystal lattice of minerals in the sediment, which

practically means permanent immobilization in the bottom sediment.

The average As(III) concentration in the interstitial water was $0.52 \mu\text{g}/\text{dm}^3$, ranging from $0.32 \mu\text{g}/\text{dm}^3$ to $1.09 \mu\text{g}/\text{dm}^3$ (Table 4). The values were higher than

those for As(III) in the water from the bottom layer at particular sites.

Concentration of As(V) in the interstitial water in the bottom sediment in Rybnik Reservoir ranged from 1.31 $\mu\text{g}/\text{dm}^3$ to 6.03 $\mu\text{g}/\text{dm}^3$ (Table 4). Highest As(V) concentration was found in the interstitial water from the surface layer of the bottom sediment and the deepest 6-8 cm layer. They were significantly higher than the ones assayed in the interstitial water from the other layers of the bottom sediment. No significant differences were found for As(V) concentrations in the interstitial water at particular sites.

The interstitial water of contaminated lakes investigated by Nikolaidis et al., was dominated by As(III) which constituted even as much as 100% of total arsenic concentration [21]. In contrast, Ruokolainen et al., [25] found As(V) as predominant form of arsenic in the interstitial water of littoral sediments. In the interstitial water of deeper layers of the sediment, under stronger reduction conditions, concentration of As(III) was higher than that of As(V) [25].

4. CONCLUSIONS

It has been found that arsenic in Rybnik Reservoir is an element that is strongly bound to the bottom sediment. The most predominant arsenic forms in the reservoir were sulfides and organically bound fraction. Release of arsenic from the bottom sediments is limited by the relatively high pH of water (7.8) in the bottom layer. Under those conditions, the mobility of arsenic is much lower than in an acidic environment.

Arsenic concentration in the interstitial water was almost twice as high as that in the water of Rybnik Reservoir. Higher values were found in the interstitial water from the surface layer of the bottom sediment, the deeper layers revealed a gradually decreasing trend. This was caused by greater stability of sorption/desorption under those conditions. The results of the speciation analysis of arsenic in the bottom sediment confirmed the above phenomenon which showed much higher percentage of residual fraction in the deepest layer of the bottom sediment compared to the surface 0-2 cm one. In contrast, the percentage of the mobile forms, exchangeable and adsorbed ones, was much higher in the 0-2 cm layer of the bottom sediment than in the 6-8 cm one.

In the surface and bottom waters of the reservoir, arsenic occurred primarily as As(V). It accounted for 70% of total concentration of inorganic arsenic in the

water of Rybnik Reservoir. It also dominated the interstitial water reaching 85% of total arsenic concentration compared to the mere 15% of As(III). High concentration of As(V) in the bottom water is difficult to explain – anaerobic conditions prevailing in the deep water zone near the dam should favour As(III), whereas comparison between As(III) and As(V) in the surface and bottom waters revealed practically no differences.

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