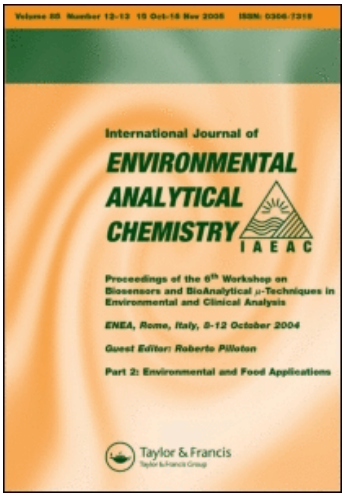

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Speciation of Inorganic Arsenic and Selenium in Contaminated Ground Water Samples—Distribution and Long-Term Stability of Species

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SPECIATION OF INORGANIC ARSENIC AND SELENIUM IN CONTAMINATED GROUND WATER SAMPLES – DISTRIBUTION AND LONG-TERM STABILITY OF SPECIES

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This paper presents the results of speciation studies of arsenic and selenium in contaminated ground water samples from Kelheim / Germany. Results are based on separation of ions by HPLC using a phosphate buffer. The separated species were collected in fractions and analysed element-specifically by HG-AAS. Dominating species were arsenate and selenate, while arsenite and selenite were less important. Long-term studies revealed that As (V), Se (IV) and Se (VI) remained stable for up to 12 months, whereas oxidation of As (III) was observed after 3 months.

Keywords: Arsenic; selenium; speciation; ground water; long-term stability

INTRODUCTION

Arsenic and selenium may exhibit toxic effects on biota in ground water samples[1,2]. If concentrations are high, humans may be affected. Arsenic is supposed to induce cancer[3]. Elevated concentrations of selenium may lead to selenosis[4]. It is well known, today, that toxicity of an element is determined by the chemical form in which it is present in the sample. According to Stoeppler & Schramel[5], it is the aim of speciation analyses to reveal the identity and the quantity of different specific compounds or oxidation states of an element. In the case of arsenic, As (III) is more toxic than is As (V). Presence of As (III) in water samples interferes with drinking water preparation; it is not effec-

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tively removed by addition of iron hydroxides. Se (IV) is considered more dangerous to aquatic organisms than Se (VI) due to its higher solubility and bioavailabilty. Those species are reported to be of greatest concern, that are able to easily penetrate the cell membrane. Among others, free ions are likely to do so. Determination and quantification of these species is therefore prerequisite to risk assessment.

In the present case, ground waters from Kelheim / Germany were analysed and arsenic and selenium species determined. The ground waters were characterized by very high concentrations of iron, manganese and sulfur due to leaching processes of pyrites, formerly used for production of sulfuric acid, and their oxidation products. Pyrites and oxidation products were deposited in the Kelheim region or were used as filling materials in road construction and railway embankments. Among other trace elements, pyrites and their oxidation products contained elevated concentrations of leachable arsenic and selenium that penetrated into ground water. High concentrations of interfering ions make direct IC determination of As and Se in environmental samples almost impossible[6]. For this reason, element-specific detection is mandatory in samples with an intricate matrix. In the present study, the ions were separated by HPLC based on phosphate buffer eluents[7–9] with element-specific detection. For this purpose, HG-AAS was selected which is highly sensitive towards inorganic arsenic and selenium species. Besides determination and quantification of species in the ground water samples, we also examined the stability of species in acidified and non-acidified samples in a series of long-term studies that lasted for 6–12 months.

EXPERIMENTAL

Sampling and Sample Storage

Ground water samples were collected in the winter (series 1 and 2), spring (serie 3), summer (serie 4) and autumn (serie 5) season 1995 at different locations at Kelheim, Lower Bavaria, Germany. The city of Kelheim is situated at the confluence of Altmühl River and Danube River in the South East of Germany.

Sampling points A, B, C and D were located at the grounds of a chemical plant where sulfuric acid was, and still is, produced. Point E was situated at the grounds of a cellulose producing plant that has been shut down, meanwhile. Sampling points G and F were located at the city centre of Kelheim. The six wells were selected since constantly elevated concentrations of arsenic and sele-

nium made long-term speciation studies possible. As will be shown later, concentrations of selenium in some wells, however, were close to, or even below, the detection limit of the method depending on location and time of sampling. Samples were pumped with a delivery of 1,2 L/sec. To avoid contamination of tubing, the pumping system was conditioned with well water. The first 50 L of each sample were discarded. Samples were filled into 1 L PE bottles, acidified to pH $\leq$ 2 with HCl and stored at 4 °C, protected from daylight. Filled bottles were immediately sealed to avoid exposure to air. While all samples of the winter, spring and summer seasons were acidified, those being collected in autumn were stored non-acidified to study possible differences in species stability. A vacuum filtration of samples through 0,45 µm filtration membranes was carried out prior to HPLC separation.

Chromatographic separation of As and Se species

Separation of species was carried out on a HPLC anion-exchange column, Hamilton PRP X-100, 250 × 4,1 mm. No guard column was used. The eluent consisted of 5 mM $NH_4H_2PO_4$ (Aldrich), 10 mM $(NH_4)_2HPO_4$ (Aldrich) and 15 mM Na_2SO_4 (Fluka) whose pH was adjusted to 5,9 with H_3PO_4 (Merck). The flow rate was 1 mL/min, generated by a Beckman solvent delivery module 114. The following retention times were determined using an UV detector, BioRad uv/vis module 1706: As (III) 2.6 min, As (V) and Se (IV) 4.0 min, Se (VI) 11.1 min. UV detection not being sufficiently sensitive in real samples, quantification of ions was carried out by HG-AAS (see below). For this purpose, the separated ions were collected in fractions (BioRad model 2110 fraction collector). Five fractions were taken every 3 min. If present, As (III) was found in Fraction 1 (0–3 min), As (V) and/or Se (IV) in Fraction 2 (3–6 min) and Se (VI) in Fraction 4 (9–12 min). Fractions 3 (6–9 min) and 5 (12–15 min) did not contain arsenic and selenium species. Thanks to element-specific detection by HG-AAS, coelution of As (V) and Se (IV) was not considered a drawback.

Element-specific detection

Analyses were carried out with a Perkin Elmer 3030B Atomic Absorption Spectrometer equipped with a hydride generator MHS 20 at λ = 193,7 nm (arsenic) and λ = 196,0 nm (selenium). For hydride generation, a solution of 3% $NaBH_4$(Merck), stabilized by 1% NaOH (Merck) was used. Each fraction's volume was extended to 10 mL by adding 7 mL 3% HCl (Merck). Samples containing Se (VI) were reduced to Se (IV) prior to analysis. Complete reduction was achieved as follows: Equal volumes (5 mL) of sample and 32% HCl (Merck) were mixed, filled in Nalgene tubes, sealed, and exposed to a water bath at 80 °C

for 1 h[10]. Purge I was 50 sec (As) or 20 sec (Se). Purge II was 40 sec (As and Se). Reaction time was 18 sec (As) or 12 sec (Se). Cell temperature was 1000 °C (As and Se). Excitation was based upon electrodless discharge lamps (Perkin Elmer). Concentration of As (III), As (V) and Se (IV) was evaluated on peak height signals.

Speciation studies of arsenic and selenium

After chromatographic separation of samples, filtrates were analysed for arsenic and selenium with HG-AAS. The sum of either arsenic or selenium species in the filtrates being in agreement with total As and Se concentrations in the ground water samples, indicated quantitative recovery. Speciation studies were subdivided into 3 series:

Serie 1:	***A2** (arsenic and selenium)*
	***E2, F2, G2** (arsenic), **B2, C3 D2** (selenium),*
	Long-term study of 12 months with ***acidified*** samples. Analysis every 2 months.
Serie 2:	***A1, A3, A4** (arsenic and selenium)*
	***E1, E3, E4, F1, F3, F4, G1, G3, G4** (arsenic), **B1, B3, B4, C1, C4, D1** (selenium)*
	Long-term study of 6 months with acidified samples. Analysis every 2 months.
Serie 3:	***A5** (arsenic and selenium)*
	***E5, F5, G5** (arsenic), **C5, D5** (selenium)*
	Long-term study of 6 months with non-acidified samples. Analysis every 2 months.

Name of sample is given in bold letters. Each analysis was performed in triplicate.

Detection limits of HG-AAS for arsenic and selenium were based on analyses of 10 blanks of HCl suprapur 3%. The corresponding values were 0,6 µg/L (As) and 0,5 µg/L (Se) with t(f = 9, P = 95%, one-sided). A 100 µL sample loop was used for HPLC. Consequently, the limit of determination of the overall method was 6 µg/L for arsenic and 5 µg/L for selenium.

RESULTS AND DISCUSSION

Arsenic and selenium concentrations in the samples

Arsenic speciation was carried out in wells A, E, F and G; selenium speciation in wells A, B, C and D. While arsenic concentration was sufficiently above the limit of determination in all samples, selenium speciation was not possible in samples

B5, D3 and D4 as selenium concentrations were nearby or below the limit of determination in these samples.

Stability of As concentration

Minimum and maximum values of arsenic concentrations measured within the analytical series (12 or 6 months, respectively) are given in the second column of Table I. Concentration means together with standard deviations are listed in the third column of Table I.

TABLE I Results of arsenic stability and speciation studies

Sample	*Concentration*	*Concentration*	*Recovery (%)*	*N*	*Species*
	Min./Max. (μg/L)	*Mean (μg/L)*	*As (III) + As (V)*		
A2	56,7 / 65,3	60,5 ± 2,8	102,7 ± 3,5	6	As (V)
E2	150 / 167	157 ± 6,4	94,2 ± 3,1	6	**As (III)** / As (V)
F2	68,1 / 83,8	76,9 ± 5,2	93,2 ± 4,9	6	**As (III)** / As (V)
G2	26,7 / 41,0	35,2 ± 5,0	104,1 ± 7,1	6	As (V)
A1	68,1 / 71,0	69,6 ± 1,5	101,7 ± 3,2	3	As (V)
A3	65,3 / 72,4	67,7 ± 4,1	105,7 ± 4,0	3	As (V)
A4	62,4 / 72,4	67,2 ± 5,0	101,3 ± 4,0	3	As (V)
E1	253 / 316	278 ± 33,5	99,0 ± 8,2	3	**As (III)** / As (V)
E3	103 / 118	108 ± 8,0	101,7 ± 4,5	3	As (V)
E4	159 / 179	169 ± 10	96,3 ± 2,9	3	**As (III)** / As (V)
F1	75,3 / 82,4	79,1 ± 3,6	104,0 ± 1,0	3	As (V)
F3	105 / 115	111 ± 5,4	93,3 ± 2,5	3	As (V)
F4	98,1 / 106	101 ± 4,4	104,0 ± 5,2	3	As (V)
G1	38,7 / 39,6	39,0 ± 0,5	106,3 ± 1,5	3	As (V)
G3	39,6 / 43,6	41,5 ± 2,2	102,7 ± 2,1	3	As (V)
G4	43,9 / 45,3	44,8 ± 0,8	94,7 ± 5,1	3	As (V)
A5	55,3 / 68,1	62,9 ± 6,7	99,7 ± 1,5	3	As (V)
E5	139 / 144	142 ± 3,3	105,0 ± 2,6	3	As (V)
F5	98,7 / 99,6	99,2 ± 0,4	101,3 ± 3,2	3	As (V)
G5	25,3 / 33,8	30,1 ± 4,4	101,3 ± 7,4	3	As (V)

Results show that total As concentrations were stable at least for up to one year in acidified samples and for up to 6 months in non-acidified samples. A total of 20 samples were analysed. In neither sample, a considerable decrease in As con-

centration was observed. Consequently, adsorption to container surfaces was negligible and PE vessels proved to be suitable to storage of ground water samples for arsenic speciation. Moreover, no loss of arsenic was observed that could have been attributed to adsorption to, or coprecipitation with, iron or manganese oxyhydroxides, even in non-acidified samples with iron concentrations > 600 µg/L. This was even more striking as both iron and manganese oxyhydroxides are reported to serve as adsorbants to arsenic[11]. Storage of our samples at 4°C was sufficient to preserve arsenic concentration.

Distribution of As species

Presence of species is shown in the last column of Table I. Where both species were detected, the dominating one is printed in bold letters.

Unique presence of As (V)

According to observations of other authors[12,13], As (V) was the predominant species in our samples, too. While wells A and G showed a uniforme distribution of As (V) with quantitative recoveries of 102,8 ± 4,2% (A) and 103,8 ± 7,3% (G), distribution in wells E and F was more complex (cf Table I and see below). Predominance of As (V) is favoured thermodynamically and by higher ionic strength of the solution[14].

Unique presence of As (III)

Just 3 samples, E2, E4 and F2, contained As (III) as the only detectable species at the beginning of the analytical series. Recoveries in these samples were slightly lower than with samples only containing As (V). Concentrations of As (III) were not stable; slow but continous oxidation to As (V) was observed after 3 months. At the end of the 12 months term, part of As (V) had increased to about 30% in E2 and F2. These results showed that acidification of samples was not sufficient to stabilize As (III) for a longer range of time. Oxidation of As (III) was induced by traces of oxygen in the samples, although exposure to air had been minimized (cf "Sampling and Sample Storage"). Susceptibility of As (III) towards oxidation has also been described by other authors[15,16].

Common presence of As (III) and As (V)

There was only one sample (E1) where presence of both As (III) and As (V) at the beginning of the analytical serie was detected. In analogy to other samples

containing As (III), partial oxidation to As (V) was observed. In this case, however, oxidation was faster. After 6 months, part of As (III) had dropped to about 70% of its original value. An accelerating effect of As (V) on oxidation of As (III) could be assumed.

Stability of Se concentration

Minimum and maximum values of selenium concentrations measured within the analytical series (12 or 6 months, respectively) are given in the second column of Table II. Concentration means together with standard deviations are listed in the third column of Table II.

TABLE II Results of selenimu stability and speciation studies

Sample	*Concentration*	*Concentration*	*Recovery [%]*	*N*	*Species*
	Min./Max. [µg/L]	*Mean [µg/L]*	*Se (IV) + Se (VI)*		
A2	10,9 / 13,8	12,5 ± 0,9	97,3 ± 6,3	6	Se (VI)
B2	281 / 334	308 ± 19,0	98,0 ± 2,9	6	Se (VI)
C3	61,5 / 66,7	64,0 ± 2,0	95,7 ± 3,2	6	Se (VI)
D2	40,5 / 46,1	42,4 ± 2,1	94,3 ± 6,9	6	Se (IV) / **Se (VI)**
A1	10,7 / 14,2	12,0 ± 1,9	83,0 ± 8,0	3	Se (VI)
A3	16,2 / 21,6	17,9 ± 3,2	91,0 ± 2,6	3	Se (VI)
A4	14,3 / 19,9	17,0 ± 2,8	93,0 ± 4,6	3	Se (VI)
B1	83,6 / 89,4	86,0 ± 3,0	93,7 ± 5,5	3	Se (VI)
B3	41,9 / 44,5	43,4 ± 1,4	91,3 ± 4,5	3	Se (VI)
B4	47,0 / 54,1	51,6 ± 4,0	97,0 ± 4,6	3	Se (VI)
C1	49,8 / 52,7	51,4 ± 1,5	90,1 ± 6,0	3	Se (VI)
C4	12,6 / 13,8	13,1 ± 0,6	89,7 ± 12,7	3	Se (VI)
D1	–/–	13,7 ± 1,2	93,3 ± 8,7	1	Se (VI)
A5	21,3 / 25,7	23,0 ± 2,4	89,0 ± 1,0	3	Se (VI)
C5	17,3 / 19,0	18,2 ± 0,9	92,7 ± 4,7	3	Se (IV) / **Se (VI)**
D5	–/–	10,5 ± 1,8	85,0 ± 8,1	1	Se (IV)

Results of long-term studies revealed that total selenium concentrations were stable at least for up to one year in acidified samples. With the exception of D1 and D5, no depletion of selenium concentration was observed in acidified or

non-acidified samples. Depletion of selenium in D1 and D5 had to be attributed to adsorption to, or coprecipitation with, iron oxyhydroxides[17]. Although being acidified, extremely high concentrations of dissolved iron (about 1800 µg/L] led to formation of precipitates in this sample. Adsorption of selenium on PE container walls has not been observed[18]. Evaluation of selenium stability in non-acidified samples was difficult since based on a few results only. Just 2 samples, (A5 and C5) contained stable Se concentrations sufficiently above the limit of determination.

Distribution of Se species

The presence of species is shown in the last column of Table II. Where both species were detected, the dominating one is printed in bold letters.

Unique presence of Se (VI)

According to observations of other authors[17,19], Se (VI) was the predominant species in our samples, too. Wells A and B showed a uniforme distribution of Se (VI) with recoveries of 91,8 ± 7,0% (A) and 95,6 ± 4,6% (B). In all cases, recoveries were < 100% indicating that minor traces of Se (IV) in these samples were present but were not amenable to analysis because of a lack of sensitivity of the method (Limit of determination 5 µg/L for selenium).

Se (VI) turned out to be stable for at least 12 months in acidified samples and for at least 6 months in non-acidified samples being in agreement with literature[20].

Unique presence of Se (IV)

There was just one sample (D5) where Se (IV) was the only species detected. Se (IV) concentration was, however, not stable in this non-acidified sample and dropped from 10,5 µg/L to below the limit of determination within 2 months while no increase in Se (VI) concentration could be observed. Depletion of Se (IV) in this sample has already been reported and had been attributed to coprecipitation due to formation of iron hydroxides.

Common presence of Se (IV) and Se (VI)

Both species could be detected in 2 samples (C5, D2). No indication of redox reactions was given as concentrations of both species remained almost constant. Verification of Se (IV) concentration, however, turned out to be difficult as it was

only slighty above the limit of determination (about 6 µg/L in each case). Nonetheless, species stability of Se (IV) could be shown to last for 12 months (acidified sample) and 6 months (non-acidified sample), respectively. It can be assumed that Se (IV) tends to be more stable in ground water samples than is As (III) and that distribution of selenium species in ground water samples is more complex than that of arsenic. As mentioned above, common presence of Se (VI) and traces of Se (IV) is very likely in most samples analysed. For final conclusions on behaviour of selenium species in ground water samples, further investigations with an adequately improved sensitivity of the analytical method will be necessary.

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