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Distribution, speciation and bioavailability of arsenic in a shallow-water submarine hydrothermal system, Tutum Bay, Ambitle Island, PNG

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1. Introduction

Shallow-water submarine hydrothermal systems, which are defined here as occurring in less than 200 m of seawater and often having a meteoric water source, are often enriched in biologically toxic elements such as As, Sb, Se, Cr, Co, Pb, Cd, Ag, Cu, Tl, Zn, Hg, and S, as well as possible limiting nutrients such as Si and Fe (Dando et al., 1999; Varnavas and Cronan, 1988; Vidal et al., 1978). These systems have been described in many areas around the world, where they are generally associated with volcanic (e.g., Dando et al., 2000; Johnson and Cronan, 2001; Tarasov et al., 1986) or tectonic activity (e.g., Vidal et al., 1978), which provide the necessary heat source. The impact of these systems may be much larger than expected, considering their location. Coastal waters are often breeding and hatching grounds for many species, in tropical areas they host coral reefs, and humans have always used these waters for fishing and recreation. The chemical composition of seawater in these important coastal areas is controlled through a combination of natural and anthropogenic processes. In areas of volcanic activity and/or high heat flow, the discharge of fluids from shallow marine hydrothermal systems may have a considerable impact on the chemical composition of the often biologically important coastal surface waters. Diffuse venting may also influence benthic organisms at very large distances away from focused venting (Tarasov et al., 1999; Varnavas and Cronan, 1988). Also, considering their abundance, emissions from shallow-water hydrothermal systems may well be a significant contributor to global budgets that has been constantly overlooked.

The shallow-water hydrothermal vents in Tutum Bay, Ambitle Island, PNG discharge approximately 1.5 kg of As per day into an area of approximately 50 by 100 m that has an average depth of 6 m (Pichler et al., 1999a,b). Of all potentially biologically toxic elements, As is the only one that is significantly enriched compared to seawater. Despite the amount of As released into the bay, corals, clams and fish do not show an obvious response to the elevated concentrations (Pichler et al., 1999b). Fish have been observed to hover over vent orifices bathing in the hydrothermal fluid, and the diversity and health of the coral reef itself is indistinguishable from reefs that are not exposed to hydrothermal discharge. The skeletons of scleractinian corals and the shells of *Tridacna gigas* clams do not show elevated concentrations of As or other trace metals when compared to specimens collected from outside Tutum Bay (Pichler et al., 2000). However, the surrounding sediments are quite different, being devoid of any calcium carbonate typical of coral reef environments.

While the general geochemistry of As in the Tutum Bay fluids and precipitates is known (Pichler and Veizer, 1999, 2004; Pichler et al., 1999a,b), only little knowledge exists about its distribution, speciation, cycling and bioavailability in surrounding seawater and sediment. The primary objective of this research, therefore, was to assess the availability of As for biological uptake from Tutum Bay sediments (cores and surface samples), seawater, pore water and vent fluids.

1.1. Setting

Submarine hydrothermal venting occurs at Tutum Bay approximately 150 m offshore from Ambitle Island in 5–10 m water depth (Fig. 1). Two types of venting are observed. (1) Focused discharge of a clear, hydrothermal fluid occurs at discrete ports, 5–15 cm in diameter. Fluid temperatures at vent orifices are between 89 and 98 °C and discharge rates are as high as 400 L/min. (2) Dispersed or diffuse discharge consists of hydrothermal fluids and streams of gas bubbles (94–98% CO_2) emerging directly through the sandy to pebbly unconsolidated sediment and through fractures in volcanic rocks. The sediments surrounding the vent site are predominantly composed of feldspar, hornblende, pyroxene and magnetite, weathering products from andecite–dacite basalts of Ambitle Island, which are coated with HFO. The nature of the sediment changes to more carbonate-dominant far away from venting (~200 m). The hydrothermal fluids are of meteoric origin and compared to seawater, vent fluids are about 10 times less saline. In addition to As, vent fluids are also enriched in Fe, Mn, Cs, Tl and Si (Pichler et al., 1999a). A more detailed description of Tutum Bay hydrothermal vent fluids and precipitates has been provided elsewhere (Pichler and Dix, 1996; Pichler et al., 1999a,b).

A control site was delineated approximately 1.6 km north, beyond the influence of hydrothermal venting (Fig. 1). The sediments associated with the control site were entirely calcium carbonate, making its composition very suitable as an end-member when compared to hydrothermal sediment.

1.2. Arsenic speciation and bioavailability

Elements such as As, S, Mn, Zn, Cr, Co, Cu, and Se can play a very biologically complex role. These elements are essential for many biological processes, but concentrations above a certain level have adverse effects, thereby converting an essential element to a toxin (Ems-

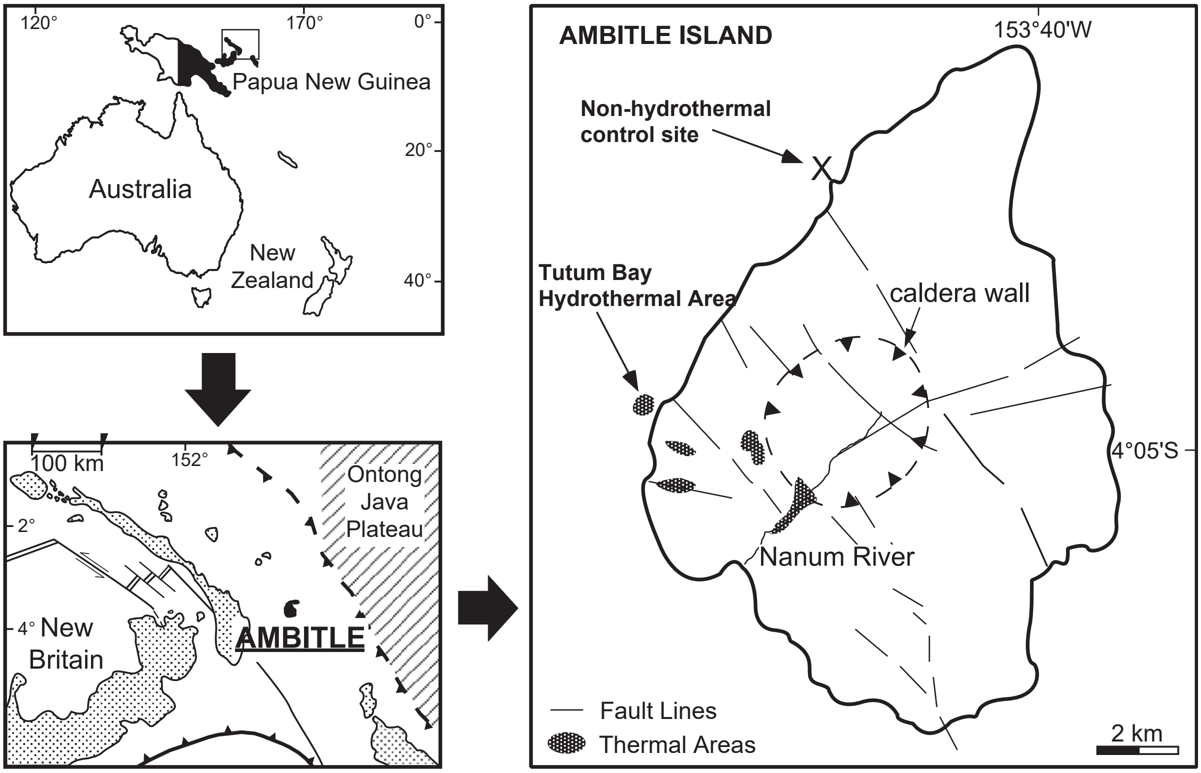

Fig. 1. Location of Ambitle Island and the shallow-water hydrothermal vents studied. Tutum Bay hydrothermal area and the control site are indicated (modified from Pichler and Dix, 1996).

ley, 1991). Recently, it has been recognized that the total concentration of an element in an ecosystem does not necessarily represent its biological availability or potential toxicity (Newman and Jagoe, 1994). This concept is known as 'bioavailability', and is a function of the abundance and chemical form of the toxin in solution (i.e., oxidation state), and the nature of its binding to sediment grains. For example, the element may be part of a very stable mineral, such as quartz, and thus is not available for biological processes (Newman and Jagoe, 1994). Alternatively, the toxin can be adsorbed to sediment grains in an easily-extractable form (Tessier et al., 1979), which would then be more available to benthic organisms (Yoo et al., 2004). Bioavailability is defined here as the degree to which an element or molecule is able to move into or onto an organism (sensu Benson, 1994). Transfer of a toxin into an organism can occur by diffusion onto/across the cell membrane, or through the food web. In solution, the free-metal ion is by far the most biologically toxic, although easily-exchangeable forms in sediments can also be harmful (Newman and Jagoe, 1994). Several elements, such as As, Cr, and Sb, are more difficult to characterize because they occur in several oxidation states in water and sediments and therefore will have a different degree of bioavailability, depending on the species present (Gebel et al., 1997). Arsenic, for example, can occur as arsenite (As^{3+} or As(III)) and arsenate (As^{5+} or As(V)), as well as several methylated forms (e.g., DMA and MMA; Francesconi and Edmonds, 1994). Of the two common oxidation states of arsenic, As(III) is more mobile and by far the more toxic, causing reduction in growth to marine organisms at aqueous concentrations less than 3 µg/L, and neurological damage in humans at concentrations as low as 100 µg/L (Gebel et al., 1997; Sanders et al., 1994). Therefore, the oxygen content and the prevailing redox condition are primary controls on the mobility and toxicity of As in an aqueous environment, because these control the oxidation state. Thus, determining the species present in the environment is necessary for understanding the bioavailability of the element (Newman and Jagoe, 1994).

Concentrations of metals in sediments usually exceed those of overlying water by 3 to 5 orders of magnitude (Bryan and Langston, 1992; Mountouris et al., 2002). Therefore the bioavailability of even a small amount of the total metal in sediment can be important. With respect to bioavailability, the metals in the most easily extracted fractions are the most important, because they are the most bioavailable and are potentially the most immediately dangerous to the biota (Bendell-Young and Harvey, 1991; Bhumbla and Keefer, 1994; Sahuquillo et al., 2002; Tessier et al., 1979). However, As concentrations in all mineral phases should be determined for any long-term prediction of arsenic behavior in sediments because changes in environmental and/or physicochemical conditions (e.g., sediment burial, reworking by storms, etc.) may alter mineral stability.

2. Methods and procedures

2.1. Sample handling and preparation

Field work was conducted in November 2003 and consisted of SCUBA diving over a period of 14 days to collect samples of vent fluid, vent precipitates, sediments, pore water, and ambient seawater from Tutum Bay (Fig. 2). Sampling was conducted along a transect stepping away from the area of focused venting to an area where the character of the sediment (i.e., color, mineralogy) seemed to be unaffected by hydrothermal activity, 225 m away (Fig. 2b). The transect was marked by aluminum stakes approximately every 30 m that were connected by a metered rope. In addition to the Tutum Bay samples, we collected a carbonate sediment approximately 1.6 km north at a location unaffected by hydrothermal activity (Fig. 1).

Temperature and pH of waters just below the sediment/water interface (~5 cm) were measured along the transect at a spacing of 1 m using an IQ Scientific Instruments® #IQ150 pH/mV/temperature probe, with automatic temperature compensation to 100 °C in an underwater housing, and a Forestry Suppliers waterproof digital thermometer, respectively.

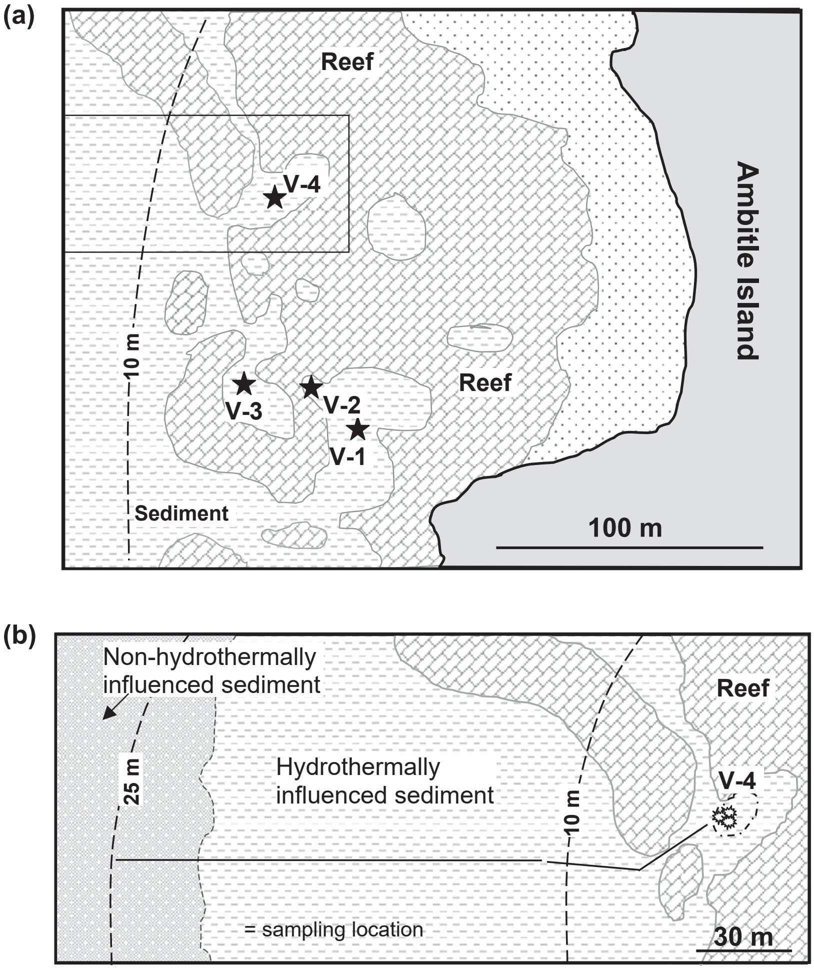

Fig. 2. (a) Location of the main venting areas of the hydrothermal system at Ambitle Island. The box in the upper left is enlarged in (b) (modified from Pichler and Dix, 1996). (b) Location of transect along which surface sediment, core samples, sediment pore-water, and ambient seawater were collected for this study. Vent fluids and precipitates were also collect at the area of focused venting.

Vent fluids were collected following the procedure of Pichler et al. (1999a). This consisted of placing an inverted Teflon® funnel over focused venting. The temperature from the top of the funnel, along with the appearance of density fronts, indicated that the flow of hydrothermal fluid discharge had displaced all seawater from the funnel. 60 ml syringes were attached to the funnel, and the vent fluid was slowly drawn into the syringe at a rate slower than vent discharge so as not to contaminate the hydrothermal fluid sample with seawater. Vent precipitates were collected in the immediate vicinity of focused venting. Although vent fluids and precipitates from this locality have been collected in the past (Pichler and Dix, 1996; Pichler et al., 1999a), they were collected again to assess consistency and temporal variability in the hydrothermal system. The direct comparison with data from this research is presented below.

Surface sediments were collected along the transect at 1, 7.5, 12, 30, 60, 90, 125, 150, 175, 200, and 225 m away from focused venting to assess the extent of hydrothermal influence on sediment chemistry (Fig. 2b). Sediment cores up to 1 m deep were taken to assess hydrothermal influence with depth at 1, 7.5, 12, 30, 60, 90, 150, and 225 m (Fig. 2b). Cores were described on-board and sampled at approximately 10 cm intervals.

At the same locations where sediment cores were taken we obtained pore-water profiles down to a depth of 1 m when possible, using Teflon® tubing inside a 1″ aluminum pipe with screened openings every 10 cm. The pore fluids were collected into syringes and, to reduce vertical mixing, a multi-syringe puller was used to extract the samples slowly and simultaneously from up to six different depths.

Ambient seawater was collected at approximately 15 cm below the ocean surface, and 1 m above the seafloor every 15 m along the entire transect. This was done simultaneously by two divers swimming along the transect using 60 ml syringes.

As soon as vent fluids, pore waters, and ambient seawaters were brought on board, unstable parameters, such as pH and alkalinity were measured. Total alkalinity was measured using a HACH digital titrator, and titrating to an endpoint of pH 4.5 (HACH, 1997). The pH was measured using a Myron-L pH meter with temperature compensation. Water samples were preserved for analysis of As abundance, As speciation, and major cations by filtering to <0.45 µm, and acidified to 1% using ultrapure hydrochloric acid (HCl). Water samples for analysis of major anions were filtered into separate bottles without acidification. All water sample bottles were sealed with electrical tape and kept cool until laboratory analysis.

2.2. Lab measurements

Sediment samples were described by optical microscopy, and using a Hitachi S-3500N variable pressure Scanning Electron Microscope (SEM), equipped with a Robinson backscatter detector and a PGT Energy Dispersive X-ray (EDX) system housed at the USF Electron Microscopy Center. The EDX analysis of hydrothermal vent precipitates was used in combination with sequential extraction to verify the primary arsenic phases.

Arsenic abundance and speciation in vent fluids, seawater, and pore-waters were determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSAnalytical 10.055 Millennium Excalibur system at the University of South Florida (USF) Center for Water and Environmental Analysis. In preparation for the determination of total As concentration, 10 ml of sample were combined with 15 ml concentrated HCl and 1 ml saturated potassium iodide (KI) solution to reduce As(V) to As(III) and diluted with deionized water (DI) to a final volume of 50 ml.

Arsenic speciation analysis was carried out by high pressure liquid chromatography (HPLC) separation of As(III), DMA, MMA and As(V) prior to detection by HG-AFS. A sample volume of 100 µL was injected without pretreatment and separated in a Hamilton PRP-X100 cation exchange using a KH_2PO_4/K_2HPO_4 buffer at a pH of 6.25.

Following homogenization and acid digestion, Fe, Ca and As in sediments and precipitates were measured by a combination of AFS, NAA and ICP-MS at Actlabs, Ontario, Canada and at USF. The element Si was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) on a Perkin Elmer Optima 2000 DV, also housed at the Center for Water and Environmental Analysis, USF.

2.3. Sequential extraction of arsenic in Tutum Bay sediments

The As fraction in sediments that is most important for bioavailability studies is the easily extractable surface-complexed fraction (Newman and Jagoe, 1994). We extracted this fraction through a cation-exchange reaction using a solution of KH_2PO_4/K_2HPO_4 at a pH of 7.2, following Gleyzes et al. (2002). This extraction step consisted of weighing 0.5 g of sediment or precipitate into a 50 ml centrifuge tube, then adding 20 ml of the reagent. The reaction was allowed to continue for

~16 h at room temperature with periodic shaking. The sample was centrifuged, and the supernatant was transferred from the centrifuge tube using a dropper. 10 ml of DI water was added to the remaining sediment, shaken, and then the rinse was added to the existing supernatant. Overall, this experiment was performed three times: 1) as a single extraction; 2) at the beginning of a four-step complete sequential extraction (see below); and 3) to test the completeness of this reaction, the KH_2PO_4/K_2HPO_4 extraction was repeated three times consecutively on the same sample.

A four-step sequential extraction, tailored specifically to the mineralogy and geochemical attributes of Tutum Bay sediments was carried out to evaluate As concentrations in the surface-bound, carbonate, Fe-oxyhydroxide (hydrous ferric oxide or HFO), and residual fractions. This extraction scheme is a combination and modification of methods developed by Tessier et al. (1979), Pichler et al. (2001), Wenzel et al. (2001), and Gleyzes et al. (2002). Often $MgCl_2$ is used on the easily extractable fraction (Tessier et al., 1979). We did not use the $MgCl_2$ reagent based on research by Gleyzes et al. (2002), who showed Mg^{2+} cannot be exchanged efficiently with the anionic species, the univalent chloride ion has low anion exchange power, and more importantly, the pH is not buffered during $MgCl_2$ extraction procedures. Low final pH values could contribute to attack the carbonate fraction, which could overestimate the exchangeable fraction while underestimating the carbonate fraction. Our sample collection, preparation, and extraction procedure consisted of the following:

1) Each sediment or precipitate sub-sample was air dried.
2) 0.1 to 1.0 g of homogenized sample, depending on the quantity of HFO and $CaCO_3$ present, was weighed into 50 ml Teflon centrifuge tubes.
3) An amount of each extracting reagent was added sequentially for the listed time and conditions (Table 1).
4) Once the reaction was complete, the sample was centrifuged at 8600 rpm for 15 min and the supernatant liquid was decanted into separate bottles for analysis following methods outlined above.
5) DI was added to the sample, and the rinse was added the supernatant.

The reagents and conditions (pH, temperature, reaction time, agitation, and rinsing) selected for each fraction are presented in Table 1. Additional reagent was added when necessary to the carbonate and HFO extraction steps (e.g., for vent precipitates or control-site samples, which consist of nearly 100% HFO and $CaCO_3$, respectively).

Analytical and instrumental quality assurance and quality control (QA/QC) was evaluated for all lab analyses by including sample duplicates and certified reference standards from Fisher Scientific®, which indicate a precision of better than 5% for HG-AFS and ICP-OES. Background signal drift was consistently <1% for all instruments. Acid blanks for digestions and sequential extractions were tested and showed no contamination for the analyzed elements. No reference material exists for the fractionation of arsenic in sediments, thus we used the marine sediment reference, PACS-2, from the Institute for National Measurement Standards-National Research Council of Canada, to track the reproducibility of our extractions. The supernatant fluids were analyzed by a combination of ICP-OES and HG-AFS.

3. Results

3.1. Temperature and pH variation of surface sediment pore-water along the transect

The temperature and pH of pore-waters in surface sediments (upper 10 cm) show a hydrothermal influence extending up to 150 m away from the vent site (Fig. 3). The temperature of these pore-waters decreases from 94 °C near the vents to a constant 31 °C (ambient seawater) at 100 m away from the vents. For the first 20 m the temperature shows dramatic variations of up to 60 °C between sampling points only a meter apart (Fig.

Table 1
Sequential chemical extraction procedure for As and Fe in sediments and vent precipitates

Step	Fraction	Extractant	Conditions	Reference
1	Easily extractable	0.1 M KH_2PO_4/K_2HPO_4	pH=7.2, 20 °C, 16 h shaking periodically rinsed with DI	Gleyzes et al., 2002
2	Carbonate	1.0 M NaOAc/HOAc	pH=5.0, 20 °C, 4 h shaking periodically rinsed with DI	Tessier et al., 1979
3	Amorphous and crystalline metal-oxides	0.2 M NH_4^+-oxalate	pH=3.25, 20 °C, 4 h shaking periodically rinsed with DI	Wenzel et al., 2001
4	Residual	Aqua regia 3:1 HCl to HNO_3	96 °C, 2.5 h rinsed with DI	Pichler et al., 2001; Tessier et al., 1979

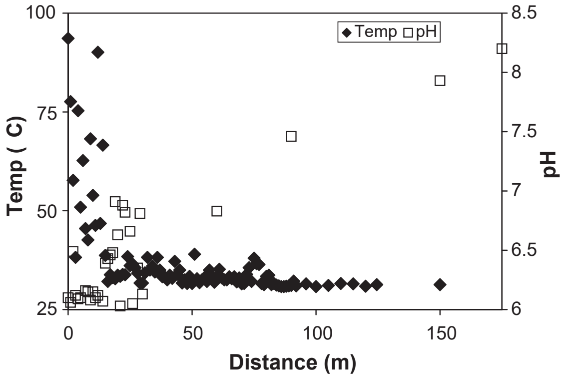

Fig. 3. Temperature and pH relationship in pore-waters of surface sediment (~5 cm depth) along transect shown in Fig. 2b vs. distance from focused venting.

3). From 20 to 100 m there is still some variation of up to 5 °C. The pH of the pore-fluids increases from approximately 6 near the vents to 8.2 along the transect. Large variations for pH of up to 1 unit were observed between 10 and 20 m. The pH values then gradually increase to ambient seawater values along the transect, with a pH lower than seawater (pH ≈ 8) extending to >100 m (Fig. 3). The temperature and pH at the control site are 30.2 °C and 8.02, respectively.

3.2. Arsenic in vent fluids, pore waters and ambient seawater

The vent at which the transect starts is vent 4 in Pichler et al. (1999a) and its arsenic concentration of 950 μg/L, exclusively present as As(III), closely matches previous data (Pichler et al., 1999a). Stepping away from vent 4, As concentrations at the seawater–sediment interface (pore-waters in the upper 10 cm) remained high (900.4 μg/L) near the vent area, but then dropped consistently to a minimum of 4.5 μg/L at 225 m (Table 2). Beginning with the pore-water profile at 30 m, As(V) is the dominant species and concentrations generally increased with depth (Table

Table 2
Temperature, pH, arsenic (As) and silica (H_4SiO_4) in pore-water profiles for points along transect shown in Fig. 2 and the control site at Picnic Island (PI), compared to Vent 4

Distance from Vent 4 (m)	Depth (cm)	T (°C)	pH	As(T) (μg/L)	As(III) (μg/L)	As(V) (μg/L)	$H_4SiO_4^\circ$ (mg/L)
Vent 4	0	98	6.0	950	950	n.d.[a]	100
1	0	38.7	6.2	n.a.[b]	n.a.	n.a.	n.a.
	10	77.6	6.1	900	900	n.d.	97
7.5	0	42.2	6.2	81	32	49	14
	10	45.5	6.2	n.a.	n.a.	n.a.	n.a.
12	0	45.5	7.4	36	2.1	34	4
	10	90.1	6.1	n.a.	n.a.	n.a.	n.a.
30	0	30.1	7.1	10	1.4	8.7	5
	10	31.7	6.1	25	1.7	23	21
	20	33	6.2	43	1.1	42	21
	30	34.5	6.2	63	1.2	61	19
	60	37.9	6.1	359	4.5	355	81
	100	40.8	n.a.	95	0.6	95	27
60	0	30.7	7.1	9.2	1.5	7.8	4
	10	33.3	6.8	16	3.1	13	15
	20	34.9	6.2	39	1.5	38	12
	30	36.6	6.2	65	2.0	63	16
	60	40.5	n.a.	66	1.2	65	16
	100	n.a.	n.a.	150	20	130	56
90	0	30.5	8.1	n.a.	n.a.	n.a.	n.a.
	10	31.1	7.5	22	2.4	20	2
150	0	n.a.	7.9	7.3	1.3	6.0	1
	10	n.a.	7.2	63	51	12	2
	30	n.a.	7.6	27	7.9	19	3
225	0	n.a.	8.2				
	10	n.a.	7.8	4.5	1.3	3.2	2
PI	0	30.2	8.0	n.a.	n.a.	n.a.	n.a.
	10	n.a.	7.6	3.3	1.9	1.4	2
	20	n.a.	7.8	2.1	1.8	0.3	2

The methylated species, DMA and MMA, were not detected.

[a] n.d. = not detected.

[b] n.a. = not analyzed.

2). Pore-waters closer to the vent site contained higher concentrations of As(III), and at 1 m, no As(V) was detected. A good correlation exists between As and Si in the pore-waters ($R^2=0.84$; Table 2).

The As concentration in Tutum Bay surface seawater ranges from 8.4 µg/L above the vent area to 2.5 µg/L at the end of the transect (Fig. 4a). This value is still significantly above the value of 1.35 µg/L, which is reported for surface seawater (Cutter, 2002). Bottom seawater shows uniformly lower As concentrations than the corresponding surface samples (Fig. 4a). Concentrations decrease from 3.1 to 1.8 µg/L. The abundance of Si along the transect mirrors that of As in both the surface and bottom samples, with a correlation coefficient of 0.98 and 0.93 for surface and bottom waters, respectively (Fig. 4a and b). Both inorganic As species, As(III) and As(V) are present in ambient seawater (Table 3). The species distribution is surprisingly constant along the transect, without variation beyond the analytical uncertainty. In surface samples, As(V) is the dominant species (~70%) whereas As(III) is the dominant species in the bottom samples (~60%). Neither of the two methylated As species, DMA and MMA, were detected in any of the samples that were selected for As speciation (i.e., vent fluid, pore waters, ambient seawater).

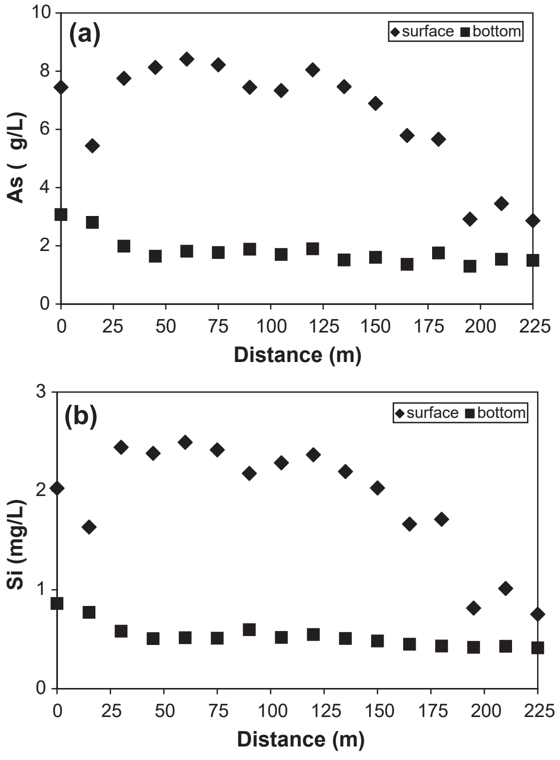

Fig. 4. (a) As concentration in surface and bottom waters along the transect shown in Fig. 2b. (b) Si concentration in surface and bottom waters along the transect shown in Fig. 2b.

3.3. Arsenic abundance and bioavailability in precipitates and sediments

The highest As concentrations in Tutum Bay are found in hydrothermal HFO that precipitates around vent orifices. Arsenic values for HFO collected directly at vent 4 are as high 33,200 ppm (Table 4, Fig. 5), although concentrations as high as 62,000 ppm were previously reported (Pichler and Veizer, 1999).

The As concentration in the surface sediments decreases from a maximum of 1482 ppm at the beginning to 52 ppm at the end of the transect (Fig. 5, Table 4). Iron exhibits a similar trend, decreasing from 18.4% to 6.6%. Calcium values increase along the transect, reflecting the increasing amount of Ca-carbonate in the sediment (Table 4). The Ca-carbonate sediment that was collect from outside Tutum Bay contains 2.2 ppm As ($n=11$; $\sigma=\pm0.25$), 33.4% Ca and 0.4% Fe.

The sediment cores displayed substantial vertical and horizontal heterogeneity, reflecting hydrothermal alteration, including precipitation of HFO and framboidal pyrite in highly altered sediment. Arsenic concentrations range from 159 to 1483 ppm near the vent, and reach 44 to 72 ppm 225 m away from the vent site (Table 4). The highest total As concentrations are concentrated in HFO layers. For example, the highest concentration of As for all core-sediments was 4025 ppm, located in a zone of extensive HFO coating in the core collected at 60 m (Table 4).

The bioavailability of As from Tutum Bay surface sediments and precipitates was estimated using the single KH_2PO_4/K_2HPO_4 extraction (Table 1). Arsenic concentrations for the easily extractable fraction ranged from 444 ppm in HFO precipitates, to 1.5 ppm in sediments at 225 m, and 0.7 ppm from the sediments at the control site. The easily extractable portion of arsenic in Tutum Bay surface sediments can be as high as 54 ppm, with a mean of 19.7 ppm when excluding the vent precipitates and control end members (Table 5, Fig. 5). This averages 3.6% of the total concentration, with a range of 1.6–4.1% (Fig. 5). Vent precipitates and the control sample had extractable As of 1.3% and 32.1%, respectively (Table 5, Fig. 5). The KH_2PO_4/K_2HPO_4 extraction for the surface-bound arsenic that was performed on the same sediments three times consecutively showed near-perfect reproducibility and values were in close agreement with the single extractions.

The four-step sequential extraction showed that of the easily extractable, carbonate, HFO, and residual

Table 3
Arsenic concentration and speciation in seawater for sampling points along the transect shown in Fig. 2 in surface and bottom seawater

Distance (m)	Location	As(T) μg/L	As(III) μg/L	As(V) μg/L	As(III) %	As(V) %
0	Surface	7.4	2.1	5.3	28.3	71.7
15	Surface	5.4	1.8	3.6	33.3	66.7
30	Surface	7.8	n.a.[a]	n.a.	n.a.	n.a.
45	Surface	8.1	n.a.	n.a.	n.a.	n.a.
60	Surface	8.4	n.a.	n.a.	n.a.	n.a.
75	Surface	8.2	1.9	6.3	23.5	76.5
90	Surface	7.4	n.a.	n.a.	n.a.	n.a.
105	Surface	7.3	n.a.	n.a.	n.a.	n.a.
120	Surface	8.0	n.a.	n.a.	n.a.	n.a.
135	Surface	7.5	n.a.	n.a.	n.a.	n.a.
150	Surface	6.9	1.9	5.0	27.5	72.5
165	Surface	5.8	n.a.	n.a.	n.a.	n.a.
180	Surface	5.7	2.4	3.3	42.1	57.9
195	Surface	2.9	1.4	1.6	46.8	53.2
210	Surface	3.5	1.3	2.2	36.9	63.1
225	Surface	2.9	1.3	1.5	46.7	53.3
0	Bottom	3.1	1.8	1.3	57.6	42.4
15	Bottom	2.8	1.5	1.4	51.7	48.3
30	Bottom	2.0	n.a.	n.a.	n.a.	n.a.
45	Bottom	1.6	n.a.	n.a.	n.a.	n.a.
60	Bottom	1.8	1.1	0.7	60.5	39.5
75	Bottom	1.8	n.a.	n.a.	n.a.	n.a.
90	Bottom	1.9	1.1	0.8	57.0	43.0
105	Bottom	1.7	n.a.	n.a.	n.a.	n.a.
120	Bottom	1.9	n.a.	n.a.	n.a.	n.a.
135	Bottom	1.5	n.a.	n.a.	n.a.	n.a.
150	Bottom	1.6	n.a.	n.a.	n.a.	n.a.
165	Bottom	1.4	n.a.	n.a.	n.a.	n.a.
180	Bottom	1.8	1.2	0.6	67.9	32.1
195	Bottom	1.3	n.a.	n.a.	n.a.	n.a.
210	Bottom	1.5	n.a.	n.a.	n.a.	n.a.
225	Bottom	1.5	1.0	0.5	64.9	35.1

[a] n.a. = not analyzed.

fractions, the As was predominantly associated with the HFO. In fact, for the HFO precipitates, 98.6% of the As was leached along with 99.7% of the Fe during this step (Table 5). The easily-extractable, carbonate, and residual fractions for vent precipitates contained 1.4%, 0.03%, and 0.1% As, respectively. The mean easily-extractable fraction for this experiment was 21.5 ppm, which is again in very good agreement with the other extraction experiments explained previously.

It is important to note that the sum of the fractions in most, but not all, cases were equal to the bulk As concentration determined by NAA. This would suggest that the residual fraction was not completely represented (digested) in some of the samples, and that the percent values would therefore be effected. However, the HFO fraction obviously contains the majority of As in Tutum Bay sediments, and ~20 ppm As is available from the easily-extractable fraction of the sediments. Residual minerals included hornblende and feldspars.

4. Discussion

4.1. The importance of diffuse venting on arsenic distribution and speciation

Diffuse discharge seems to play a critical role in the distribution of As throughout Tutum Bay waters and sediments. The As concentration in Tutum Bay surface sediments is elevated to a distance >200 m, with a mean value of 527 ppm. This is approximately one order of magnitude more As than observed at the end of the transect and two orders of magnitude higher than the As concentration at the control site (2.2 ppm). Discharge of hydrothermal fluid through the sediment is visible to at least 30 m away from focused venting, while temperature and pH is highly variable along the transect to almost 100 m (Fig. 3). However, the most compelling evidence that suggests diffuse venting is a major contributor of As in Tutum Bay sediments is the high As concentration in pore fluids up to 150 m away

Table 4
Arsenic, Fe and Ca composition in Tutum Bay sediment cores that were collected along the transect shown in Fig. 2, compared to Picnic Island

Distance (m)	Depth (cm)	As (ppm)	Fe (%)	Ca (%)
0	0	33,200	29.7	3.0
1	0	1483	18.4	4.8
	15	159	12.3	6.4
	25	203	12.8	6.4
7.5	0	783	12.2	5.9
	5	872	11.9	6.9
	12	431	9.0	5.0
	25	148	11.0	4.9
	35	178	13.7	5.7
12	0	680	8.4	6.0
	2	473	8.7	6.8
	16	747	9.0	6.0
	20	416	8.3	10.9
	26	1064	13.1	8.6
	38	273	14.7	4.5
30	0	539	8.3	6.9
	2	483	11.2	7.1
	10	719	9.8	6.7
	30	537	7.3	8.0
	50	624	6.8	7.2
	68	788	6.9	6.0
60	0	614	10.5	8.2
	5	635	11.5	8.0
	25	1043	11.2	7.1
	31	3668	15.3	7.2
	45	2053	18.3	6.1
	64	736	13.5	5.2
	75	1255	11.9	5.8
	80	1580	10.9	4.8
	85	4025	14.9	3.1
	92	530	7.0	1.9
90	0	443	10.3	11.0
	5	464	11.8	9.0
	25	524	11.4	8.9
	50	590	9.9	22.6
	79	1245	10.5	7.3
125	0	468	6.0	5.8
150	0	402	6.5	7.6
	5	411	6.5	8.9
	20	411	6.9	11.1
	35	369	6.0	12.7
	50	374	6.5	10.4
175	0	360	8.8	5.6
200	0	163	6.2	12.6
225	0	52	6.6	19.7
	5	72	6.5	19.4
	13	48	4.3	25.4
	23	44	5.6	24.8
Picnic Island averages[a]		2.2	0.4	33.4

[a] $n = 11$.

from the vent site (62.8 µg/L; Table 2). Altered core sediments with HFO coatings contain elevated As concentrations to the end of the transect at 225 m. Hydrothermal discharge through the sediments is also reflected in the lack of Ca-carbonate near the vent, only appearing in the sediment at 175 m. This is likely a result of the low pH of hydrothermal fluids preventing the formation and/or prolonged existence of calcium carbonate in the sediment. In addition to high As concentrations in surface sediments at the end of the transect, elevated Fe concentrations also exist (e.g., 6.6% at 225 m compared to 0.4% at the control site).

Vent fluids at Ambitle Island are characterized by very high As concentrations. Interestingly, however, the ambient seawater immediately surrounding the vent site has As values which are three orders of magnitude lower and are near commonly reported values for normal seawater of ~2 µg/L (Andreae, 1977; Cutter, 2002; Plant et al., 2003). Arsenic speciation in bottom waters seems to be slightly affected by diffuse flow, with higher As(III) concentrations when compared to average seawater (5–10%; Table 5; Plant et al., 2003). The use of Si as a tracer of hydrothermal venting is valid provided there is a sufficient concentration difference between the hydrothermal fluid and seawater, which is the case at Ambitle Island (Pichler et al., 1999a; Sedwick and Stuben, 1996). The low Si and As concentrations in bottom waters show that there is little hydrothermal fluid leaving the sediments, although pore water and sediment chemistry reflects diffuse flow (Tables 2, 4, and 5). This likely reflects the absorption capabilities of HFO at depth (Pichler et al., 1999b).

The elevated As abundance in Tutum Bay surface seawater can be explained by the buoyancy-driven rise of hydrothermal fluids due to differences in temperature and salinity (Pichler et al., 1999a). If the As in surface

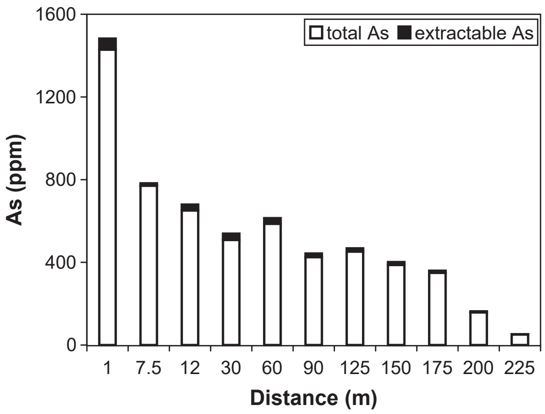

Fig. 5. The variation of As concentration in the easily-extractable sediment fraction and total concentration of As in surface sediments along the transect shown in Fig. 2b.

Table 5
Four-step sequential extraction results in ppm for vent precipitates (VP), surface sediments along the transect shown in Fig. 2, compared to the Picnic Island (PI) control site

Distance (m)	Easily extractable		Carbonate		HFO		Residual	
	As	Fe	As	Fe	As	Fe	As	Fe
VP	444	0.1	9.3	134	31,783	281,479	3.5	719
1	54	67[a]	4.7	13	461	36,024	3.7	7769
7.5	12	n.d.[b]	0.7	10	340	35,916	0.6	7406
12	29	n.d.	2.7	14	446	31,048	2.3	3951
30	30	n.d.	2.3	14	433	35,981	n.d.	3892
60	27	n.d.	1.3	9.5	375	32,574	n.d.	5116
90	18	n.d.	0.9	6.5	257	28,340	n.d.	5046
125	16	n.d.	0.7	8.7	282	21,895	0.4	1864
150	14	n.d.	n.d.	n.d.	270	23,090	0.6	1572
175	10	n.d.	0.02	62	195	23,570	0.1	1841
200	5.5	n.d.	n.d.	49	104	21,144	0.2	1555
225	1.5	n.d.	n.d.	19	17	21,715	n.d.	2761
PI	0.7	n.d.	n.d.	87	n.d.	1928	n.d.	65

[a] This value suggests the HFO fraction may have contributed some As to the easily extractable fraction. However, repeat experiments showed approximately the same amount of As being extracted from this sample (±3 ppm).

[b] n.d.=not detected.

waters of Tutum Bay is hydrothermally derived, the As speciation should be characterized by elevated As(III), in particular at the surface. About 30% of the As occurs as As(III), which is approximately one order of magnitude higher than the concentration of As(III) typically found in average seawater (Table 5; Plant et al., 2003). However, As in surface waters still have higher As(V) concentrations than expected if the As is hydrothermal (100% As(III)). As(III) will be moderately unstable in the presence of oxygen, which is enriched more in surface waters. Photo- or biological oxidation of As(III) to As(V) can also occur within a few hours in coastal surface waters (Cutter, 1992; McCleskey et al., 2004; Sanders et al., 1994). This might explain the elevated As(V) concentration in the surface waters of Tutum Bay.

The pore-waters of Tutum Bay are enriched in As with depth, suggesting that diffuse discharge of hydrothermal fluid occurs throughout Tutum Bay. In addition, abundant HFO coatings occur in the core, and are associated with elevated As concentrations (e.g., 4000 ppm As in the core at 60 m; Table 4). The enrichment is likely due to diffuse hydrothermal discharge, precipitation of HFO upon mixing with seawater, and adsorption of As. As a comparison, higher concentrations of As frequently occur in pore-waters extracted from unconsolidated sediments than in overlying surface waters (see Plant et al., 2003). However, the relative concentration increase between pore-water and the overlying water column are much more enhanced in hydrothermal areas (e.g., 6.4 mg/L in Lake Ohakuri, New Zealand; Aggett and Kriegman, 1988). However, if the higher As concentrations in pore-waters of Tutum Bay are from hydrothermal fluids, we would expect predominantly As(III). To the contrary however, pore-waters are dominated by As(V). An important aspect to consider is the role that microbes and bacteria may play in oxidizing As(III) to As(V) in the sediments, in particular in those areas with hydrothermal diffuse discharge where mixing of reduced fluids and seawater may create redox gradients. Microbes that obtain energy through oxidation or reduction of As have been described in several hydrothermal systems (Oremland and Stolz, 2003; Plant et al., 2003).

Compared to coastal regions unaffected by hydrothermal input, which show As concentrations in the range from 3 to 15 ppm (Sanders et al., 1994), the As concentrations of sediments at Tutum Bay are two orders of magnitude higher (mean=527 ppm). Similar enrichments have also been reported in the sediments from Santorini hydrothermal field, with a maximum concentration of As=927 ppm and a mean of ~460 ppm (Varnavas and Cronan, 1988). Varnavas and Cronan (1988) also suggest that hydrothermal As is scavenged into the sediments by freshly precipitating HFO. Johnson and Cronan (2001) show a maximum concentration of 997 ppm As in shallow submarine hydrothermally influenced sediments at Champagne Hot Springs of Dominica (Lesser Antilles), but provide no transect data to examine the extent of hydrothermal influence. McCarthy et al. (2005—this issue) has also shown decreasing As with increasing distance away from focused hydrothermal venting at Champagne Hot Springs.

4.2. Mechanism for arsenic enrichment in sediments

We suggest the main control on the distribution of As in Tutum Bay sediments is the upward diffusion of hydrothermal fluid, precipitation of HFO upon contact with oxidizing seawater, and adsorption of As onto HFO. Mixing of the hydrothermal fluids and seawater causes rapid oxidation of Fe(II) and therefore the precipitation of HFO, and possibly the subsequent complete removal of As from the hydrothermal fluids. The scavenging of As by HFO has been well documented (De Vitre et al., 1991; Feely et al., 1994; Sracek et al., 2004). In oxidizing environments, the primary mechanism for attenuation of As is its adsorption onto HFO (Sracek et al., 2004).

Our sequential extractions have shown that >98% of the As is associated with coprecipitated HFO in vent precipitates, and a mean of 93.5% for surface sediments (range = 88.2 to 96.3; Table 4). Long-term stability of this adsorbed As can be effected by abiotic reactions (oxidation, reduction, precipitation, and dissolution) and biotic reactions (microbial transformations), as well as the physical disturbance of sediments (Mok and Wai, 1994; Sanders et al., 1994). If redox conditions remain oxidizing, the HFO will remain stable. Upon burial, however, oxidizing sediments could potentially be subjected to reducing conditions. Previous work has shown that the reduction of HFO upon burial can cause the release of any adsorbed or coprecipitated As (Plant et al., 2003). Recent work also confirms the association of As with HFO in oxic sediments, its release to the interstitial water when Fe(III) is reduced to Fe(II) upon burial of the sediments, and its upward diffusion to the sediment–water interface (Sanders et al., 1994). There it is reprecipitated, under oxic conditions, with newly formed HFO, or is released to the water column under prevalent reducing conditions.

Dissolved As can also be co-precipitated with pyrite (Sanders et al., 1994), and we have observed framboidal pyrite in some sediments of Tutum Bay. In reduced environments, sulfides control the distribution of As (Plant et al., 2003). Physical disturbance of the sediments by storm, typhoon, or flooding may move the underlying sediments to an oxidizing environment where the sulfides undergo oxidation, thus releasing the As.

4.3. Bioavailability of arsenic in Tutum Bay

The concentration of bioavailable As from surface sediments in Tutum Bay excluding vent precipitates ranges from 5.5 to 54 ppm, with a mean of 19.7 ppm (Table 5). We can see that because As, but no Fe, was leached during the easily-extractable step of the sequential extraction, that this portion of As is surface-bound, whereas the rest is likely co-precipitated with the HFO. Solid-phase toxicity to marine organisms is low when compared to the potential toxicity of the free-metal in the aqueous phase (Benson, 1994; Newman and Jagoe, 1994). Therefore, the elevated concentrations of As and the abundance of the more toxic As(III) in surface waters of Tutum Bay may have the most impact on biota.

Arsenic is an example of an element that effects mainly the base of the food chain (Sanders et al., 1994). Exposure of an ecosystem to above normal levels of As may induce stress and results in a reduction in diversity and the increased abundance of a limited group of opportunistic taxa (Engle, 2000; Pearson and Rosenberg, 1978). However, from the viewpoint of toxicity, the most sensitive link in the chain is phytoplankton, with reduction in growth exhibited at concentrations of arsenate as low as 3 μg/L (Sanders et al., 1994). This is very significant given the fact that the surface waters of Tutum Bay have approximately 8 μg/L As, and one order of magnitude more As(III) when compared to average seawater. While invertebrates appear to be more resistant to dissolved As (death at >100 μg/L; Gebel et al., 1997), they may be effected by changes in phytoplankton community structure that are changed due to high As concentrations. Future work should therefore include measurements of the plankton community structure, abundance, and diversity as compared to a control area.

However, it appears as though the majority of As discharged by the hydrothermal system is rapidly locked up into the solid phase due to mixing of hydrothermal waters with seawater throughout Tutum Bay, and therefore biota is essentially buffered from the potential deleterious effects.

5. Summary and conclusions

The discharge of potentially toxic elements such as As by shallow-water hydrothermal systems has to date received little attention, despite the large number of vents reported from around the world. By studying the abundance, distribution, and bioavailability of As in Tutum Bay, Ambitle Island, PNG, we assessed the potential impact of a hydrothermal system discharging large amounts of a single toxin to biota for the first time. We have found that: 1) As concentrations in surface sediments along a transect ranges from 1483 to 52 ppm (mean = 527 ppm), and decrease exponentially away from focused venting, with the highest enrichments in HFO vent precipitates (32,000 ppm). 2) The bioavailable portion of As in Tutum Bay surface sediments is an average of 3.6% of the total, which equals a mean bioavailable concentration of 19.7 ppm. 3) The As abundance in surface waters of Tutum Bay is elevated by four times above average seawater as far as 170 m away from focused venting, with a maximum of 8.4 μg/L. The hydrothermal fluids are high temperature (98 °C) and low salinity (3.5), which causes the fluids to quickly rise to the surface of Tutum Bay due to buoyancy effects. The As concentrations in bottom waters are similar to average seawater concentrations of 2 μg/l (Andreae, 1977; Cullen and Reimer, 1989; Plant et al., 2003). Arsenic species in surface waters are about 70% As(V), and 30% As(III). The methylated species DMA and MMA were not detected. Bottom waters are even more enriched in As(III), with only approximately 40% As(V). The enrichment of As(III) in bottom waters is likely caused by diffuse venting of hydrothermal fluids, while As speciation in surface waters could be controlled by photo- or bio-oxidation. 4) The As concentration increases with depth in sediment pore-waters, and is characterized by As(V) as the major As species, possibly due to microbial activity. Arsenic in core sediments is enriched in HFO layers which precipitate upon mixing of reducing hydrothermal fluids with oxic seawater (max = 4025 ppm). The water seeping through the sediments is enriched in As, Fe, and Si, and the As is being locked up in hydrous ferric oxides before the fluid reaches the sediment–seawater interface.

These findings emphasize the importance of measuring the distribution, bioavailability, and element cycling throughout an entire hydrothermal system, and not just from vent fluids and precipitates. The most important control on this distribution, at least with respect to As, is the discharge and precipitation of HFO upon mixing of hydrothermal fluids with seawater. Arsenic is bioavailable by two major pathways throughout Tutum Bay: 1) easily-exchangeable As from hydrothermally influenced sediments to as far away as 200 m from focused venting, and 2) in surface seawaters, which may allow for biological uptake by phytoplankton and transfer up the food web.

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