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Speciation of volatile arsenic at geothermal features in Yellowstone National Park

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Abstract

Geothermal features in the Yellowstone National Park contain up to several milligram per liter of aqueous arsenic. Part of this arsenic is volatilized and released into the atmosphere. Total volatile arsenic concentrations of 0.5–200 mg/m^3 at the surface of the hot springs were found to exceed the previously assumed nanogram per cubic meter range of background concentrations by orders of magnitude. Speciation of the volatile arsenic was performed using solid-phase micro-extraction fibers with analysis by GC–MS. The arsenic species most frequently identified in the samples is $(CH_3)_2AsCl$, followed by $(CH_3)_3As$, $(CH_3)_2AsSCH_3$, and CH_3AsCl_2 in decreasing order of frequency. This report contains the first documented occurrence of chloro- and thioarsines in a natural environment. Toxicity, mobility, and degradation products are unknown.
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1. Introduction

Volatile arsenic species (arsenic species with a boiling point below 150 °C) have been known since the early 19th century. After several incidents of sudden deaths in Germany and Great Britain, the German scientist Gmelin (Gmelin, 1839) correlated an observed "mouse-like" odor in the rooms where the deaths occurred with the possible presence of volatile arsenic and its potential for human poisoning. Following this clue, Fleck (Fleck, 1872) demonstrated that molds growing on wallpapers that were painted with arsenic pigments such as Scheel's green, and Schweinfurt or emerald green (copper aceto-arsenites) were able to produce a volatile arsenic compound. Fleck suggested that the produced gaseous compound was arsine but was not able to identify it. Finally, Gosio isolated various microbial cultures that produced this gas, named "Gosio gas" in his honor (Gosio, 1893). Biginelli (1900) purged the Gosio gas produced by the molds through acidified HgCl solution and identified the resulting precipitate, incorrectly, as diethylarsine $(C_2H_5)_2AsH$. About 30 years later, Challenger et al. (1933) reviewed Biginelli's work and positively identified the gas produced as trimethylarsine $(CH_3)_3As$. The mold, earlier named by Gosio as *Penicillium brevicaule* was later renamed as *Scopulariopsis brevicaulis*) (Challenger, 1945). Even though it seems unlikely today that trimethylarsine was the major cause for the observed deaths because of its low toxicity potential (Cullen and Bentley, 2005), this initial suspicion triggered the early research on volatile arsenic compounds.

Volatile arsenic species are highly mobile in the environment. Abiotic transformation from inorganic to vola-

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tile arsenic compounds is rare and is more likely microbially catalyzed. Laboratory experiments predict that the occurrence of volatile arsenic species in natural aquatic systems is limited because of their reactivity towards oxygen which decreases with increasing methylation (Parris and Brinckman, 1976). Studies in natural environments have focused on pure inorganic, mono-, di-, and trimethylated arsines. These compounds form as intermediates of the arsenic biomethylation pathway which is a stepwise progression of reduction and oxidative methylation with the theoretical end product $(CH_3)_3As$ (Table 1). Inorganic AsH_3, with a boiling point of −62.5 °C is the most volatile of the arsenic gases and is unstable under atmospheric conditions. As a potent hemolytic agent it is the most toxic inorganic arsenic species. Exposure to 320 mg/m^3 (100 ppm) for less than 30 min has been reported to be lethal for humans (Ellenhorn, 1997). The exposure limit for an 8 h workshift is 0.16 mg/m^3 (0.05 ppm) (Klimecki and Carter, 1995). Of the methylated compounds, $(CH_3)_3As$ is the species most commonly found in environmental samples because of its resistance to oxidation (gas-phase oxidation rate constant: 10^{-6} M^{-1} s^{-1} (Parris and Brinckman, 1976)). Trimethylated arsine has been detected

- in incubated sewage sludge: 3.3 ng/L (1.6×10^{-5} mg/m^3) $(CH_3)_3As$ compared to 0.76 ng/L (2.4×10^{-6} mg/m^3) AsH_3, 0.68 ng/L (2.6×10^{-6} mg/m^3) CH_3AsH_2, and 0.51 ng/L (2.2×10^{-6} mg/m^3) $(CH_3)_2AsH$ (Michalke et al., 2000),
- in geothermal gases (Hirner et al., 1998),
- in domestic waste heap gases: total volatile arsenic: 16.2–48.5 μg/L (0.05–0.15 mg/m^3) (Feldmann et al., 1994),
- in thermophilic and mesophilic digester gas: total volatile arsenic: 0.006–0.025 and 0.016–0.030 mg/m^3, respectively (Feldmann and Kleinmann, 1997).

Acute toxicity potential for trimethylarsine seems to be low (LD_{50} 20,000 mg/L), especially compared to that of AsH_3 (LD_{50} 5–45 mg/L) (Cullen and Bentley, 2005). Compounds such as As_2H_4, $CH_3As_2H_3$, and $(C_2H_5)_2AsH$ are only known from laboratory syntheses (Kösters et al., 2003).

In synthetic solutions the ratio of arsenohalides to arsenohydrides increases with increasing HCl concentrations. The so-called "arsenic butter" ($AsCl_3$) becomes the predominant volatile arsenic species at high HCl concentrations (Arcand, 1957; Tesfalidet and Irgum, 1988). Furthermore, contact of arsine with HCl vapor can result in the formation of $AsCl_3$ directly in the gas-phase (Mester and Sturgeon, 2001). Monomethylchloroarsine CH_3AsCl_2 and dimethylchloroarsine $(CH_3)_2AsCl$ have been found in laboratory experiments using natural samples (Killelea and Aldstadt, 2002; Mester and Sturgeon, 2001). Because the sediment samples were sterilized before the experiment the authors concluded that the formation of halides must have been abiotic. The release of halides has been found to increase with increasing temperature. Despite the high affinity of arsenic and sulfur, little is known about inorganic or organic sulfur arsines. Cullen and Reimer (1989) stated that the rate of arsine evolution from $(CH_3)_2AsSR$

Table 1
Volatile arsenic species: methyl hydrides form as intermediates of the As biomethylation pathway (Challenger mechanism) which is a stepwise alteration of reduction and oxidative methylation

		Inorganic compounds	Methylated compounds		
			1 CH_3	2 CH_3	3 CH_3
gaseous	halogen	$AsCl_3$ (b.p.133°C) AsF_3 (b.p. 57.8°C) AsF_5 (b.p. -53°C)	CH_3AsCl_2 (b.p. unknown, >133°C)	$(CH_3)_2AsCl$ (b.p. 130°C)	
	sulfur		$CH_3As(SR)_2$ (b.p. unknown)	$(CH_3)_2AsSR$ (b.p. unknown)	
	hydrogen	As_2H_4 (b.p. 100°C), AsH_3 (b.p. -62.5°C)	CH_3AsH_2 (b.p. -2°C)	$(CH_3)_2AsH$ (b.p. 36°C)	$(CH_3)_3As$ (b.p. 52°C)
aqueous	As(III)	H_3AsO_3	$CH_3As(OH)_2$	$(CH_3)_2AsOH$	
	As(V)	H_3AsO_4	$CH_3AsO(OH)_2$	$(CH_3)_2AsOOH$	$(CH_3)_3AsO$

The fully methylated $(CH_3)_3As$ is the end product of the biomethylation pathway. Arsenic shows a high affinity for S (RSH = cysteine or glutathione) and halogens (X) also in the gas-phase forming inorganic and organic compounds. So far, they have only been found under extreme conditions (high temperatures for inorganic As-S and As-X compounds, high HCl conditions for organic As-X compounds) or in syntheses (organic As-S compounds); b.p. = boiling point.

(RS- = cysteine or glutathione) is lower than from $(CH_3)_2AsOOH$, and that the arsines produced are $(CH_3)_3As$ and $(CH_3)_2AsH$, not volatile S-As compounds. The volatile dimethylarsenomercaptane, $(CH_3)_2AsSCH_3$, has been synthesized and observed in laboratory experiments (Ashe and Ludwig, 1986; Kösters et al., 2003) but has not been identified previously in natural samples. The toxicities of the chloro- and thioarsines have not yet been studied. This lack of data may be explained by the presumed insignificance of these compounds in natural systems. The present study proves the natural occurrence and predominance of methylchloro- and thioarsines besides $(CH_3)_3As$ in geothermal gases.

Gases were sampled over hot springs and fumaroles in Yellowstone National Park, USA (for location see electronic annex EA-1). The geothermal activity is the surface expression of the final stage of the third Yellowstone caldera cycle. This caldera formed about 630,000 years ago as the present-day terminus of the active Yellowstone hotspot (Smith and Siegel, 2000). High aqueous arsenic concentrations (from leaching of the volcanic rocks) were first detected in Yellowstone in 1888 (Gooch and Whitfield, 1888). Arsenic concentrations in acid, sulfate dominated waters typically are in the lower tens of microgram/liter range, but they can reach up to 9 mg/L in chloride-dominated waters of near-neutral pH (Stauffer and Thompson, 1984; Fournier, 1989; Ball et al., 1998; Ball et al., 2002).

2. Materials and methods

2.1. Total volatile arsenic concentrations

For quantification, volatile arsenic species were collected with gas hoods placed over hot springs. Following the diffusion gradient the collected gases were continuously transferred to a 100 mL Teflon bottle containing a diluted oxidizing solution of 1 mL NaOCl (6–14% active Cl; Riedel-de-Haen) and 99 mL deionized water. Another bottle with 100 mL of 0.1 M NaOH solution was similarly used for trapping volatile HCl and other volatile acid gases (H_2S, H_2SO_4). Sampling of aerosols instead of the target dry gases was excluded by using water traps mounted in front of the oxidizing bottles. The equipment was left in the field for 52–262 h of cumulative sampling. Samples were then filled in polyethylene bottles, stored in the refrigerator until transfer to the laboratory, and analyzed by graphite furnace atomic absorption spectrometry (GF-AAS) for arsenic or photometry for chloride within a maximum of 6 weeks. Stability for this period of time was proven by laboratory experiments (Planer-Friedrich, 2004). The GF-AAS detection limit is 2 μg As/L, the photometry detection limit is 0.5 mg Cl/L. The so-obtained concentrations in NaOCl or NaOH solutions were re-calculated to original concentrations in the gas-phase by determining the net diffusion rate according to Fick's first law:

$$J = -D \cdot \frac{\Delta c}{\Delta x} = \frac{m}{t \cdot A},$$

where J is the net diffusion rate [mg/(s cm^2)]; m is the mass (mg) = concentration of aqueous, oxidized compound (mg/L) · volume of trapping solution (100 mL); t is the exposure time (s); A is the flow cross-section of tube connecting sampling site and trapping solution; tube diameter = 2 mm ($r = 0.1$ cm); $A = r^2 \cdot \pi = 0.0314$ cm^2 (cm^2); D is the diffusion coefficient (cm^2/s); Δc is the concentration gradient between sampling site and trapping solution (mg/cm^3); Δx is the diffusion length; length of the tube connecting sampling site and trapping solution (cm).

Assuming a 100% effective dissolution and oxidation, confirmed by laboratory experiments, the concentration of the volatile compound above the trapping solution is zero during the whole sampling time. Thus, the concentration gradient (Δc) equals the concentration (c) at the sampling site in milligram per cubic meter. Necessary input parameters are diffusion length (x) and area (A), exposure time (t), mass (m), and the diffusion coefficient (D) that is dependent on temperature above the sampling site, and the predominant arsenic or chloride species. The precision of the so-calculated concentration is mainly determined by the analytical precision of the arsenic determination by graphite furnace atomic absorption spectrometry or the chloride determination by photometry (±1–2%) and the calculation of the diffusion coefficients. The Fuller, Schettler, and Giddings (FSG) equation was used for a semi-empirical estimation of the diffusion coefficient based on molecular volumes (Fuller et al., 1966; Tucker and Nelken, 1990)

$$D = 0.001 \frac{T^{1.75} \cdot M_r^{0.5}}{P \cdot (V_A^{1/3} - V_B^{1/3})^2},$$

where D is the diffusion coefficient (cm^2/s); T is the absolute temperature (K) above sampling site, estimated as the average of water temperature at the sampling site and average ambient air temperature (15 °C); M_r is $M_r = \frac{M_A + M_B}{M_A \cdot M_B}$, M_A = molecular weight of air (approximately 28.97 g/mol); M_B = molecular weight of compound of interest (g/mol); P is the pressure (bar); V_A is the molar volume of air (approximately 20.1 cm^3/mol); V_B is the molar volume of the compound of interest (cm^3/mol) = molecular weight (g/mol): vapor density (g/cm^3).

Typical values for diffusion coefficients of inorganic and organic gases in air are between 0.1 and 0.2 cm^2/s. To achieve a higher accuracy, information about the exact composition of the gas including the percentage of each species (e.g., AsH_3, mono-, di-, trimethylarsine, etc.) would be needed. A sensitivity analysis was done for arsenic assuming an uncertainty of ±10 °C for the temperature estimation above the sampling site and the two extreme cases that all volatile As is present as the lightest volatile As species AsH_3 ($M_B = 77.945$ g/mol; $V_B = 77.945$ g/mol: 2.70 g/cm^3 (Sax, 1986) = 28.87 cm^3/mol) or as the heaviest volatile As species $AsCl_3$ ($M_B = 181.28$ g/mol; $V_B = 181.28$ g/mol: 6.25 g/cm^3 (Clayton and Clayton, 1981) =

29 cm^3/mol). Calculated diffusion coefficients ranged from 0.115 cm^2/s to 0.172 cm^2/s with a mean of 0.147 ± 0.015 cm^2/s. Assuming HCl being the predominant volatile chlorine species, mean diffusion coefficients were 0.176 ± 0.010 cm^2/s for the temperature range sampled.

2.2. Volatile arsenic speciation

A total of 57 gas samples from 31 locations were collected for species-selective determinations by solid-phase micro-extraction (SPME) fibers, a technique first described by Arthur and Pawliszyn (1990). The commercial SPME design is similar to a GC injector syringe with a fused silica fiber of approximately 1 cm length coated with different stationary phases. Coatings of polydimethylsiloxane (PDMS) or polydimethylsiloxane-carboxen (CAR) have been used successfully before for trapping chloroarsines in the laboratory (Mester and Sturgeon, 2001, 2002; Mester et al., 2000). A ternary fiber of polydimethylsiloxane-carboxen-divinylbenzene (DVB) proved especially effective in sorbing trimethylarsine (Sur et al., 2003). For our own laboratory experiments, arsines were created by hydride generation from dimethyl arsenic sodium trihydrate ($(CH_3)_2AsNaO_2{\cdot}3H_2O$, Fluka) using sodium borohydrate as reducing agent. In accordance with previous publications (Talmi and Bostick, 1975; Van Elteren et al., 1994; Pantsar-Kallio and Korpela, 2000) it was found that reduction of dimethyl arsenate yielded different arsine species. At a pH of 2 (0.01 M HCl) mono- and trimethylated arsines were detected besides the expected dimethylated arsine. In the presence of excess chloride (0.1–1 M HCl, pH 0–1) the predominant arsine species were dimethylchloroarsine and methyldichloroarsine. Regarding species-selective preferential sorption, PDMS fibers proved efficient for sorbing chloroarsines whereas di- and trimethylated arsines were only observed on PDMS–CAR and PDMS–CAR–DVB fibers (Table 2). Monomethylated arsine with a boiling point of +2 °C was observed on PDMS–CAR–DVB fibers only. Twelve PDMS, 31 PDMS–CAR, and 14 PDMS–CAR–DVB fibers were used in the field.

For application in the field a custom-made SPME fiber holder was used (Fig. 1) connected to the same setup of gas hood and water trap as described in section 2.1. The fiber is protected inside a syringe needle and the syringe plunger is used to expose the fiber. Sampled gas passes the fiber, and non-sorbed components leave the fiber holder by way of the third arm of a T-shaped valve that functions as the gas outlet. After a certain time of exposure (ranging from 2 to 98 h) to the geothermal gases, fibers were retracted in their metal shaft, detached from the fiber holder, immediately cooled, and kept in the refrigerator at +6 °C for one to a maximum of two days until analysis by gas chromatography mass spectrometry (GC–MS).

A GC–MS Varian 3400 and a Varian CP 3800 at the National Water Quality Laboratory in Denver, Colorado, and a HP 5890 at the Department of Chemistry, Montana State University, Bozeman, were used. The GC column was

Table 2
Characteristics of the different coatings on solid-phase micro-extraction (SPME) fibers (PDMS = polydimethylsiloxane, DVB = divinylbenzene, CAR = carboxen)

Stationary phase	Film thickness	Phase description	pH	Maximum temperature (°C)	Operating temperature (°C)	Conditioning temperature (°C) (cleaning step prior to analysis)	Conditioning time (h)	Application range for volatile arsines (from laboratory experiments)
PDMS	100 μm (GC/HPLC)	Non-bonded	2–10	280	200–280	250	0.5	Mainly chloroarsines
CAR/PDMS	75 μm (GC) 85 μm (HPLC)	Bonded	2–11	320	250–310	300	1–2	dimethyl-, trimethyl-, chloro-, and thioarsines
PDMS/CAR/DVB	50/30 μm (GC)	Bonded	2–11	270	230–270	270	1	mono-, dimethyl-, trimethyl-, chloro-, and thioarsines

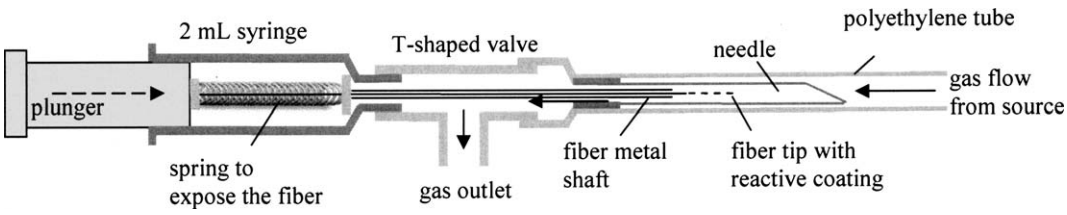

Fig. 1. Custom-made SPME fiber holder for application in the field.

a non-polar low bleed capillary column (HP5-MS) of 30 m length, 0.25 mm diameter, and a film thickness of 0.25 μm. Helium (purity ⩾99.999%) was used as carrier gas at a pressure of 0.15 bar and a flow rate of 1 mL/min. Desorption temperature was 250 °C for 20 s. The column was heated from an initial temperature of 40 °C held for 3 min in splitless mode to 250 °C at 10 °C/min with a split of 1:20. The final temperature of 250 °C was held for 10 min to clean the fiber. Masses from 70 to 180 were scanned at a scan rate of 2.1 s^{-1}. Total analysis time including cleaning was 34 min.

2.3. Aqueous arsenic speciation

For the aqueous phase standard water chemistry parameters were determined. The aqueous arsenic species arsenite (As(III)), arsenate (As(V)), and mono- and dimethylated arsenic were separated using their different sorption behavior on ion exchangers (Le et al., 2000). Arsenate and monomethylated arsenic predominate at pH values above 2–3 as negatively charged complexes and thus sorb on anion exchangers. Arsenite predominates up to a pH of 9 as zero-valent complex and is thus not retained by ion exchangers. Dimethylated arsenic also predominates as zero-valent complex up to a pH of 6 but shows unspecific sorption on both cation and anion exchangers because of its two methyl groups. Passing a water sample first through a cation, then an anion exchanger, and collecting the flow through, all four species can be determined. A strong acid resin-based cation exchanger with a particle size of 45–150 μm and an exchange capacity of 1.9 meq/mL (Alltech) was used to sorb dimethylated arsenic followed by a silica-based anion exchanger with a particle size of 50 μm and a total capacity of 0.14 meq/g (Supelco) to sorb arsenate and monomethylated arsenic. Each 4 mL cartridge contained 500 mg exchanger material between 1 mm thick porous disks. Prior to sampling the ion exchangers were conditioned with 50% methanol and washed with distilled water. In the field, 20 mL of the sample was filtered through a 200 nm cellulose acetate filter (Membrex) before passing the ion exchangers with a flow rate of approximately 0.5–1 mL/min. The flow through containing the As(III) fraction was collected in a 50 mL polyethylene bottle. The ion-exchange cartridges were separated, wrapped in aluminum foil, and stored at 6 °C together with the polyethylene bottle. In the laboratory, the cation exchanger was eluted with 1 M HCl for obtaining the dimethylated arsenic fraction. The anion exchanger was first eluted with 60 mM acetic acid for the monomethylated arsenic fraction, then with 1 M HCl for the arsenate fraction. Elution was done at the most four weeks later. Stability over this time period was demonstrated before (Le et al., 2000) and confirmed by additional experiments in this study. Analysis was done by atomic absorption spectrometry (Zeiss AAS EA4 spectrometer with graphite furnace (GF-AAS) and platform technique, detection limit 2 μg/L). The relative standard deviation between arsenic, calculated as the sum of the four species As(III), As(V), mono- and dimethylated arsenic, and total arsenic from ICP-AES (for arsenic concentrations >100 μg/L) was 3.2% on average for all samples with a maximum of 9.7%. The relative standard deviation between the sum of the four arsenic species and total arsenic from GF-AAS was 3.1% on average with a maximum of 11.5%. Additionally, 50 mL of sample were filtered, stabilized with 1 mL HNO_3 suprapur, and stored dark and cool for analysis of As(III) and As(V) by hydride generation atomic absorption spectrometry (HG-AAS) using a Perkin-Elmer Analyst 300 with a FIAS-100 flow injection analysis system hydride generator (detection limit 0.1 μg/L).

Further aqueous arsenic speciation was obtained by speciation computations with PHREEQC 2.8.03 (Parkhurst and Appelo, 1999) using database WATEQ4F V.2.46 (As species: $H_4AsO_3^+$, H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}, $As_3S_4(HS)_2^-$, and $AsS(OH)(HS)^-$ (Nordstrom and Archer, 2003)). Input parameters and independent components considered were pH, temperature, pe, F, Cl, Br, NO_3, SO_4, Al, B, Ba, Ca, Cd, Cu, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Zn, Si, H_2S, CO_2, and the redox couples As(III)/As(V) (determined by HG-AAS) and Fe(II)/Fe(III) (determined by photometry on-site).

3. Results and discussion

3.1. Total volatile arsenic

Using oxidation in NaOCl, volatile arsenic was found at all sites sampled ranging from a wetland with low geothermal influence (Hazle Lake) to acid fumaroles (near Nymph Lake with a minimum pH of 1.9) as well as acid (Ragged Hills, Gibbon Geyser Basin) and alkaline (Lower Geyser Basin with a maximum pH of 8.7) hot springs (for location see electronic annex EA-1). Total volatile arsenic concen-

trations directly above the geothermal features were between 0.5 and 200 mg/m^3, with an average of 36 mg/m^3 (Planer-Friedrich, 2004). For most sites, significant concentration differences were observed during repeated sampling. The database is yet too low to discuss any seasonal trends. Both concentration decreases (e.g., RH01 from 74 to 26 to 5 mg/m^3) and increases (e.g., NL04 from 4 to 90 mg/m^3) have been observed from June through July to September (electronic annex EA-2). All concentrations observed are significantly increased compared to estimated average global background concentrations of 2.8 ng/m^3 in the Northern hemisphere and 1 ng/m^3 in the Southern hemisphere (Chilvers and Peterson, 1987). They are also much higher than any of the few previously reported values such as for waste heaps (up to 0.050 mg/m^3) and digester gas (up to 0.025 mg/m^3 for mesophilic digestion and up to 0.030 mg/m^3 for thermophilic digestion (Feldmann et al., 1994; Feldmann and Kleinmann, 1997)). The average volatile arsenic concentrations decreased rapidly with increasing vertical and horizontal distance from the source and dropped below detection limit (0.1 μg/m^3) within 1–2 meters.

3.2. Problems with quantitative interpretation of volatile arsenic species

From the species-selective sampling by SPME fibers, volatile arsenic was positively identified in only 23 of the 57 gas samples taken. Four different volatile organic arsenic species were present under a wide range of pH, temperature and redox conditions: $(CH_3)_2AsCl$, $(CH_3)_2AsCl$, $(CH_3)_3As$, and $(CH_3)_2AsSCH_3$. Artifact built-up of the chloro- and thioarsines by reaction of sorbed methyl-arsines with HCl or H_2S on the fiber during storage or later thermo-desorption can be excluded. The gases HCl with a boiling point of −85.1 °C and H_2S with a boiling point of −60.2 °C are not retained on the fibers at ambient air temperature, similar to AsH_3 as discussed below. Blank fibers, not exposed in the field but otherwise treated the same way as the samples showed no built-up of volatile arsenic artifacts.

Quantification of the volatile arsenic species detected proved impossible. One important reason was the lack of certified standards for the predominant chloro- and thioarsines. For tests on the general suitability of SPMEs, chloroarsines were generated in the laboratory as described in Section 2.2. After an experiment, one fiber can only be analyzed once. With the established desorption program, the first desorption is complete, a second desorption shows no more arsenic peaks. Reproducibility tests can, thus, only be conducted by exposing several fibers (with possibly different aging effects of the coating) to the same solution or by conducting several consecutive experiments with one and the same fiber. Because SPME fibers do not quantitatively sorb the target compounds but only a share that is determined by the equilibrium between the aqueous, the gaseous and the solid fiber phase, reproducibility of the amount of generated volatile arsenic species within a certain period of time is crucial. Reproducibility tests in the laboratory, thus, show relatively large standard deviations as demonstrated in Fig. 2 for $(CH_3)_2AsCl$ ($2.3 \times 10^6 \pm 1.5 \times 10^6$, STD 66%). The largest peak (No. 5a) was obtained when a brand-new fiber was used. Already after one desorption and reconditioning cycle the peak obtained

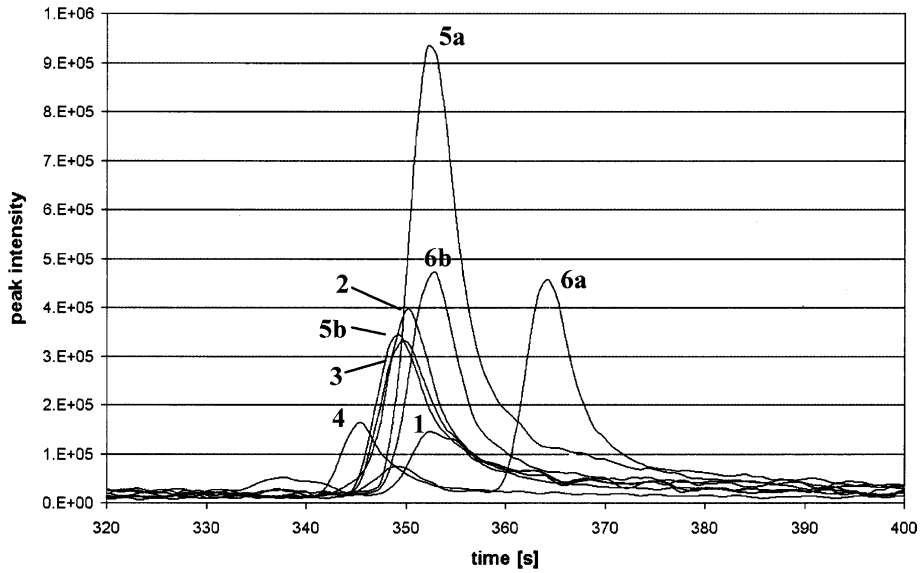

Fig. 2. Reproducibility of a $(CH_3)_2AsCl$ peak generated from 200 mL dimethyl arsenate solution (100 μg/L As) by reduction with $NaBH_4$ at pH 0 (headspace volume 100 mL, exposure time 40 min, desorption program see Section 2.2), retention times vary (351 ± 5 s) due to temperature, and gas flow fluctuations as well as slight differences in starting the run time; experiments No. 1–3: fibers analyzed immediately after each experiment, No. 4: fiber stored for 24 h in the refrigerator before analysis, No. 5a–b: two fibers exposed to the same experiment (fiber No. 5a brand-new) and analyzed immediately after the experiment, No. 6a–b: two fibers exposed to the same experiment and stored for 64 h in the refrigerator before analysis.

with this fiber (No. 6a) was comparable to those obtained with other fibers used several times before. Eliminating this peak from the reproducibility tests, the calculated standard deviation drops to 47%. No further peak decrease was observed during use (up to 30 experiments per fiber). Storing the fibers up to 64 h (No. 4, No. 6a and b) yielded measurable peaks within the range of standard deviation. Without certified standards elimination of arsine generation uncertainties is not possible, thus no further optimization could be achieved. However, the laboratory experiments have shown the general suitability of the SPME fibers, that the peaks were qualitatively detected after each experiment, and that the order of magnitude of peak intensity can be used for semi-quantitative comparison.

One major additional problem for quantitative interpretation of natural gas samples from the field is competitive sorption between different arsenic species and with various other volatile compounds. These interferences might also be a reason for the fact that no preferential sorption on the different SPME fiber coatings was observed in the field in contrast to the laboratory results. Again, interference could only be quantified with certified arsine standards. Further problems are different sorption temperatures depending on the sampling site and unknown equilibration times. While equilibrium between aqueous, gaseous, and solid fiber phase was reached within minutes in the laboratory, it took longer in the field. Comparative sampling was carried out with two CAR fibers at one site (Fig. 3). When sampling the site for 94 h the occurrence of $(CH_3)_2AsCl$ could be proven, while interrupting sampling after 2.3 h most peaks were identical but smaller. Arsine, if present, was below recording limit. Sampling time for all other sites were 22–98 h with an average of 70 h. Considering that two of the largest peaks (RH05, RH06, and electronic annex EA-2) were recorded after 23 h of sampling, sampling times of more than one day might not be necessary. Alternatively, the occurrence of individual species could undergo diurnal or longer variations making the time of the day or the day when collecting the fibers an important factor. No such statistically significant relationship between time of recovery and occurrence of volatile arsenic species could unambiguously be proven for the present data.

3.3. Qualitative interpretation of volatile arsenic species occurrences

On a significance level of 0.95, no significant rank correlation was observed between the occurrence of an individual arsenic species and the analyzed water chemistry parameters (electronic annex EA-2). Positive identification of arsines showed both high spatial and temporal variability. The volatile arsenic species most frequently identified in 22 out of 23 samples was $(CH_3)_2AsCl$, and not $(CH_3)_3As$ as expected from previous studies. Trimethylarsine was only found in 8 out of 23 samples exclusively over geothermal features with total volatile arsenic concentrations less than 50 mg/m^3 (Fig. 4a). For establishing a significant correlation there are too few samples and the peak-area comparison is only semi-quantitative as explained before but it appears that larger $(CH_3)_3As$ peak areas are observed when As(III) is the predominant aqueous As species (Fig. 4b) and the percentage of mono- and dimethylated arsenic in solution is low (electronic annex EA-2).

The least abundant species was CH_3AsCl_2, detected in 3 out of 23 samples with a peak area 20–40% smaller than

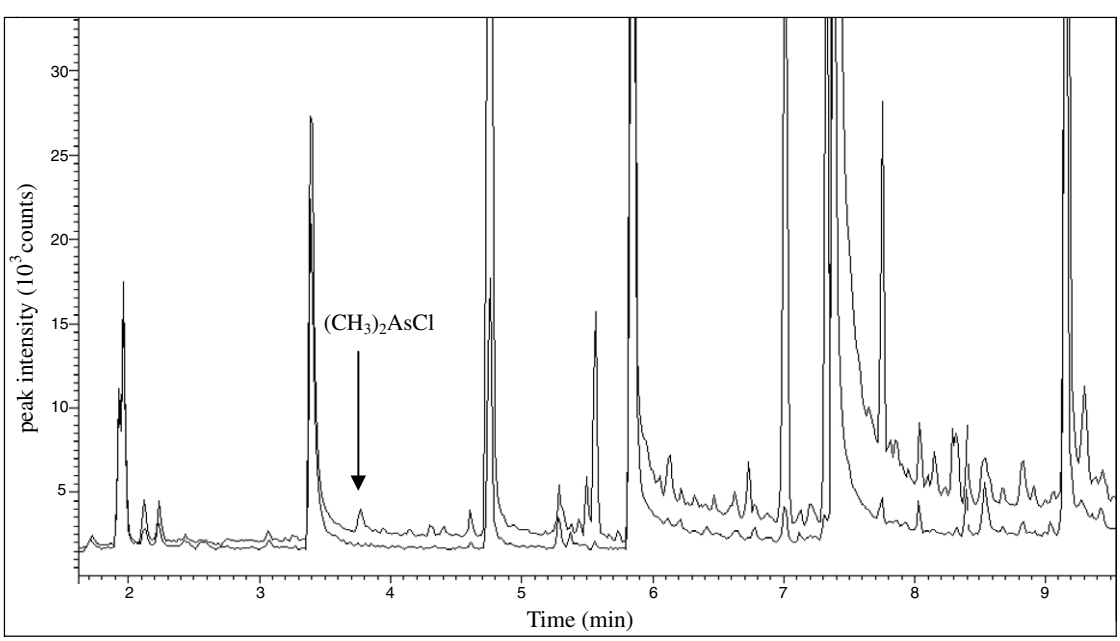

Fig. 3. Comparison of sampling one site (RH05, for location see electronic annex EA-1) for 94 h (upper line) and 2.3 h (lower line); while most peaks are identical, though smaller, the $(CH_3)_2AsCl$ peak (marked with an arrow in the chromatogram) is below recording limit for the shorter sampling time.

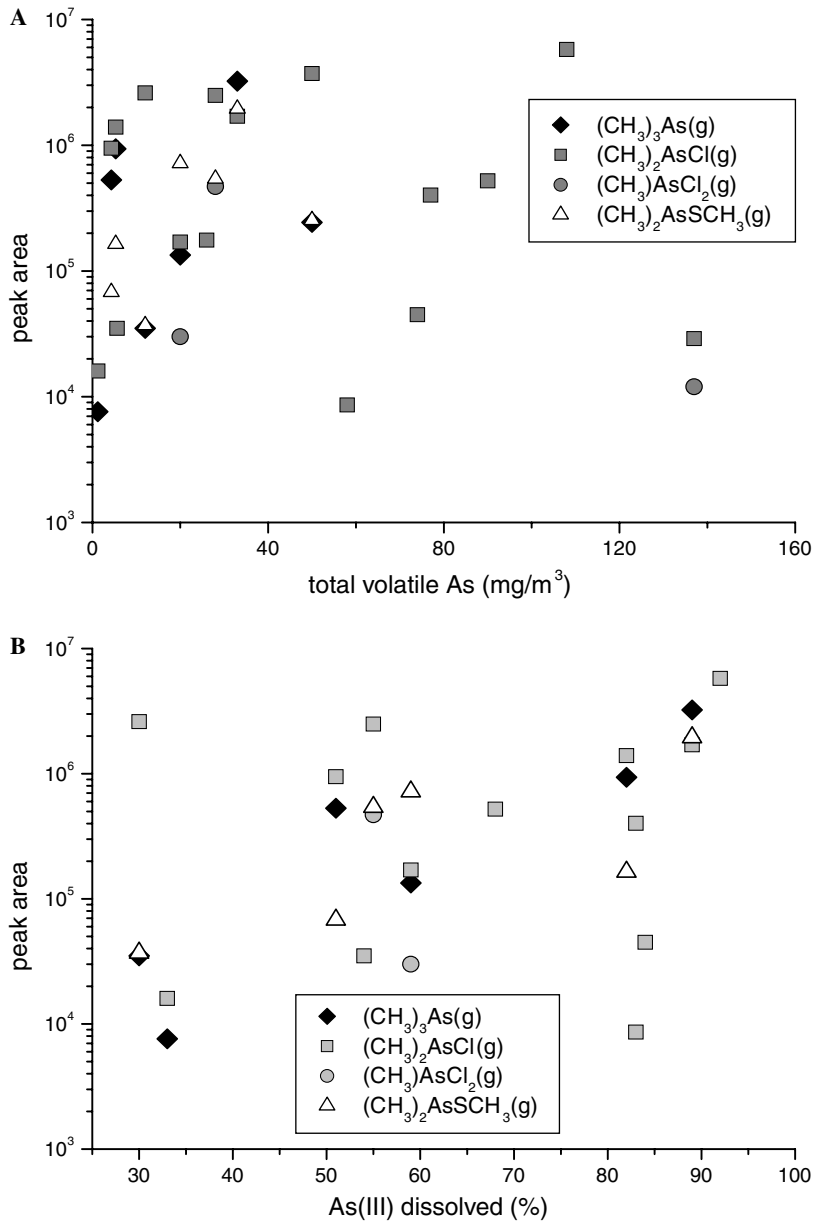

Fig. 4. Scatter plots for the occurrence of individual volatile arsenic species at (A) varying total volatile As concentrations and (B) varying ratios of aqueous As(III) concentrations. *Note*. Peak areas are given for semi-quantitative comparison in the order of magnitude only, quantitative interpretation is not possible due to missing certified standards.

that of $(CH_3)_2AsCl$ (Fig. 5). While the mono-chlorinated species $(CH_3)_2AsCl$ formed already at aqueous chloride concentrations of 2 mg/L, CH_3AsCl_2 was only detected at chloride concentrations in the aqueous phase greater than 190 mg/L. No significant rank correlation was found between the occurrence of volatile chloroarsines and the concentration of aqueous chloride or HCl vapor. Both methylated chloroarsines were found over a chloride-dominated geothermal feature with a pH of 8.7 ("Bath Spring," Lower Geyser Basin). This result contradicts previous laboratory experiments where volatile chloroarsines only formed under extremely low pH values at a surplus of HCl.

Seven out of 23 samples showed the presence of a thioarsine compound in gases sampled at Yellowstone National Park (Fig. 6). The fragment pattern observed by GC–MS matches dimethylarsenomercaptane $(CH_3)_2AsSCH_3$. This compound has structurally been characterized by nuclear magnetic resonance (NMR), Raman and mass spectrometry (Ashe and Ludwig, 1986), and been observed after derivatization of compost samples in the laboratory (Kösters et al., 2003). Under natural conditions it has never been detected before. The species always occurred together with large peak areas of $(CH_3)_2AsCl$ and with one exception also of $(CH_3)_3As$. It was only detected over hot springs with more than 0.45 mg/L aqueous S^{2-}. The occurrence of dimethylarsenomercaptane did not show any significant rank correlation with pH, sulfate or any of the modeled aqueous arsenic sulfur species (electronic annex EA-2).

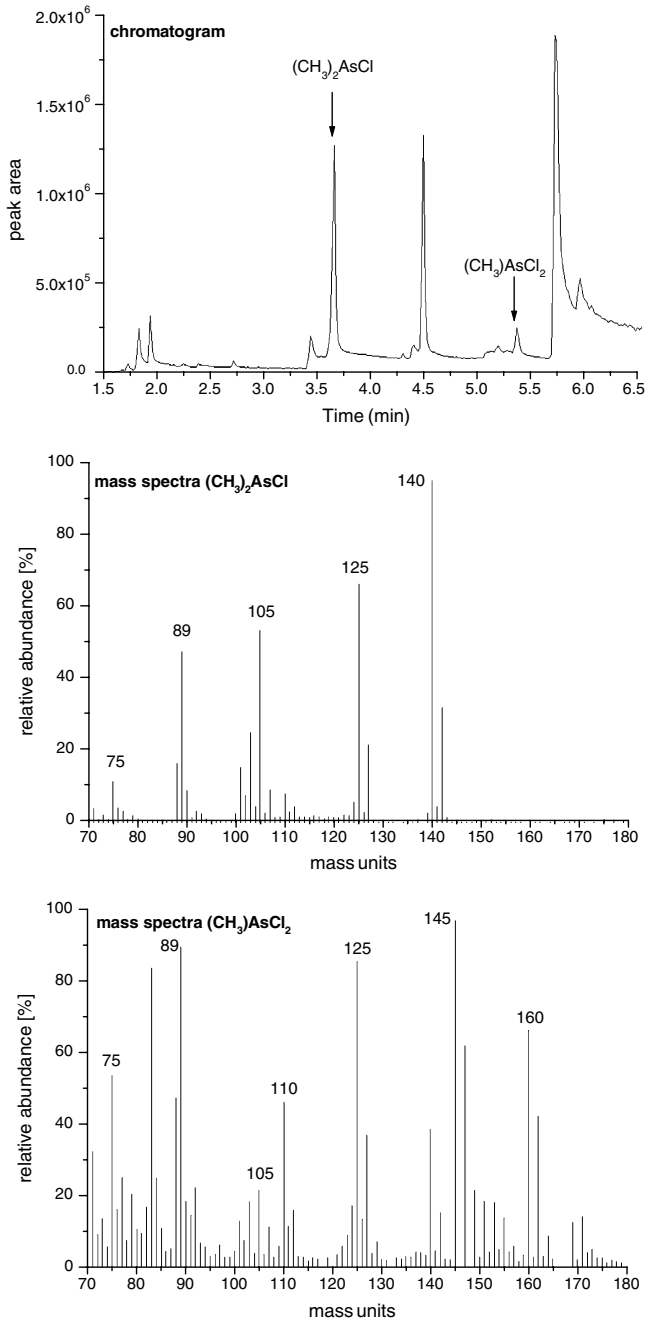

Fig. 5. GC–MS analytical results for geothermal gases from Hazle Lake sampled with a PDMS–CAR–DVB SPME fiber; a predominance of volatile $(CH_3)_2AsCl$ and significantly lower concentrations of $(CH_3)AsCl_2$ were found in all samples taken throughout Yellowstone National Park.

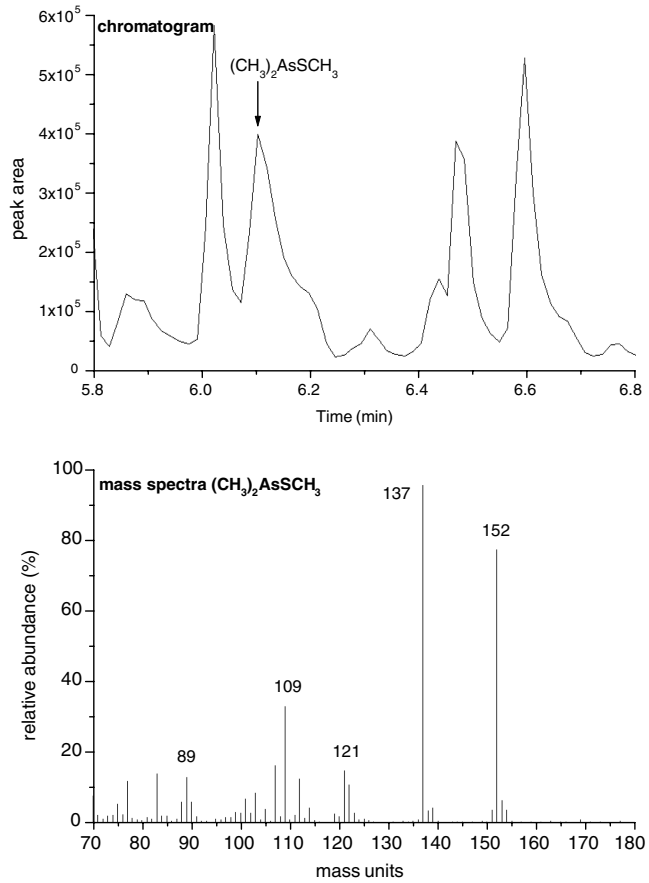

Fig. 6. GC–MS analytical results for a sample from Nymph Lake, showing evidence of dimethylarsenomercaptane $(CH_3)_2AsSCH_3$ in natural aquatic environments (sample was collected with a PDMS–CAR SPME fiber). Characteristic patterns are the fragmented $[(CH_3)_2As\text{-}\ ^{32}S]^+$ (*m*/*z* 137) and the non-fragmented $[(CH_3)_2As\text{-}\ ^{32}SCH_3]^+$ (*m*/*z* 152). The predominance of *m*/*z* 137 compared to *m*/*z* 139 and *m*/*z* 152 compared to *m*/*z* 154 reflects the natural abundance of ^{32}S (95.0%) compared to ^{34}S (4.2%). The fragment at *m*/*z* 109 supports the hypothesized formation of a $[HAs\text{-}SH]^+$ or a $[H_2AsS]^+$ fragment by co-ordination of hydrogen atoms previously detached from the methyl groups (Kösters et al., 2003).

Volatile inorganic arsenic species, such as AsH_3 or $AsCl_3$ (Table 1), were not detected in any of the chromatograms. One of the central questions is why volatile arsenic species could only be identified in 23 of 57 samples, whereas the remaining 34 samples showed no known volatile arsenic species. This result contradicts those from the total volatile arsenic determinations which showed that arsenic is degassing from all features. The non-detection of all volatile arsenic species by means of SPME fibers could be a sampling artifact. Volatile arsenic compounds such as AsH_3, CH_3AsH_2, and $(CH_3)_2AsH$ have low boiling points of −55, +2, and +36 °C, respectively. Even though the SPME fibers were stored in the refrigerator and analyzed only 1–2 days after sampling, degradation, or volatilization could have occurred prior to analysis. The low affinity of AsH_3 to SPME fibers, especially under ambient temperatures, has been reported before (Sur et al., 2003). Hence, efficiency of capture and preservation of the most volatile species on fibers is a central problem. Alternatively or additionally, standard mass spectra databases contain only a limited number of mass spectra for volatile arsenic species. Rarely observed species, like $(CH_3)_2AsSCH_3$, are not included in the databases yet and can only be identified if the peaks are manually searched for their mass spectra. All chromatograms showed numerous peaks besides those assigned to known volatile arsenic species. Automatic peak identification only helped to identify some of the large peaks at the end of the chromatogram as siloxanes (hexam-

ethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and decamethylcyclopenta-siloxane). These siloxanes have also been detected before in the laboratory, especially when using new fibers, and are a typical indication for constant low-bleeding of the sorption material with a continuous slow degradation of the fiber coating. All other peaks were not unambiguously identifiable by retention times and mass spectra. Some of those unidentified peaks might hide additional volatile arsenic compounds with as yet unavailable mass spectra.

3.4. Origin of volatile arsenic

Compounds like As(g), As_2(g), AsS(g), As_4S_4(g), and $As(OH)_3$(g) could form at greater depths and at temperatures above 150 °C. A prerequisite would be that the gases rise quickly in a process of excess enthalpy boiling and do not equilibrate with the aqueous phase at the surface. An experimental study showed that partial pressures for As(g), As_2(g), As_3(g), As_4(g), $AsCl_3$(g), AsF_3(g), AsF_5(g), AsH_3(g), As_4O_6(g), AsS(g), and As_4S_4(g) (thermodynamic data (Spycher and Reed, 1989)) and for $As(OH)_3$(g) (Pokrovski et al., 2002) in equilibrium with the sampled aqueous phase at the surface would be negligibly low. According to these calculations the predominant inorganic gas-phase in 87% of the samples would be $As(OH)_3$(g) with a partial pressure of 6.8×10^{-14}–8.0×10^{-17} vol%. The second highest partial pressure was found for As_4S_4 with 10^{-11}–10^{-30} vol%. Arsine was third in abundance of the modeled inorganic gaseous arsenic species with partial pressures of 10^{-23}–10^{-34} vol%. Thermodynamic calculations (Spycher and Reed, 1989) showed that even at temperatures up to 300 °C considering removal of at least 97% of the solution by boiling, no significant arsenic fractionation into the gas phase occurs. Neither could any of the above-mentioned high-temperature volatile arsenic species be identified on the SPMEs. With the exception of AsH_3 (boiling point −62.5 °C) and AsF_5 (boiling point −53 °C) all of the inorganic volatile arsenic species mentioned before have boiling points significantly higher than 50 °C and should thus sorb on the SPME if they were present.

Purely abiotic formation of organic volatile arsenic species has been reported in the presence of methyliodide (Hamasaki et al., 1995) and is indicated by the detection of organic arsenic halides from sterilized sediments (Killelea and Aldstadt, 2002; Mester and Sturgeon, 2001). There are no investigations published on the likelihood of a transfer of the methyl group from methyliodide (formed from methane and iodine) or any other methyl donor to arsenic, especially under the specific conditions found at Yellowstone. In thermodynamic equilibrium calculations on abiotic arsenic fractionation in the gas-phase organic volatile arsenic species have been excluded (Spycher and Reed, 1989). Their formation was argued to be negligible by analogy from modeling $Sb(CH_3)_3$, one of the few volatile organometallics for which thermodynamic data were available and which yielded very low fugacities. Based on the observed predominance of the four volatile organic arsenic species in the geothermal gases in Yellowstone, the previously proposed insignificance of volatile organoarsines must be questioned if their formation is abiotic.

From all data presently available, microbially catalyzed formation seems most likely. It is unclear yet whether the chloro- and thioarsines are formed in solution by reaction of methylated arsenic species and aqueous chloride or sulfide or in the gas-phase by reaction of volatilized methylated arsenic species and HCl or H_2S vapor. Both ways seem plausible. So far, no microorganisms that are known to volatilize arsenic from other experiments have been identified in geothermal features at Yellowstone. A significant rank correlation between occurrence of volatile arsenic and hydrogeochemical parameters such as pH, Eh, or temperature could indicate a group of microorganisms (acidophiles, thermophiles, and hyperthermophiles) most likely responsible for arsenic volatilization. But no such correlation was observed. Neither a minimum threshold for detection of volatilization nor a linear or exponential correlation between aqueous and gaseous arsenic concentrations could be detected. If the formation is biotic, most likely different microorganisms living under a wide range of environmental conditions with different abilities to volatilize individual arsenic species are involved.

3.5. Potential toxicity

Our observations show that occurrence of complex volatile organoarsenic species such as methylated chloro- and thioarsines is more common than previously assumed. Additional complex inorganic and organic arsenic species might form at high temperature and pressure in the presence of carbon sources (CO_2, CH_4, and hydrocarbons), sulfur sources (H_2S, S, and S_2O_3), and chloride sources (Cl^-, residual phase). Concentrations directly at the source are within the range of acute toxicity compared to AsH_3 but decrease rapidly to levels below detection limit within a few meters horizontally and vertically from the source. The toxicities of the methylated arsines are considerably lower than arsine, but nothing is presently known about the toxicities of the chloroarsines and the thioarsine. While humans rarely approach geothermal features that closely for long exposure times, animals might be endangered because they breathe air that is closer to the ground and they gather around the warm geothermal features, especially during winter. The observed decrease in life expectancy of elk populations in areas with a large number of geothermal features compared to control populations is attributed to high arsenic concentrations in forage species found in aquatic and riparian habitats (Kocar et al., 2004) and to compromised dentition caused by high fluorine concentrations in the waters and exacerbated by consumption of forages with high levels of abrasive silica (Garrott et al., 2002). A chronic effect of high volatile arsenic concentrations has not yet been considered. Further extended speciation and quantification combined

with microbiological investigations will lead to an improved understanding of possible interactions between the biosphere and arsenic degassing from Yellowstone and other active geothermal areas.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.02.019.

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