

Volatile Metals and Metalloids in Hydrothermal Gases

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Volatile metals and metalloids were sampled from hot springs, fumaroles, and a hydrothermally influenced wetland in Yellowstone National Park. The sampling was based on diffusion through gas sampling chambers. Collected gases were stabilized by dissolution and oxidation in 1:100 diluted NaOCl. Special procedures were developed to analyze the oxidized samples by GF-AAS and HG-AAS. For ICP-MS, samples had to be blank-corrected for polyatomic isotope interferences, especially by $^{23}\text{Na}^{35}\text{Cl}^+$ and $^{23}\text{Na}^{37}\text{Cl}^+$ on ^{58}Ni and ^{60}Ni and by $^{40}\text{Ar}^{23}\text{Na}^+$ on ^{63}Cu . From the concentrations trapped in solution, net diffusion rates were calculated by Fick's first law. The highest concentrations reached a maximum of 8 g/m³ for volatile silicon. Volatile nickel, tungsten, zinc, copper, and molybdenum, previously only known from anthropogenic sources, occurred naturally in the hydrothermal gases in ranges of tens to hundreds of μg/m³. Replicate measurements indicated significant temporal variations in concentrations, probably the result of complex changes in the hydrothermal regime as well as varying microbial activity. Global correlations between gaseous and superficial aqueous phases were missing.

Introduction

The occurrence of volatile metals and metalloids in the environment is known both from anthropogenic sources, such as combustion of fossil fuels, metal-producing industry, exhaust fumes, cropping, agriculture, waste deposits, sewage, and digester gases, as well as from natural sources, such as volcanic exhalations, hydrothermal sources, natural fires, wetlands, or seawater. Hydrides of the metalloids B, As (1, 2), and Sb (3), as well as of the metals Sn (1, 4) and Bi (3), have been detected in nature. Mostly methylated volatiles of the metalloids As (1, 2, 5, 6), Ge (2, 7), Sb (2, 6, 7), Si (2, 8), and Te (1, 6), the metals Bi (1, 6, 7, 9), Pb (10–12), Sn (7, 11, 13), Ga (11), and In (11), as well as the transition metals Cd (1) and Hg (12), are environmentally relevant. Nickel carbonyl complexes are known from anthropogenic sources such as cigarette smoke (14), urban air (15), sewage gases (16), or gases from the petroleum industry (17). Volatile carbonyl complexes with Mo and W have been detected in domestic waste deposit (18) and sewage (16) gases.

Commonly, volatile metals and metalloids occur in reductive environments, even though methylation and volatilization of inorganic As and Sb has also been detected under completely aerobic conditions, e.g., metabolized by the fungus *Scopulariopsis brevicaulis* (19, 20). Strictly speaking, all volatile compounds are thermodynamically unstable with respect to oxidation, UV irradiation, thermal influence,

hydrolysis, reaction with radicals, and demethylation. Those with slower reaction kinetics can be detected under natural conditions. Mean dissociation energies can be taken to estimate the stability of organometallics, because the weak bond between the metal or metalloid and the C atom is easily replaced by much stronger bonds between C–O or C–X (X = halogens). With increasing mean dissociation energies the stability of (CH₃)_nM complexes increases for M being Bi < Cd < Pb < In < Zn < Sn < Sb < As < Se < Ge < Ga < Si < C. While trimethylbismuth decomposes spontaneously in an exothermal reaction, compounds with higher mean dissociation energies than Sn undergo only endothermal dissociation reactions and are consequently more stable. The increasing polarity between metal and C atom as well as the presence of other ligands, like humic or fulvic acids, can further destabilize the compounds. Higher alkylated species are generally considered less stable than methylated species (21).

Reported concentrations for volatile metals and metalloids in the environment range from tens of ng/m³ (e.g., Pb or Hg in urban air (11, 22), Hg in estuaries (11), Hg, Te, Pb in domestic waste gases (23), Ga, Sr, Ba, Pb, and Hg in suburban air (24, 25)) to μg/m³ (e.g., As, Sn, Sb, Bi (23) and Mo, W (18) in waste disposal gases or Mg and Al in suburban air (24, 25)), and even mg/m³ (Si in waste disposal gases (8)). Hydrothermal gases are likely candidates for high concentrations of volatile metals and metalloids because significant amounts are leached from surrounding rocks and volatilized at high temperatures. Investigations on quantification of volatile metals and metalloids in hydrothermal gases are, however, rare. Volatile As concentrations up to 79 ng/kg have been reported from noncondensable gases in several hot-water fields in California (26). Volatile methyl Hg was found in hydrothermal gases at lakes in New Zealand. Volatile As and Sb were detected and speciated in hydrothermal gases over hot springs in British Columbia (2).

For the present paper volatile metals and metalloids released in hydrothermal gases at the Yellowstone National Park were quantified, and correlations between gaseous and aqueous phase were investigated.

Materials and Methods

A total of 60 water and 55 gas samples were collected from hot springs, fumaroles, and a hydrothermally influenced wetland in Yellowstone National Park (WY).

Water Samples. Temperature, pH, conductivity, redox potential, and dissolved oxygen were determined onsite using a WTW MultiLine P4 device with a SenTix 97/T pH electrode, a TetraCon 325 conductivity cell, a Pt 4805/S7 redox probe, and a CellOx 325 oxygen probe, respectively. Additionally, water samples were filtered (200 nm cellulose acetate filter, Membrex), stabilized with 1 mL of HNO₃ suprapur in 50 mL acid cleaned polyethylene bottles, and stored in the refrigerator until analysis by ICP-MS (Perkin-Elmer ELAN 6000) or, for arsenic, by GF-AAS (Zeiss AAS EA4 spectrometer with graphite furnace and platform technique).

Gas Samples. Volatile compounds were collected using polyethylene boxes (30 cm long, 20 cm wide, and 10 cm high) placed upside down as gas sampling chambers over hot springs and fumaroles (Figure 1). Maximum water depth of the features sampled was 5 cm, thus boxes were placed on the ground and no floating device was needed. Surrounding water or water-saturated sediment provided a gastight seal. Gases could only leave the gas sampling chamber through a PTFE tube outlet on top of the box. Gases

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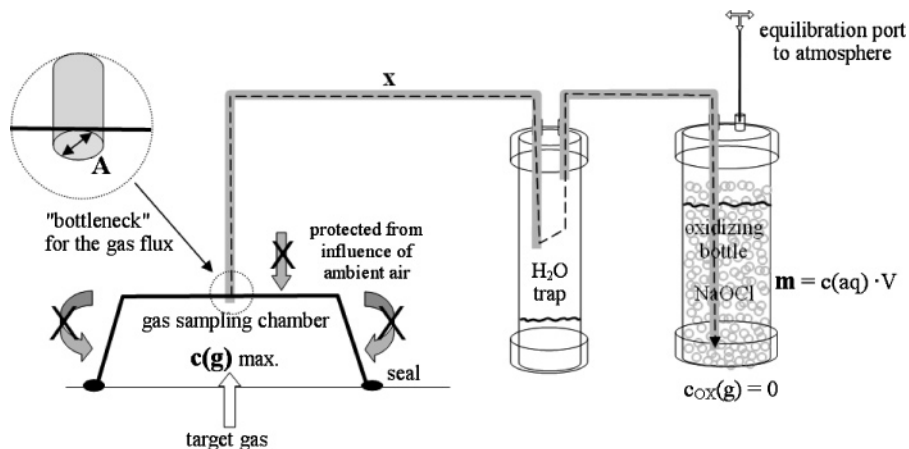


FIGURE 1. Schematic of sampling setup (not to scale). Volatile compounds are sampled by passive diffusion-based sampling. A gas sampling chamber is used to eliminate disturbances from ambient air, but the restricting flow cross-section is the diameter of the hose connecting sampling source and oxidizing bottle. Volatile compounds are trapped in 1:100 diluted NaOCl. To keep the pressure over the sampling site close to natural conditions an equilibration port, open to the atmosphere, is used at the far end of the oxidizing bottle. Concentrations in the gas phase are calculated from aqueous concentrations in the oxidizing solution by Fick's first law ($c = mx/tAD$).

collected were conducted to a PTFE oxidizing bottle filled with 100 mL of oxidizing solution to dissolve and oxidize the volatile compounds. The oxidizing solution was NaOCl (6–14% active Cl; Riedel-de-Haën) diluted 1:100 with deionized water. Additionally, PTFE rings of 4 mm diameter and 2 mm height in the solution helped to increase reaction time and sampling efficiency. Sampling efficiency was optimized for the volatile arsenic species AsH_3 , $(CH_3)_2AsH$, and $(CH_3)_2AsCl$, and was found to be better than 80% in laboratory experiments using 30 mbar differential pressure (28). In the field, no pumping or pressure was applied to the gas sampling system. The equipment was left in the field for 52–262 h of cumulative sampling. No detectable gas flow was monitored at the outlet of any oxidizing unit during that sampling time. Sampling of volatiles was based only on equilibration of concentration gradients between the gas phase under the gas sampling chamber and the oxidizing solution by diffusion. Sampling efficiencies were thus assumed to be significantly higher than the 80% determined in a pressurized system in the laboratory, close to 100%, because of much lower gas flow and longer reaction times compared to the laboratory experiments. To confirm that assumption, a second sampling bottle was mounted behind the first bottle at six sites in the field to detect any possible breakthrough. All solutions showed concentrations comparable to the blank 1:100 diluted NaOCl solution for the elements discussed below, confirming effective trapping in the first oxidizing bottle. Sampling of aerosols instead of the target dry gases was excluded by using empty polyethylene bottles mounted in front of the oxidizing bottles as water traps (Figure 1). Little to no water was trapped for most sampling sites. For the roadside fumaroles at Nymph Lake (NL02, 03, 04, Table 2) about 30 mL of water was trapped over 3–4 days sampling. The conductivity of this water was a few $\mu S/cm$ only and one such condensate analyzed for trace elements with ICP-MS showed all elements below detection limit. Previous laboratory experiments had already confirmed that volatile arsenic passes deionized water without dissolution and oxidation (28).

After diffusion sampling, solutions were re-filled into two 50 mL PE bottles and stored nonstabilized in the refrigerator until analysis 4–6 weeks later. Stability over this time was confirmed for As in laboratory experiments before (28). Field blanks were obtained by filling NaOCl in an oxidizing bottle with two closed valves on the outlets of the oxidizing bottle preventing inflow or outflow of gases. The blanks were left outside for the same periods of cumulative sampling and treated the same way as the samples, but were not exposed

to the hydrothermal gases. The NaOCl gas samples were analyzed by graphite furnace AAS (Zeiss AAS EA4) and/or hydride generation AAS (Perkin-Elmer Analyst 300 with a FIAS-100 flow injection analysis system hydride generator) for arsenic. Twenty-one selected gas samples were sent to Actlab, Canada, for ICP-MS analysis (Perkin-Elmer ELAN 6000) on Si, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, Se, Mo, Pd, Cd, In, Sn, Sb, Te, W, Pt, Au, Tl, Pb, and Bi.

Results and Discussion

Evaluation of the Method's Performance. The performance of the method largely depends on three main factors: (1) initially, the sampling setup including possible disturbances of the natural gas flux, (2) the analytics, here, mainly the interfering effect of the oxidizing solution, and (3) the conversion of dissolved, oxidized concentrations back to initial concentrations in the gas phase. Before interpreting the detected concentrations of volatile metals and metalloids, an evaluation of problems encountered with the method's performance will be discussed.

As with any sampling method, sampling itself disturbs natural conditions. The gas sampling chambers helped to exclude meteorological factors that might have biased sampling, especially precipitation, humidity, wind direction, and wind speed. However, the installation of the gas sampling chamber also possibly alters the gas flux from its undisturbed rate by changing the air pressure, the temperature, and the volatile metal gradient, by diverting gas flow around the gas sampling chamber, or by causing build-up of water vapor within. Trying to ensure a seal between the gas sampling chamber and the underground to minimize atmospheric input at the source leads to physical disturbance, possibly with the alteration of gas flow (29). Care was taken to keep physical impact of the above to a minimum. After installing the gas sampling chambers, 0.5–1 h was given for the system to re-equilibrate before attaching the oxidizing bottles to start sampling. To avoid increase of air pressure underneath the gas sampling chamber, the sampling setup had an equilibration port to the atmosphere at the far end of the oxidizing bottle (Figure 1). Accumulation underneath the gas sampling chamber which could further lead to decomposition of the volatile metals and metalloids over long sampling times cannot be completely excluded. However, it is unlikely because of the high concentration gradient between the source with maximum volatile concentrations and the oxidizing bottle, where those concentrations were reduced to zero by immediate dissolution and oxidation. An alternative

TABLE 1. Potential Matrix-Specific Polyatomic Interferences during ICP-MS Analysis in a NaOCl Matrix^a

isotope	abundance	matrix (NaOCl)-specific interference
⁵¹ V	99.76%	³⁵ Cl ¹⁶ O ⁺
⁵⁸ Ni	67.77%	²³ Na ³⁵ Cl ⁺
⁶⁰ Ni	26.16%	²³ Na ³⁷ Cl ⁺
⁶³ Cu	69.1%	⁴⁰ Ar ²³ Na ⁺
⁶⁹ Ga	60.16%	³⁵ Cl ¹⁶ O ¹⁸ O ⁺ , ³⁵ Cl ¹⁷ O ₂ ⁺ , ³⁷ Cl ¹⁶ O ⁺
⁷¹ Ga	39.84%	³⁵ Cl ¹⁸ O ₂ ⁺ , ³⁷ Cl ¹⁶ O ¹⁸ O ⁺ , ³⁷ Cl ¹⁷ O ₂ ⁺ , ³⁶ Ar ³⁵ Cl ⁺
⁷⁰ Ge	20.51%	³⁵ Cl ¹⁷ O ¹⁸ O ⁺ , ³⁷ Cl ¹⁶ O ¹⁷ O ⁺ , ³⁵ Cl ₂ ⁺
⁷² Ge	27.4%	³⁷ Cl ¹⁷ O ¹⁸ O ⁺ , ³⁵ Cl ³⁷ Cl ⁺
⁷⁴ Ge	36.56%	³⁷ Cl ₂ ⁺

^a Data compilation and further references can be found in ref 40.

to passive sampling with the potential danger of accumulation underneath the gas sampling chamber could be active gas sampling. However, a comparative study on active and passive sampling of volcanic CO₂ (30) showed that active pumping created a forced in-diffusion and thus a flux overestimation of often more than 1 order of magnitude compared to passive sampling. The values obtained with the proper precautions taken to minimize sampling impact as mentioned before are thus considered as the best possible approximation to natural conditions in our case.

For analysis, compensation of NaOCl matrix effects had to be considered. Even though the oxidizing solutions were already 1:100 diluted some matrix effects were still observed upon analysis by GF-AAS, HG-AAS, and ICP-MS. For GF-AAS, relatively high dry ashing temperatures (1500 compared to 1350 °C with the same device for standard water samples) for a total duration of 70 s (compared to 40 s for standard samples) were needed to achieve separation of the arsenic signal from unspecific sorption peaks due to the high salt concentrations. To avoid arsenic losses during this thermal treatment a twice increased modifier concentration, 8 μL of a 1 g Pd/L stock solution (Pd(NO₃)₂), was added to 15 μL of sample solution. Experiments with NH₄NO₃ to improve the separation of unspecific and specific signals showed no success (26). For HG-AAS, pre-reduction with 2.4 mL of 10% HCl, and 1 mL of KI in ascorbic acid on 0.5 mL of sample (diluted to a total of 5 mL with deionized H₂O) was required and samples were allowed to pre-reduce for 1 h before analysis to achieve a reproducible, complete reduction. Volatile arsenic concentrations reported in the following are the ones from HG-AAS.

The ICP-MS samples (including blanks) were diluted 1:1 with deionized water before they were sent off to Actlab, Canada, for routine analysis (Code 6, water samples). For the elements discussed below matrix-specific polyatomic interferences could occur for V, Ni, Cu, Ga, and Ge through formation of molecular ions such as ClO⁺, NaCl⁺, ArNa⁺, ArCl⁺, ClO₂⁺, or Cl₂⁺ of the same mass-to-charge ratio (Table 1). To compensate for these interferences, a blank (prepared as 1:100 diluted NaOCl and further subdiluted 1:1 before shipment to ICP-MS) was included in the analysis batch. The blank showed concentrations below or close to detection limit for V, Ga, and Ge, indicating that interferences with chlorine-oxide molecular ions can be neglected. Increased blank concentrations for Ni (130 μg/L) and Cu (18.5 μg/L), however, showed that the Na-containing molecular ions NaCl⁺ (interferes with ⁵⁸Ni and ⁶⁰Ni) and ArNa⁺ (interferes with ⁶³Cu) have a significant impact on the ICP-MS analysis of these elements (Supporting Information part EA1). All samples were blank-corrected. Additionally, water samples were routinely spiked with internal standards to correct for matrix differences over the entire mass range. A repeat of every 10th sample was analyzed. As control materials, a National Research Council of Canada standard (SLRS-4) was

run every 25 samples and the NIST water standard 1640 was run at the beginning and the end of each batch.

For a quantitative interpretation, the concentrations of the volatile compounds dissolved in NaOCl [μg/L] had to be converted into gaseous concentrations in μg/m³ calculating the net diffusion rate according to Fick's first law (SI part EA2). Assuming a 100% effective dissolution and oxidation, as explained before, the concentration of the volatile compound above the trapping solution is zero during the whole sampling time. Thus, the concentration gradient equals the concentration at the sampling site. Necessary input parameters are, besides sampling time, the diffusion length and area. As can be seen in Figure 1, the bottleneck that determines the rate of gas diffusion is the approximately 60 cm long and relatively small (Ø 2 mm) PTFE tubing connecting the gas sampling chamber and the oxidizing bottle. Gas diffusion coefficients can be assumed to be generally between 0.1 and 0.2 cm²/s or calculated depending on species and temperature according to the Fuller, Schettler, and Giddings equation (29, 30). Such a diffusion coefficient calculation for arsenic gives a mean value of 0.147 ± 0.015 cm²/s (SI part EA2).

Certainly, the presented method is influenced by more potential errors than largely standardized methods for sampling an aqueous phase. However, comparing cost and efficiency it still proved to be a valuable tool for screening volatile metals and metalloids, provided proper precautions are taken to guarantee largely undisturbed natural gas flow and compensation of matrix effects during analysis.

Detected Volatile Metals and Metalloids. Volatile metals and metalloids were detected in varying concentrations at all sampling sites ranging from a wetland with low hydrothermal influence (Hazle Lake) to acid fumaroles (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 (Figure 2, Table 2, Table 3). Using nonparametric Spearman and Kendall correlation with a significance level of 5% revealed no general correlations between the amount of degassing metals and metalloids and any water chemistry parameter such as pH, temperature, redox potential, or concentrations of dissolved metals and metalloids.

The highest concentrations, with up to 8 g/m³, were found for volatile silicon. These concentrations are significantly higher than, e.g., previously detected concentrations of several mg/m³ in waste disposal gases (8). They compare in concentration to H₂S, which was determined as the 3rd most frequent gas component in Yellowstone's hydrothermal gases (Table 4; (31)). A silicon fluorine species (SiF₄) has been identified as a common trace component of fumarole gases on volcanoes before (SO₂/SiF₄ ratios up to 170:1), arising from interactions between magmatic HF and silica-rich wall rocks (32). This SiF₄ species has been reported to increase with decreasing reservoir temperatures and is not abundant at magmatic temperatures. Interestingly, for the June/July sampling, we observed higher volatile Si concentrations at Lower Geyser Basin (LG01–LG03, Table 2) with reported reservoir temperatures of 125–200 °C than at Ragged Hills (RH01-1, RH04-1, RH05-1) where reported reservoir temperatures are 270–300 °C (33). Following this, the consistently higher volatile Si concentration at Ragged Hills in September (RH01-3, RH04-3, RH05-3) can be explained by decreasing reservoir temperatures following the "seasonal disturbance". This is an annual Norris Geyser Basin-wide hydrothermal disturbance that occurs commonly in late summer (August/September) and is coupled to mixing of deep thermal waters with waters of lower temperature from shallower reservoirs (34). This inverse trend between volatile Si concentrations and reservoir temperature could be an indication for the

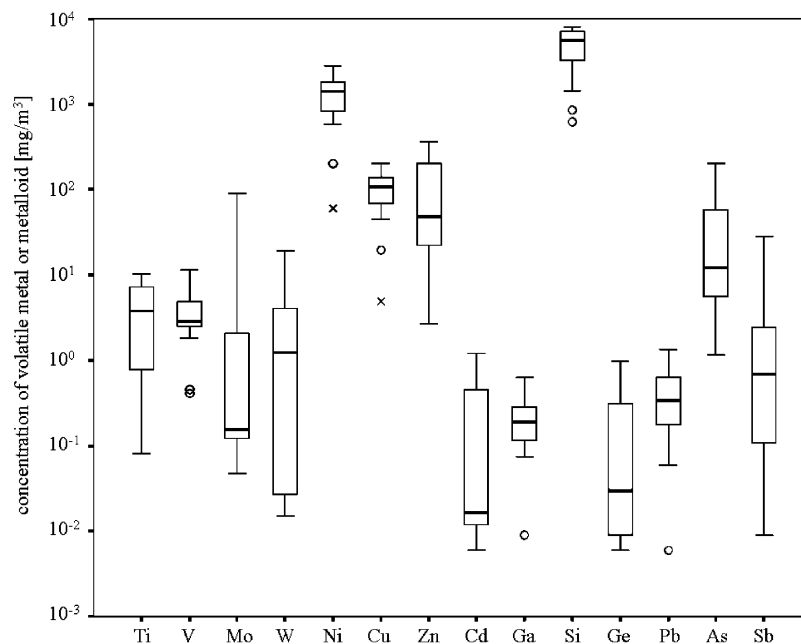


FIGURE 2. Box plot showing median, quartiles, minima, and maxima for volatile metals and metalloids detected in hydrothermal gases at Yellowstone National Park (circles = outliers, i.e., cases with values between 1.5 and 3 box lengths from the upper or lower edge of the box; crosses = extremes, i.e., cases with values more than 3 box lengths from the upper or lower edge of the box).

TABLE 2. Concentrations (mg/m³) of Volatile Metals and Metalloids in Hydrothermal Gases^a

site	Ti	V	Mo	W	Ni	Cu	Zn	Cd	Ga	Si	Ge	Pb	As	Sb
GG04-4	0.79	0.45	<0.16	4.0	60	5.0	14	<0.02	0.15	3800	0.04	<0.02	18	0.98
HL01-1	0.70	2.7	<0.42	6.6	200	20	200	0.36	0.12	1420	<0.04	0.35	12	1.0
HL01-3	2.3	6.8	<0.70	19	580	46	215	<0.07	0.12	3160	<0.07	0.33	1.2	<0.07
LG01-2	4.0	4.9	<0.54	7.3	1100	100	27	0.95	0.55	7570	0.34	0.17	11	2.5
LG02-2	8.4	5.1	<0.51	2.9	840	69	24	<0.05	0.40	6570	0.09	0.39	12	0.50
LG03-2	5.5	3.7	26	2.0	860	69	10	<0.04	0.64	6510	0.43	0.18	7.8	0.76
NL02-1	<0.28	2.7	<0.28	<0.06	780	58	340	1.2	<0.03	620	<0.03	1.3	33	0.14
NL03-1	<0.27	1.8	<0.27	<0.05	1270	93	360	0.14	<0.03	850	<0.03	0.09	5.6	<0.03
NL04-1	2.7	0.41	<0.30	1.2	1590	120	4.9	1.2	0.07	3490	<0.03	0.06	4.3	0.14
NL05-1	10.3	3.0	<0.41	<0.08	1800	140	22	0.46	0.22	6850	0.14	0.49	7.0	<0.04
RH01-1	7.2	2.6	13	6.1	1560	110	120	<0.03	0.16	4820	<0.03	0.45	75	15
RH01-3	7.6	2.3	<0.59	<0.12	2790	200	71	<0.06	0.23	7310	<0.06	0.21	5.2	<0.06
RH04-1	3.6	2.7	1.7	0.28	1350	105	30	<0.02	0.27	3250	<0.02	0.71	37	0.63
RH04-3	3.2	2.5	<0.47	1.3	2360	160	2.7	<0.05	0.29	6370	0.32	0.23	58	1.2
RH05-1	<0.31	4.0	4.3	2.1	1490	110	34	0.63	0.09	3840	<0.03	0.20	5.3	0.11
RH05-3	6.1	3.7	90	1.0	2220	140	190	<0.04	0.18	8130	0.98	0.68	110	4.8
RH07-2	9.8	8.1	<0.42	<0.08	1590	110	94	<0.04	0.19	7680	0.07	0.70	200	29
RH20-4	5.5	11.5	2.1	<0.09	2200	150	205	<0.05	0.31	7130	0.31	0.64	130	3.7

^aSite codes = area abbreviation and sampling site number-sampling time. Area: GG = Gibbon Geyser Basin, HL = Hazle Lake, LG = Lower Geyser Basin, NL = Nymph Lake, RH = Ragged Hills. Sampling time: 1 = June 2003, 2 = July 2003, 3 = September 2003, 4 = October 2003. Analysis done by ICP-MS, except for arsenic which was done by HG-AAS.

presence of SiF₄, but further information can only be obtained by species-selective Si determination.

Volatile nickel, previously mainly known from anthropogenic sources (14, 15, 17), showed the second highest concentrations in the hydrothermal gases with an average of 1–2 g/m³. Significantly increased dissolved nickel concentrations of up to 600 µg/L correlate with the volatile nickel concentrations. Previously not considered much for their environmental relevance, volatile zinc and copper compounds were found in considerable concentrations in the 100 mg/m³ range. An observed positive correlation between gaseous silicon, nickel, and copper might indicate similar origin or formation conditions, possibly from magmatic HF or HCl. Data from thermodynamic modeling of magma degassing and fumarolic processes already suggested that Ni and Cu are transported mainly as simple chlorides (NiCl₂, CuCl) in HCl-rich volcanic gases (34).

Fifth in abundance was the main target element, arsenic, with concentrations between 0.5 and 200 mg/m³, and an average of 36 mg/m³. The overall volatile arsenic concentrations detected were much higher than any of the few previously reported ones such as for waste heaps (up to 0.050 mg/m³) and digester gas (up to 0.025 mg/m³ for mesophilic digestion and up to 0.030 mg/m³ for thermophilic digestion (1, 23)). No correlation was found between total dissolved and volatile concentrations. The amounts of arsenic degassed from the hot springs with the lowest (18 µg/L, Nymph Lake) and the highest (11 mg/L, Ragged Hills) total dissolved arsenic concentrations are comparable at 90 and 108 mg/m³, respectively. The amount of degassing arsenic also proved to be noncorrelated with the redox potential. The highest concentration with 200 mg/m³ was measured over a hot spring of only slightly suboxic conditions (+200 mV at RH07, Table 3) while volatile arsenic concentrations over hot springs

TABLE 3. Concentrations ($\mu\text{g/L}$) of Dissolved Metals in Hydrothermal Waters^a

site	pH	redox	temp.	cond.	Ti	V	Mo	W	Ni	Cu	Zn	Cd	Ga	Si [mg/L]	Ge	Pb	As	Sb
GG04-4	3.6	295	88	1126	17	0.7	32	12	0.9	1	3.9	0.1	0.6	91.2	15	1.4	530	29
HL01-1	3.1	435	20	1030	13	0.7	0.3	5.2	1.5	0.70	8.7	0	0.8	68.9	7.1	0.35	200	2.6
HL01-3	3	194	25	1890	16	1.5	0.60	11	4.7	1.7	15	0.1	0.9	101	14	0.93	535	6.3
LG01-2	7.3	-148	91	1426	14	0.3	74	424	4.7	2.0	-1	0.1	11	116	58	<0.01	1830	80
LG02-2	8.7	-219	91	1472	13	0.4	79	431	10	2.4	-1	0.1	21	114	61	<0.01	1690	72
LG03-2	7.3	-211	91	1375	13	0.3	88	391	29	4.3	-1	0.2	15	114	55	<0.01	1560	67
NL02-1	2.5	399	64	1596	14	3.4	1.3	9.8	115	10	7.2	0	3.7	105	3.7	0.51	190	13
NL03-1	3	507	74	461	8.0	2.4	0.5	1.1	61	5.8	9.4	0	0.1	47.1	0.6	0.56	50	0.4
NL04-1	3	149	42	375	6.1	0.8	1.6	0.5	57	4.8	4.7	0	0.1	48	0.4	0.19	37	0.3
NL05-1	2	556	71	3860	44	13	4.0	0.7	180	20	53	0.3	15	152	9.8	8.3	195	0.5
RH01-1	2.7	267	64	1608	22	1.7	21	0.5	87	10	32	0.2	0.2	146	17	0.35	980	9.0
RH01-3	2.7	317	72	1440	19	1.6	3.8	0.3	85	9.7	30	0.1	0.2	144	15	0.20	580	8.8
RH04-1	2.4	725	45	2440	19	3.4	22	31	100	11	21	0.1	4.0	163	18	1.5	1895	25
RH04-3	2.3	327	50	2650	32	5.4	23	45	130	13	26	0.1	7.4	173	19	2.2	1780	29
RH05-1	2.9	268	65	1963	12	1.3	7.0	21	165	17	115	0	0.3	72.7	26	2.4	6940	36
RH05-3	2.9	301	88	1703	18	5.1	4.7	27	400	40	180	0.3	0.5	72.9	20	3.2	11085	61
RH07-2	2.3	203	84	1310	22	2.6	0.5	0.4	205	15	6.9	0	2.2	35.1	0.6	5.7	140	1.3
RH20-4	3.3	567	67	2110	34	0.9	225	52	600	61	11	0.3	0.7	254	51	0.14	1625	115

^aSite codes are the same as those in Table 2. Analysis done by ICP-MS, except for arsenic which was done by GF-AAS. Redox = redox potential in mV; temp. = temperature in °C; cond. = conductivity in $\mu\text{S/cm}$.

TABLE 4. Mean Values from 12 Gas Analyses of Major and Minor Gas Components Determined (by ref 33) in 1994 and 1997 in Yellowstone National Park for Comparison with Concentration Ranges of Volatile Metals and Metalloids (Table 2)^a

	mean mol %	standard deviation	mean mg/m ³
CO ₂	97.83	2.02	1,900,000
N ₂	1.226	1.60	15,000
H ₂ S	0.525	0.50	8,000
CH ₄	0.235	0.37	1,700
Ar	0.024	0.04	430
O ₂	0.058	0.12	830
NH ₃	0.006	0.01	42.5
H ₂	0.083	0.10	75.0
He	0.004	0.01	7.35

^a Values were recalculated from mol % to mg/m³ using their mole masses and the average number of moles gas per m³ (44.64 mol/m³).

with fully reductive (-200 mV at Lower Geyser Basin, Table 3) and fully oxidative conditions (+725 mV at RH04, Table 3) were in the lower to medium range. Figure 3 shows an influence of pH with volatile arsenic concentrations of more than 30 mg/m³ occurring only at hydrothermal features with a pH less than 3.5, but a significant linear correlation was not confirmed by statistic tests.

In lower concentrations and not at all sites, volatile molybdenum, tungsten, antimony, titanium, vanadium, cadmium, lead, germanium, and gallium were detected as shown in Figure 2. Other previously known environmentally relevant volatile species were not detected. Bismuth and selenium were detected neither in the gaseous nor in the aqueous phase. Tellurium, indium, and tin did not form volatile species even though concentrations in the aqueous phase were increased. From the compounds palladium, platinum, gold, thallium, and chromium known to form volatile species under laboratory conditions (35) only chromium was identified in concentrations around 10 mg/m³ in Yellowstone's hydrothermal gases.

Origin of Volatile Metals and Metalloids. As discussed above no global linear correlation was found for the partitioning of metals and metalloids between the aqueous and the gas phase. Obviously the sampled gas phase is not in equilibrium with the aqueous phase at the surface. Information about reservoir temperatures and formation

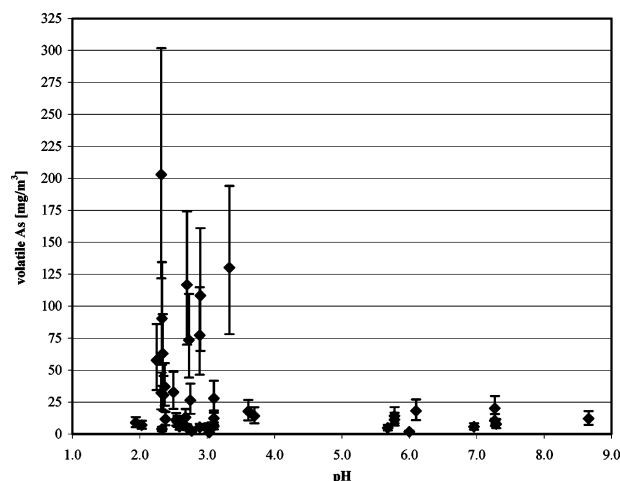


FIGURE 3. Concentrations of arsenic degassing from hydrothermal features in correlation with their corresponding pH. Significantly increased concentrations (> 30 mg/m³) were only found over hydrothermal features with a pH < 3.5; error bars calculated assuming the uncertainties given in the methods section.

depth of the hydrothermal fluids could be helpful to further explain differences in gas composition. Geothermometers can be used for calculating reservoir temperatures if on one hand full equilibrium with respect to the mineral system albite-potassium feldspar-muscovite-clinocllore-silica was reached at formation depth and on the other hand the fluids rise quickly in a process of excess enthalpy boiling and do not equilibrate with the aqueous phase at the surface. Using a ternary Na-K-Mg diagram for classification according to Giggenbach (38, 39) only the four samples from Lower and Gibbon Geyser Basin can be considered as being in full equilibrium. The classification was confirmed by thermodynamic modeling where the respective mineral phases were found to be in equilibrium or supersaturated. Unfortunately, four samples is insufficient to define a general trend such as increased volatilization with increasing reservoir temperature.

Part of the samples from Ragged Hills and all samples from Nymph Lake and Hazle Lake were classified as immature waters in the Giggenbach diagram (38, 39). Replicate analyses of gases from these nonequilibrated hydrothermal features (HL01, RH01, RH04, and RH05 in Table 2) showed significant temporal variations in gas concentrations. Compared to the

sampling in June 2003, the concentrations of most volatile metals and metalloids were 2 to more than 20 times higher in September 2003. Apart from complex changes in the hydrothermal regime ("annual disturbance" as discussed for Si before), formation and quantity of the volatile metals and metalloids most certainly are influenced by microbial activity. Up to today, however, there are no investigations published as to the identification of microorganisms able to volatilize any of the volatile metals and metalloids detected.

This study has shown that it is possible to sample volatile metals and metalloids with a relatively simple, low-cost, and fast screening method if proper precautions are taken for passive diffusion-based gas sampling, compensation of oxidizing solution matrix effects, and conversion of dissolved, oxidized to gaseous concentrations. Volatile Si, Ni, Zn, Cu, and As were detected in tens to hundreds of $\mu\text{g}/\text{m}^3$. Global correlations between aqueous and gaseous phase have not been observed, even though some trends of volatile Si occurrence dependent on reported reservoir temperatures might exist. Future investigations should focus on quantitative species-selective investigations to further elucidate the origin and fate of the volatile metals and metalloids.

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Supporting Information Available

Table of dissolved metal and metalloids concentrations; gas concentration conversion according to Fick's first law. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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