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Determination of arsenic bioavailability in mineral springs in the Czech Republic

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Abstract: Mineral springs Hronovka and Regnerka located in the northeast Bohemia, Czech Republic are characteristic for high content of arsenic. The diffusive gradient in thin films technique (DGT) was used for determination of arsenic bioavailable fraction in both mineral water samples. Despite the high concentration of iron in both mineral water, the arsenic content measured by DGT (c_{DGT}) corresponded to the total arsenic concentration measured directly by ET-AAS in the grab sample of mineral water (c_{GRAB}) with the final ratio c_{DGT}/c_{GRAB} 1.09 for Hronovka, and 1.06 for Regnerka. These results indicate that the composition of the mineral water prevents the complexation of arsenic and iron and so arsenic in tested spring waters is completely bioavailable.

Key Words: arsenic, bioavailability, DGT, mineral spring

INTRODUCTION

In the Czech Republic, there are many natural mineral springs, some of which are traditionally used for their healing effects in spa towns. In the area of northeast Bohemia, we can find arsenic-rich mineral springs. According to the former Czechoslovakian national standard (ÚNMZ 1966) the mineral spring can be considered as arsenic spring if the arsenic content exceeds the limit of 0.7 mg/l. The current classification of mineral waters does not take into account the arsenic content (Česká Republika 2001). Legislation of the Czech Republic sets the maximum hygienic level of arsenic in drinking water to 10 µg/l (Česká Republika 2014), which is also consistent with recommendations of World Health Organization (WHO 2011).

Generally, arsenic in natural water is present in arsenite AsO_3^{3-} and arsenate AsO_4^{3-} oxoanion forms (Smedley and Kinniburgh 2002). The composition of mineral spring is influenced by the geological and hydrogeological location of the spring (Fugedi et al. 2010). Mineral water generally contains a high concentration of sulfates, carbon dioxide, chlorides or iron, which can affect the speciation and bioavailability of arsenic. In the surface geothermal waters rich in sulfides, arsenic is rather than oxyanions present as thioanions with the predominance of thioarsenates (Guo et al. 2017). The presence of ferric compounds in the aquatic environment also has a significant influence on the mobility of arsenic (Farrell et al. 2013) and thus the bioavailable fraction of arsenic can be lower compared to the total arsenic concentration in mineral springs.

In this study, the diffusive gradient in thin films technique (DGT) was used for determination of arsenic bioavailable fraction in the samples of mineral springs. The principle of the DGT technique is based on the diffusion of metals through a diffusive gel and their subsequent accumulation on a resin gel containing functional groups for targeted analytes. In real ecosystems, primarily mobile and labile forms of the metal, such as free and hydrated ions and complexes with natural ligands smaller than the pore size of the diffusion gel are able to diffuse through the diffusion gel and subsequently are bound in the resin gel (Zhang and Davison 2000). Resin gels containing iron oxyhydroxide functional

groups were used for arsenic determination. Iron oxyhydroxide is able to adsorb arsenite as well as arsenate compounds by ion-exchange mechanism and is commonly used for arsenic removal from drinking water (Giles et al. 2011).

MATERIAL AND METHODS

Reagents

All chemicals were of analytical grade or higher. Standard solution of As^{III} (c = 1000 ± 4 mg/l in 2% (v/v) HNO_3 (Sigma-Aldrich, Germany)) was used for calibration. Palladium 10 g/l (Analytika, Czech Republic) was used as a matrix modifier for ET-AAS determination of arsenic, sodium tungsten dihydrate (Sigma-Aldrich, Germany) was used for graphite furnace surface coating. Test kit NANOCOLOR® Sulfate LR 200 (Macherey-Nagel, Germany) was used for photometric determination of sulfate. All solutions were prepared using Milli-Q water produced by Millipore Milli Q system (Millipore, Bedford, MA, USA), the 65% nitric acid (VWR, Czech Republic) was distilled by apparatus Type BSB-939IR (Berghof, Germany).

Acrylamide 40% (w/v) (Merck, Germany), ammonium persulfate (Honeywell Fluka, Germany), N,N,N′,N′-tetramethylethylenediamine (TEMED) (Sigma-Aldrich, Germany), DGT cross-linker (2%) (DGT Research Ltd., UK) and iron oxyhydroxide based resin (Lanxess, Germany) were used for DGT gel preparation. Sodium chloride and sodium hydroxide (Penta, Czech Republic) were used as elution agent for the release of arsenic from resin gels.

Instrumentation and DGT devices

Measurement of arsenic was performed using atomic absorption spectrometer 280Z AA (Agilent Technologies, USA) with a graphite furnace atomizer and Zeeman background correction. The resonance line of As was set at 193.7 nm with a spectral bandwidth of 0.5 nm and the arsenic lamp (Agilent Technologies, USA) as a light source operated with a current 10 mA.

DGT pistons with an exposure area of 3.14 cm^2 (DGT Research Ltd., UK) and polyethersulfone membrane filters of 0.45 μm pore size and 0.013 cm thickness (Pall Corporation, USA) were used for experiments.

Diffusive and resin DGT gels

Diffusive gels consist of 10 ml of gel solution (15% of acrylamide, 0.3% of cross-linker and Milli-Q water), 70 μl of 10% (w/v) ammonium persulfate and 25 μl of TEMED and were produced according to the protocol stated in (Zhang and Davison 1999). Resin-containing gels were prepared in a similar manner with the addition of iron oxyhydroxide resin.

To elute the arsenic from DGT resin gel, the mixture of sodium hydroxide (10 g/l) and sodium chloride (10 g/l) in the combination with microwave-assisted extraction at 130 °C for 16 min was used.

Determination of arsenic

The determination of As content in eluates of DGT resin gels was complicated by the loss of arsenic content during the pyrolysis step and interferences caused by the matrix of elution agent (10 g/l NaOH + NaCl). Therefore, the optimized ET-AAS method combining the palladium modifier (1% (v/v)), cool-down step (130 °C) incorporated to temperature program and graphite tube coating by tungsten carbides was used. The parameters of ET-AAS method and procedure of arsenic determination are described in detail in Smolíková et al. The concentration of arsenic in the grab sample of mineral water was determined in the same way due to the high content of chlorides.

Samples

Samples of mineral springs Hronovka and Regnerka were collected in July 2019 in the park Jiráskovy sady, Hronov, Czech Republic. For direct determination of arsenic content, the samples were acidified to 1% (v/v) HNO_3 concentration (VWR, Czech Republic). All samples were collected to acid-cleaned glass bottles and stored refrigerated until analysis.

Figure 1 Mineral springs Hronovka and Regnerka (A) and their location (B) (https://mapy.cz)

Determination of bioavailable arsenic in mineral spring water

The DGT units (iron oxyhydroxide resin gel placed on the top of the plastic piston, covered by diffusive gel and membrane filter, and capped by outer sleeve with an exposure window) were deployed to into 3 liters of the mineral water under constant stirring for 2, 4 and 6 h (5 replicates for each sampling time). After accumulation, the DGT units were removed from mineral water, disassembled and disks of resin gel were rinsed with Milli-Q water and eluted. The concentration of arsenic in the eluate represents the arsenic mass accumulated per resin gel disk (M, ng). This value was used for calculation of the arsenic concentration in mineral spring determined by DGT (c_{DGT}, µg/l) using Equation (*1*), where Δg is the thickness of diffusive layer (0.093 cm), D is the diffusion coefficient of the analyte, A is the exposed area (3.14 cm^2) and t is the deployment time (e.g., 21,600 s). Since arsenic speciation analysis was not performed, the average diffusion coefficient (D = 6.41×10^{-6} cm^2 s^{-1}, determined in 0.01 M $NaNO_3$ solution (pH 5.0)) of four arsenic species (As^{III}, As^{V}, monomethylarsonic acid, and dimethylarsinic acid) which are available for iron oxyhydroxide resin gel was used for calculations.

$$c_{DGT} = \frac{M\,\Delta g}{D\,A\,t} \qquad (1)$$

To evaluate the bioavailable fraction of arsenic in mineral spring water, the c_{DGT} value was then compared to the arsenic concentration measured directly by ET-AAS in the grab sample of mineral water (c_{GRAB}).

RESULTS AND DISCUSSION

Characterization of mineral water samples

Samples of mineral springs Hronovka and Regnerka were characterized by determination of pH, iron (determined by F-AAS Agilent Technologies, USA), sulfates, phosphates, chlorides, nitrates and nitrites (Horáková 2007) (Table 1).

Table 1 Characterization of mineral springs Hronovka and Regnerka

	Hronovka	Regnerka
pH	6.45	6.13
Fe [mg/l]	8.61	14.22
SO_4^{2-} [mg/l]	61.0	58.0
PO_4^{3-} [mg/l]	0.07	0.05
Cl^- [mg/l]	61.35	78.22
NH_4^+ [mg/l]	0.39	0.29
NO_3^- [mg/l]	0.13	< LOD
NO_2^- [mg/l]	0.13	0.09
Conductivity [µS/cm]	1570	1714

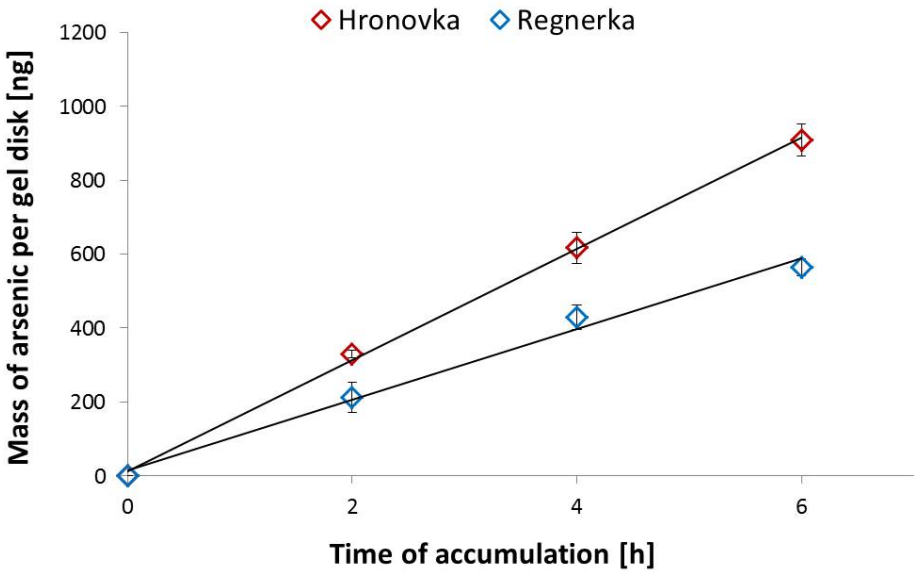
Legend: LOD – Limit of detection = 0.1 mg/l

The high concentration of iron in both samples could influence the availability of arsenic towards DGT. The previous laboratory experiments showed that the availability of arsenic towards iron oxyhydroxide resin gel is decreased by ~22% when 1mg/ l Fe^{3+} is added to the 0.01 mol/l $NaNO_3$ solution (pH 5.0) which is used as a standard environment for determination of diffusion coefficients of DGT resin gels.

Time-dependence experiment

Time-dependence experiment (Figure 2) was performed because the linearity of target analyte accumulation over time is the fundamental assumption of the DGT use.

Figure 2 Time-dependence experiment



The results showed that the mass of arsenic accumulated per gel disk increased linearly over the accumulation time, with a coefficient of determination R^2 = 0.990–0.999 for Hronovka and Regnerka, respectively. The linear course of arsenic accumulation on DGT resin gels indicates the steady-state flux of analyte under perfect sink conditions was achieved and there was no factor adversely affecting the arsenic accumulation into DGT unit (e.g., competition, saturation, kinetic effects).

Determination of bioavailable arsenic

In order to compare the concentration of arsenic measured by DGT (c_{DGT}) to the concentration measured directly by ET-AAS in the grab sample of mineral water (c_{GRAB}), the ratio of both values was calculated (Table 2).

Table 2 The comparison of the arsenic concentration obtained by DGT and by direct ET-AAS measurement

	c_{DGT} (µg/l)	c_{GRAB} (µg/l)	c_{DGT}/c_{GRAB}
Hronovka	192.54 ± 9.18	175.18 ± 10.51	1.09
Regnerka	120.81 ± 4.83	113.71 ± 9.32	1.06

Because speciation analysis of arsenic compounds was not performed, the average diffusion coefficient of four arsenic species was used for the calculations of c_{DGT}. The use of this *D* value can only generate a maximum error of 11.6% compared to the result obtained when using the diffusion coefficient of particular arsenic species. Nevertheless, the obtained ratios close to 1.00 indicates that the bioavailable fraction of arsenic concentration determined by DGT corresponds to the total arsenic concentration analyzed in grab sample of mineral water. Although previous laboratory experiments with standard solutions containing only arsenic and iron led to the reduction of arsenic availability to DGT, in real samples of mineral spring water the arsenic was fully available to the DGT despite the naturally high concentration of iron in both samples of mineral spring water. It is assumed

that this phenomenon is caused by the presence of other components (e.g., sulfates, phosphates) in the samples. The effect of sulfates and phosphates on arsenic accumulation to ferric oxide has been described in the literature (Wilkie and Hering 1996, Youngran et al. 2007).

CONCLUSION

Bioavailability of arsenic in two mineral springs Hronovka and Regnerka was evaluated using diffusive gradient in thin films technique. The linear accumulation of arsenic on iron oxyhydroxide resin gel over time indicated that the DGT measurement had a quantitative character. Although it was expected that the bioavailability of arsenic in mineral water will be reduced by the high iron content, the obtained ratios of c_{DGT}/c_{GRAB} showed that the bioavailable fraction of arsenic determined by DGT corresponds to the total arsenic concentration in grab sample in mineral water. For this reason, it is assumed that the composition of the mineral water prevents the complexation of arsenic and iron, and so arsenic is completely available to DGT as well as to the biota.

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