



Suitability of the shallow water hydrothermal system at Ambitle Island (Papua New Guinea) to study the effect of high $p\text{CO}_2$ on coral reefs



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ABSTRACT

Volcanic CO₂ seeps were successfully used to predict coral reef response to ocean acidification, although toxic elements, often characteristic of hydrothermal vents were rarely reported. We measured the physicochemical conditions, seawater carbonate chemistry and trace elements in Tutum Bay, Papua New Guinea. There, intense emission of hydrothermal fluids and CO₂ expose the coral reef to a seawater pH_T between 7.6 and 7.7.

Arsenic and silica were enriched by up to six times in surface seawater, while bottom concentrations were lower and thus similar to coral reefs worldwide. Manganese, cesium, iron and zinc concentrations fell into the range of other coastal environments. Our measurements suggest that Tutum Bay is a suitable site to study the response of coral reefs to high $p\text{CO}_2$. Considering that arsenic is a common metal in hydrothermal fluids, its characterization should be included in any study that uses volcanic CO₂ seeps as natural laboratories for ocean acidification.

1. Introduction

Oceanic uptake of anthropogenic carbon dioxide (CO₂) and the associated alteration of ocean carbonate chemistry (i.e., ocean acidification, OA) might affect various physiological parameters at different life stages of marine organisms, from reproduction through larval phases and to their adult stages involving molecular, physiological, developmental and behavioral processes (Doney et al., 2009). Ocean acidification is also expected to cause changes in biodiversity and ecosystem functioning at global scales within this century (Yang et al., 2016). Calcifying species, such as coral reefs, which harbor a large part of the world's ocean biodiversity (Reaka-Kudla, 1997), will likely be most affected by OA since calcification and dissolution rates seem to be linked to seawater carbonate chemistry (Allemand et al., 2011). In general, many laboratory experiments and field observations showed a decline in coral net calcification (e.g., De'ath et al., 2009; Erez et al., 2011) and an increase in the dissolution rates of carbonate skeletons (Enochs et al., 2015; Wisshak et al., 2012) and reef sediments (Eyre et al., 2018) associated with lower aragonite saturation states.

Currently, our ability to predict the impact of OA on coral reefs remains limited and predictions are still uncertain. This is because the quasi totality of studies that have been conducted were unable to recreate in their experiments the variability (physical, chemical,

biological) of real-world coral reefs; the number of biotic and abiotic factors which can affect the coral metabolism in the wild (e.g., light irradiance, natural food, natural changes in the main environmental parameters, etc.); and the complex, sometimes poorly understood, interactions among species and habitats. In 2008, Hall-Spencer and co-authors used submarine shallow volcanic CO₂ vents at Ischia in the Gulf of Naples, Italy as a natural analogue for future, more acidic conditions. There natural CO₂ vents with continuous emissions of near-pure CO₂ from below the seafloor alter the ambient seawater chemistry, thus providing an environment to study long-term responses to future acidification levels (Barshis, 2015; Stillman and Paganini, 2015). Although several natural limitations exist to use CO₂ vents as analogues for future conditions of ocean acidification (OA) they seem to provide important new information about its effects (e.g., Fabricius et al., 2014; Hall-Spencer et al., 2008; Vizzini et al., 2013). This is because the acidified seawater conditions found at such sites occur on sufficiently large spatial and temporal scales to integrate ecosystem processes, such as allowing resident species to acclimatize or adapt (e.g., Calosi et al., 2013; Rodolfo-Metalpa et al., 2011).

Following the pioneering studies at Ischia, other CO₂ vents were used to assess organism response to OA. Other vent sites include Vulcano, Panarea and Columbretes in the Mediterranean Sea (Boatta et al., 2013; Caramanna et al., 2012; Linares et al., 2015), one in New

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Zealand (Brinkman and Smith, 2015), two in Japan (Agostini et al., 2015, 2018; Inoue et al., 2013), two in Papua New Guinea (PNG) at the d'Entrecasteaux Island (Fabricius et al., 2011), Taiwan (Chen et al., 2015), Indonesia (Januar et al., 2016), Azores (reviewed by Couto et al., 2015), Mexico (Pettit et al., 2013; Prol-Ledesma et al., 2013), and at the Commonwealth of the Northern Mariana Islands (Enochs et al., 2015). With the exception of the two identified vent sites in PNG, which allowed to partially replicate field observations (Fabricius et al., 2011), in general each vent site is unique and limited in space. Vent sites differ in their geographical occurrence (temperate, tropical and sub-tropical), depth, habitat, geomorphology, species distribution, making it difficult to compare conclusions between studies.

In order to better identify commonality in OA response and to isolate factors that are responsible for any specific ecosystem effect future research needs to replicate such observations in a larger number of natural laboratories, such as new CO₂ vents, semi-closed lagoons (Barkley et al., 2015) or extreme environments (Camp et al., 2018, 2017). With this in mind, we examined a CO₂ vent site surrounding an apparent rich and diverse coral reef in Tutum Bay, Ambitle Island, New Ireland Province in PNG, first described by Pichler and Dix (1996). For this site already exists a complete chemical description of the hydrothermal fluids, sediments pore waters including trace elements contents as well as a general census of some key-habitat species, including archaea and bacteria (e.g., Akerman et al., 2011; Karlen et al., 2010; Meyer-Dombard et al., 2012; Pichler et al., 2006).

Previous studies of Tutum Bay found that the concentrations of Si, Mn, Cs, Fe, Zn, and particularly As were much higher in the hydrothermal fluid and that they were slightly elevated in Tutum Bay seawater when compared to “normal” seawater (Pichler et al., 1999a; Price and Pichler, 2005; Price et al., 2013). The problem of metal pollution, however is not specific to coral reefs around CO₂ vents as many reefs worldwide (e.g. Costa Rica, Panama, Red Sea, Thailand, New Caledonia) can have high metal levels (Ali et al., 2011; Biscéré et al., 2017, 2015; Fujita et al., 2014; Guzmán and Jiménez, 1992; Moreton et al., 2009; Tanaka et al., 2013; Whittall et al., 2014). While many experimental studies have emphasized the harmful effect of high concentrations of metals on coral reproduction and early life stages (Gissi et al., 2017; Reichelt-Brushett and Harrison, 2005, 2004, 2000; Reichelt-Brushett and Hudspeth, 2016), it has also been shown that some of them can play key roles in the functioning of corals (Biscéré et al., 2018, 2017; Ferrier-Pagès et al., 2001). Zinc for example is essential for the health and growth of corals as it is a cofactor of > 300 enzymes involved in several metabolic pathways (Houlbrèque et al., 2012).

Here we evaluated the environmental and physicochemical conditions in Tutum Bay based on data collected during two research periods in September 2016 and May 2017. The aim of this research was: i) to assess the seawater carbonate chemistry of Tutum Bay and to define a coral reef area which is chronically affected by OA-like conditions and therefore suitable to be established as a living and natural laboratory for OA studies; and ii) to assess the concentrations of trace elements in seawater in the study area. In addition, the potential biological effect of contaminants on coral reefs is also discussed in reference to the literature on the effects of metals on sessile marine organisms.

2. Materials and methods

2.1. Study site

Submarine hydrothermal venting activity is located in Tutum Bay, Ambitle Island (04° 03' S, 153° 34' E; NW) of New Ireland Province, PNG (Fig. 1). Tutum Bay is characterized by a well-developed and diverse fringing coral reef surrounded by medium- to coarse-grained mixed carbonate-volcaniclastic sand and gravel (Pichler et al., 1999a; Pichler and Dix, 1996). There are at least four main hot vents at around 8 m depth, and hundreds of both dispersed and diffuse seeps. Hot vents discharge a clear, two-phase fluid from discrete ports, 10 to 15 cm in

diameter, while seeps discharged streams of gas bubbles emerging directly through the sandy to pebbly unconsolidated sediment. Gas composition ranged from 93 to 98 % CO₂, with minor amounts of nitrogen (N₂, 2 to 5 %), methane (CH₄, < 2 %), oxygen, < 1 %), a trace of helium and, most importantly, no traces of sulfur compounds, such as H₂S (Pichler et al., 1999a).

In September 2016 and May 2017, we worked in Tutum Bay on board the research vessel *Alis*, for eight and seven days respectively. A reference site, which had a similar topography but with seawater pH at its normal value (i.e., 8.0 pH_T unit) was found one kilometer to the south of Tutum Bay.

2.2. Acquisition of field data and sample collection

During the first research period in September 2017, a 50 m long benthic transect was fixed in shallow water at around 4 m depth (Fig. 1). Here, three SeaFET (stations 1, 2, and 3) measuring pH_T (total scale) and one YSI 600 OMS-M probe (YSI Inc., USA), measuring depth, salinity, oxygen and temperature in combination to the SeaFET (Sea-Bird Electronics, Inc., USA) at station 1 (St 1) were deployed measuring at 10 min intervals for 6 days. Seawater samples were collected twice a day along the benthic transect. In the same way seawater samples were also collected from nine fixed stations around the benthic transect (stations A-I, Fig. 1). Seawater samples were also collected two times a day at the reference site where another YSI 600 OMS-M probe was secured at 5 m depth for 36 h. pH values were immediately measured onboard, while water samples were preserved for the measurement of total alkalinity (see below).

To assess the hydrothermally derived physicochemical gradients at the study site, a 3-D sampling grid (Fig. 1) was constructed using metered rope in combination with a Bad Elf® WAAS GPS. Six transects (T0 to T5) with a 10 m spacing were established and samples were collected at different tide levels during three subsequent days (Fig. 1). Three, four and two transects were sampled respectively on the 17th, 18th and 19th September 2016. During the three days of sampling, surface and bottom seawater (36, 48 and 24 samples, respectively) were collected simultaneously by a team of two divers into 20 mL syringes at 0.2 m below sea surface and at 0.5 m above seafloor. In particular, transect 2 (T2 in Fig. 1) was always sampled during the three consecutive days to assess any potential temporal variability. The water level (tide) was monitored at one-minute intervals during the three sampling days using a combination of two Onset HOBO pressure loggers, one measuring water pressure and the other measuring barometric pressure. This combination allowed for compensation of changes in atmospheric pressure and measurements were used to corroborate depth variations measured by the YSI 600 OMS-M probes. In addition to seawater samples taken inside the study area, normal seawater was also sampled at the reference site and from the four main hydrothermal vents. Those samples (i.e., reference and vents) were considered the respective end members for the physicochemical composition of Tutum Bay seawater.

In order to collect the fluid discharged from the main hydrothermal vents without any contamination by ambient seawater, samples were collected by inserting a Teflon tube as far as possible into the vent orifice or covering the vent orifice with a Teflon funnel. Samples were collected into 60 mL syringes once the temperature of the discharge through either the tube or funnel was identical to the maximum temperature of each vent. On return to the Research Vessel, the pH and electrical conductivity were measured immediately using a Myron Ultrameter 6P (Myron L® Co., USA). The samples were then filtered to < 0.2 μm and a 10 mL aliquot was acidified with ultrapure HNO₃ and stored in high density polyethylene bottles for later laboratory analyses.

During the second research period in May 2017, one SeaFET and one YSI probe were secured close to the benthic transect (station 4) used in September 2016, while another set of instruments were deployed at the reference site and left there during four consecutive days. Unfortunately, due to technical issues, the SeaFET recorded only for

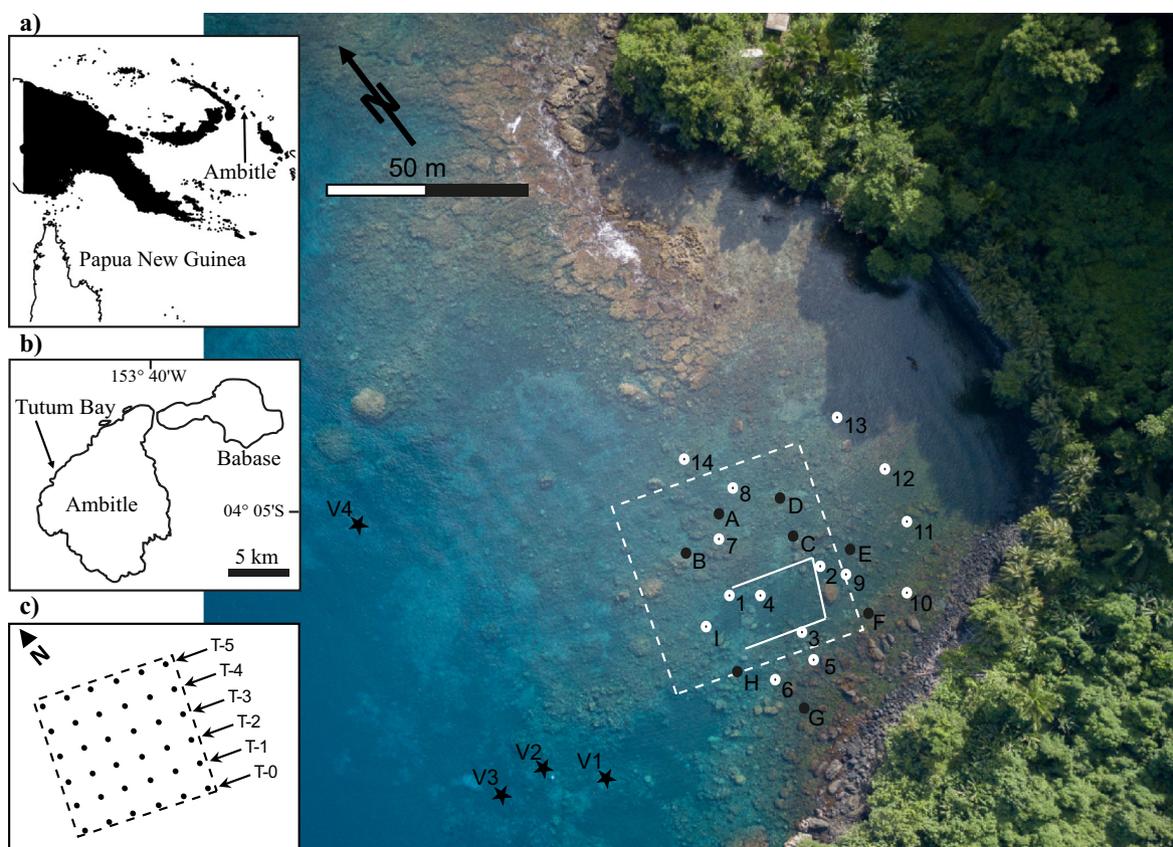


Fig. 1. Aerial picture of Tutum Bay showing the benthic transect (white line), the area investigated for trace elements in seawater (dashed square, also in panel C), and the position of the stations where the pH was measured. Black dots are stations where the pH was measured two times per day during September 2016 (St. A-I); white dots are stations where the pH was measured using SeaFETs during September 2016 and May 2017. Stars indicate the position of the four main vents. The reference site was about one kilometer south of Tutum Bay.

24 h. Two other instruments were subsequently moved each 24 h period (from ca. 10 am) among sites within the bay to collect ten 24-hour cycles of pH and temperature (stations 5 to 14). The GPS position of each site was recorded using a portable Garmin GPSMAP 60CSx and recorded aerially by drone imaging (a buoy was positioned at the sea surface) (Fig. 1).

2.3. Carbonate chemistry measurements

After collection seawater samples were brought on board the research vessel and temperature as well as pH were measured immediately. pH was measured in total scale (pH_T) for stations A to I by the SeaFET instruments; in contrast pH was measured using National Bureau of Standards (NBS) along the grid of collection for the hydrothermally derived physicochemical gradients. pH in total scale (pH_T) was measured using a pH-meter and electrode (Methrom 913 pH meter) calibrated using TRIS buffers (A.G. Dickson, batch #T28, Scripps Institute of Oceanography). Discrete water samples were also taken at the start and end of each SeaFET deployment to corroborate or correct the pH_T measurements. pH in NBS scale (pH_{NBS}) was measured using a Hanna Instruments Halo Bluetooth probe in conjunction with the Hanna Lab app on an Apple iPad. The pH probe was calibrated at the beginning and checked at the end of each series of measurements. In between each sample, fresh seawater collected at the reference site was measured as a reference check for electrode drift.

Seawater samples were filtered through 0.45 μm Whatman filters using a Nalgene vacuum system and stored at 4 °C in the dark for further testing at the Institut de Recherche pour le Développement (IRD) in New Caledonia. Total alkalinity (A_T) was determined using an auto titrator (TIM865 TitrLab, Radiometer). Three replicate 20 mL sub-

samples were analyzed at 25 °C. The pH was measured at 0.02 mL increments of 0.01 N HCl. Total alkalinity was calculated from the Gran function applied to pH from 4.2 to 3.0, as meq L^{-1} from the slope of the pH vs HCl curve. Results were corrected against A_T standards provided by A.G. Dickson (batch #155). Parameters of the carbonate system [pCO_2 , CO_3^{2-} , HCO_3^- and saturation state of calcite (Ω_{calc}) and aragonite (Ω_{arag})] were calculated from pH_T (min, mean and max values per station); mean A_T , temperature and salinity (34 ‰) were tested using the free-access CO2SYS package.

2.4. Trace element measurements and concentration maps

The seawater reference, study area samples and vent samples were analyzed for silica (Si) and arsenic (As) content in the Geochemistry and Hydrogeology laboratory at the University of Bremen. Silica was analyzed by ICP-OES using a Perkin Elmer Optima 7300 instrument. The samples were diluted 10-fold to decrease salt loading of the instrument. To improve the detection of Si, its ionization was facilitated by adding 5 % methanol to each sample (e.g., Hu and Liu, 2004; Wu and Pichler, 2014). Instrument drift and memory effects were monitored by adding a blank and drift monitor solution after each 10 samples. The NIST Trace 1643e and IAPSO K15 solutions were used as external certified references. Based on repeat measurements and comparison to 1643e the analytical uncertainty was determined to be better than 2 % for the Si analyses. Arsenic was analyzed by hydride generation – atomic fluorescence spectrometry (HG-AFS) using a PS Analytical Millennium Excalibur instrument following a well-established method (Price et al., 2007). The accuracy and precision of the measurements were verified by adding a blank and drift monitor solution after each 10 samples and using the NIST Trace 1643e and IAPSO K15 solutions as external

certified references. Analytical uncertainty was determined to be better than 5 %.

Contour maps for pH_{NBS} , As and hydrothermal component, i.e., the percentage of hydrothermal fluid (HF) present in Tutum Bay seawater were created with the computer code Surfer using data collected from transects T0, T2, T3 and T5 on September 18th 2016. Kriging was used for interpolation between sampling points to cover a total area of 70×70 m (e.g., Bárdossy and Bárdossy, 1984). The element silica (Si) was chosen as an indicator of hydrothermal fluid because its concentration difference between the reference seawater and hydrothermal fluid was the largest of all elements previously measured in Tutum Bay (Pichler et al., 1999a). Considering the short distances of < 100 m and thus short residence times in the actual area of interest, conservative behavior was assumed for Si (see also the discussion). Based on the Si concentrations the hydrothermal component in Tutum Bay seawater was calculated using a simple mass balance equation:

$$C_{\text{TBW}} = x C_{\text{SW}} + y C_{\text{HF}} \quad (1)$$

where x and y are the respective fractions of ambient seawater and hydrothermal fluid, C_{TBW} is the Si concentration in Tutum Bay seawater; C_{SW} , the Si concentration in reference seawater and C_{HF} , the silica concentration in the hydrothermal fluid.

In the same way, the abundances of for Li, Be, Rb, Sr, Mo, Sb, Cs, Ba, Tl, Al, V, Mn, Fe, Co, Ni, Cu, Zn, Pb and U were also calculated based on their previously reported concentrations (Pichler et al., 1999a) and using the mass balance Eq. (1). All data were presented as mean \pm standard deviation if not specified.

3. Results

3.1. Tutum Bay seawater carbonate chemistry

Data recorded from the three SeaFETs along the benthic transect in September 2016 (six days, stations 1, 2 and 3) and in May 2017 (six days, station 4) showed that pH_{T} values were always below the ones measured at the reference station (Table 1; pH_{T} 8.01 ± 0.03 , suggesting that the area was permanently exposed to acidic conditions (Fig. 2, Supplementary Table S1a, Supplementary Figs. S1, S2). Mean pH_{T} and Ω_{arag} values were respectively 7.64 ± 0.1 and 1.83 ± 0.36 (Sts 1–4 pooled). The highest and lowest pH data measured were 7.35 pH_{T} (St 4) and 7.93 pH_{T} (St 3), corresponding at a range in Ω_{arag} of 0.95 and 3.14, respectively. All around the benthic transect, at stations A to

I, which had been measured twice per day during six consecutive days in September 2016, the mean pH_{T} varied between 7.57 ± 0.09 (St F) and 7.79 ± 0.04 pH_{T} (St A) (Supplementary Table S1b).

Data from the SeaFETs recorded in May 2017 from different stations in Tutum Bay (St 15 to 14; Supplementary Fig. S3, Supplementary Table S1c) showed that the average pH_{T} of seawater in Tutum Bay ranged from 7.51 ± 0.14 (St 5) to 7.83 ± 0.09 (St 14), corresponding to 0.5 to 0.2 pH units lower than at the reference station (8.01 ± 0.03). The average Ω_{arag} range for Tutum Bay was 2.14 ± 0.66 (Table 1).

Tidal range in Tutum Bay varied by a maximum of 1 m (Fig. 2), which corresponded to a water pressure of ca. 10 KPa (0.1 bar). This change in water pressure was concomitant to a change in pH, i.e., higher pH values were recorded consistently at high tide.

Salinity (34 ‰), temperature (30 to 31 °C), A_{T} (2158.5 and 2182.6 $\mu\text{mol kg}^{-1}$, for Sts Ref and the Tutum Bay stations, respectively) and dissolved oxygen (5 to 6 mg L^{-1}) did not significantly differ between Tutum Bay and the reference site (data not shown).

3.2. Chemical composition of Tutum Bay seawater

Average seawater ($n = 2$) from the reference site had a pH_{NBS} of 8.08 pH units and Si and As concentrations were 0.04 mg L^{-1} and $1.42 \mu\text{g L}^{-1}$, respectively (Supplementary Table S2). The average vent water ($n = 4$) had a pH_{NBS} of 6.17 and Si and As concentrations were $97.6 \pm 1.1 \text{ mg L}^{-1}$ and $928 \pm 7.7 \mu\text{g L}^{-1}$, respectively. Thus, relative to reference seawater, Si was enriched in the hydrothermal fluids by a factor of about 2400 and As by about 650. Electrical conductivity, which is an approximate measure of total dissolved solids (TDS) was one order of magnitude higher in the reference seawater than in the hydrothermal fluids. Relative to the reference seawater, only Mn ($3.2 \mu\text{g L}^{-1}$), Cs ($1.8 \mu\text{g L}^{-1}$), Fe ($1.8 \mu\text{g L}^{-1}$) and Zn ($1.8 \mu\text{g L}^{-1}$) were somewhat enriched (Table 2), while the remaining trace elements were similar to ambient seawater.

3.3. Effects of the hydrothermal fluids on the seawater pH, Si and as concentrations in Tutum Bay

The Si and As concentrations, as well as pH systematically and significantly differed between surface and bottom water samples. At any point at the study site area, surface water had always significantly (ANOVA, $p < 0.001$) lower pH and higher Si and As concentrations than bottom water (Fig. 3; Supplementary Fig. 4; Supplementary Table

Table 1
Seawater carbonate chemistry at the reference site (St Ref), and at the stations monitored in Tutum Bay.

Station		T (°C)	pH_{T}	pCO_2 μatm	CO_2 $\mu\text{mol kg}^{-1}$	HCO_3^- $\mu\text{mol kg}^{-1}$	CO_3^{2-} $\mu\text{mol kg}^{-1}$	C_{T} $\mu\text{mol kg}^{-1}$	Ω_{calc}	Ω_{arag}
St Ref (158)	Mean	30.37	8.009	412	10	1629	214	1854	5.25	3.52
	SD	0.12	0.035	43	1	33	13	21	0.32	0.22
	Min	29.84	7.917	347	9	1575	181	1820	4.44	2.97
	Max	30.93	8.066	532	13	1712	235	1906	5.78	3.87
St 1–4 (3174)	Mean	30.53	7.637	1140	29	1912	111	2052	2.74	1.83
	SD	0.12	0.100	306	8	55	22	40	0.54	0.36
	Min	30.19	7.346	515	13	1716	58	1920	1.42	0.95
	Max	30.91	7.933	2369	59	2044	191	2162	4.69	3.14
St A–I (108)	Mean	30.52	7.713	973	24	1873	128	2024	3.13	2.10
	SD	0.12	0.110	305	8	64	26	46	0.64	0.43
	Min	30.34	7.463	553	14	1740	75	1935	1.85	1.24
	Max	31.00	7.908	1774	44	2002	181	2121	4.44	2.97
St 5–14 (1589)	Mean	30.60	7.679	1025	25	1867	130	2022	3.19	2.14
	SD	0.23	0.161	478	12	99	40	69	0.98	0.66
	Min	30.08	7.155	336	8	1572	39	1829	0.97	0.65
	Max	31.48	8.081	3770	93	2090	249	2222	6.11	4.10

Note: Carbonate chemistry parameters were calculated with CO_2sys using the temperature and pH_{T} data collected either by the SeaFETs at 10-min logging interval (stations 1–4 and 5–14), or two times a day by SCUBA diving (stations 4–12), or both (station Ref). Other setting were: mean total alkalinity ($A_{\text{T}} = 2158.5$ and $2182.6 \mu\text{mol kg}^{-1}$, for St. Ref and Tutum Bay stations, respectively; $n = 28$ and 95 , respectively), and salinity (34). Mean pH were calculated after conversion of data to hydrogen ion concentrations. Number of samples n is in brackets.

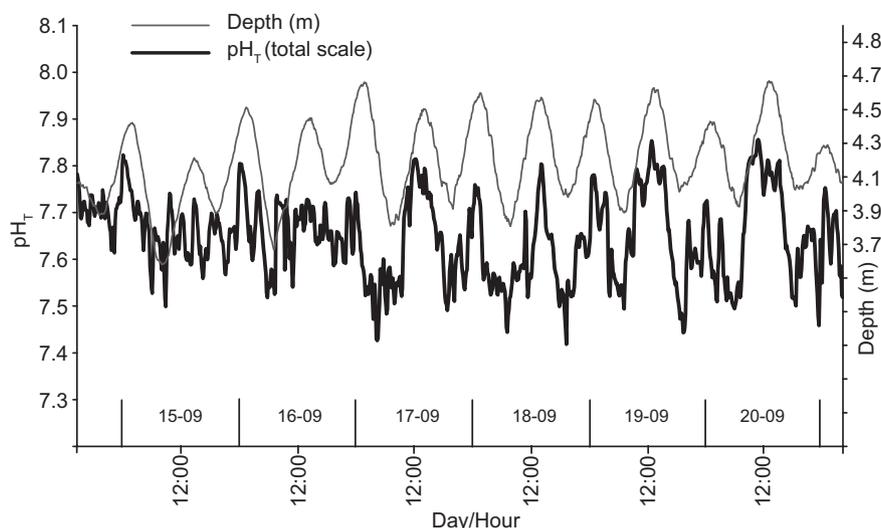


Fig. 2. Sea level and pH_T (total scale) variations recorded in Tutum Bay at station 1 from the 14th to the 21st September 2016. YSI 600 OMS-M probe was coupled to SeaFET recording at 10-min logging interval depth (m). The tick mark on the X-axis inside the chart denoted midnight.

Table 2

Trace elements measured (Si and As; see Supplementary Table S3) and calculated at the reference station, from the vents and at the study site in Tutum Bay.

Element ($\mu\text{g L}^{-1}$)	Reference seawater	Vent water	Study site seawater			
			Mean	St. Dev.	Min	Max
Si (mg L^{-1})	0.04	97.6	0.8	0.3	0.3	2.2
As	1.4	928	7.5	2.5	2.8	15.1
Li	137	980	143	3.0	137	155
Be	0.3	1.3	0.3	0.0	0.3	0.3
Rb	104	350	106	0.9	104	109
Sr	7991	7088	7984	3.2	7971	7991
Mo	10.4	4.7	10.3	0.0	10.2	10.3
Sb	0.5	8.1	0.6	0.0	0.5	0.7
Cs	0.6	57.9	1.0	0.2	0.6	1.8
Ba	10.0	54.9	10.4	0.2	10.0	11.0
Tl	0.3	4.5	0.3	0.0	0.3	0.3
Al	17.0	31.2	17.1	0.1	17.0	17.3
V	1.7	0.3	1.6	0.0	1.6	1.6
Mn	1.6	440	5.1	1.6	1.6	11.2
Fe	15.0	1458	26.6	5.1	15.0	46.6
Co	0.03	0.33	0.03	0.0	0.03	0.04
Ni	1.8	0.9	1.8	0.0	1.8	1.8
Cu	0.2	1.8	0.2	0.0	0.2	0.3
Zn	0.3	31.1	0.5	0.1	0.3	1.0
Pb	0.1	0.4	0.1	0.0	0.1	0.1
U	2.9	0.2	2.9	0.0	2.9	2.9

Note: To calculate the mean, standard deviation, minimum and maximum values, all data from the transect T0-T5, both bottom and surface seawater, were pooled.

S2). The average concentration of As in surface water was $8.99 \pm 2.30 \mu\text{g L}^{-1}$ and in bottom water $5.94 \pm 1.67 \mu\text{g L}^{-1}$, a difference of approximately 34 %. The average concentration of Si in surface water was $1.06 \pm 0.33 \text{mg L}^{-1}$ and in bottom water $0.64 \pm 0.21 \text{mg L}^{-1}$, a difference of approximately 39 %. The average pH_{NBS} in surface water was 7.58 ± 0.17 and in bottom water 7.71 ± 0.11 , a difference of approximately 24 %. With 50.6mS cm^{-1} compared to 50.8mS cm^{-1} , surface seawater had a slightly lower electrical conductivity than bottom water. The amount of hydrothermal fluid present in seawater of the study area ranged between 0.3 % and 1.5 % and showed the same layering as pH and As.

Transect 2 (T2 in Fig. 1c) was sampled on three consecutive days to assess temporal variability (Supplementary Table S3). The values for pH, Si and As, both for bottom and surface samples, varied by up to 30

% between the sample dates. This variation was systematic in the sense that the ratio between Si and As remained approximately constant, and that both Si and As concentrations at the study site were negatively correlated to pH (Fig. 4). Therefore, their concentrations were directly related to the observed variation in pH as a result of tide level (see above).

4. Discussion

Extreme environments such as CO_2 vents have become popular since the first study offshore Ischia, Italy by Hall-Spencer et al. (2008) revealed the opportunities offered by these natural sites in assessing the ecosystem scale effects of ocean acidification. Even though CO_2 vents are not perfect analogues of future conditions, they should be one of the best natural settings to investigate individual physiological responses and ecosystem functioning changes to extreme conditions. The main limitations in using these systems as proxies to assess the future of coral reefs are: i) the large variation in pH, often approaching undersaturated conditions or even ambient unaffected pCO_2 values; ii) the limited area of the reef actually affected by the vent emissions (i.e., tens to hundreds of meter squares); and iii) the water quality of the area, as shallow-water hydrothermal vents can frequently introduce large amounts of potentially toxic elements and gases (e.g., Dando et al., 1999; Pichler et al., 1999c).

With regards to Tutum Bay, our measurements and observations showed that Tutum Bay is an opportune candidate to study the effects of ocean acidification on reef organisms, although the fluids emitted by the vents marginally enrich the sea water in Tutum Bay with arsenic and other trace elements.

4.1. Temporal and spatial variability of pH in Tutum Bay

Hydrothermal activity is a dynamic process that can undergo changes in physicochemical conditions through time either waxing or waning due to changes in geological conditions (e.g., German and Von Damm, 2003). Particularly, volcanic activity can have profound short-term effects (Chiodini et al., 2006). Since 1994, when the lead author of this study started the first of seven expeditions to Tutum Bay, hydrothermal activity and thus the physicochemical conditions in Tutum Bay have remained stable. Discharge rates, as well as the chemical composition of hydrothermal fluid and gas has remained constant. Radio-carbon age dating has estimated the last eruption of Ambitle volcano to be approximately 2300 years ago (Licence et al., 1987) and it is likely

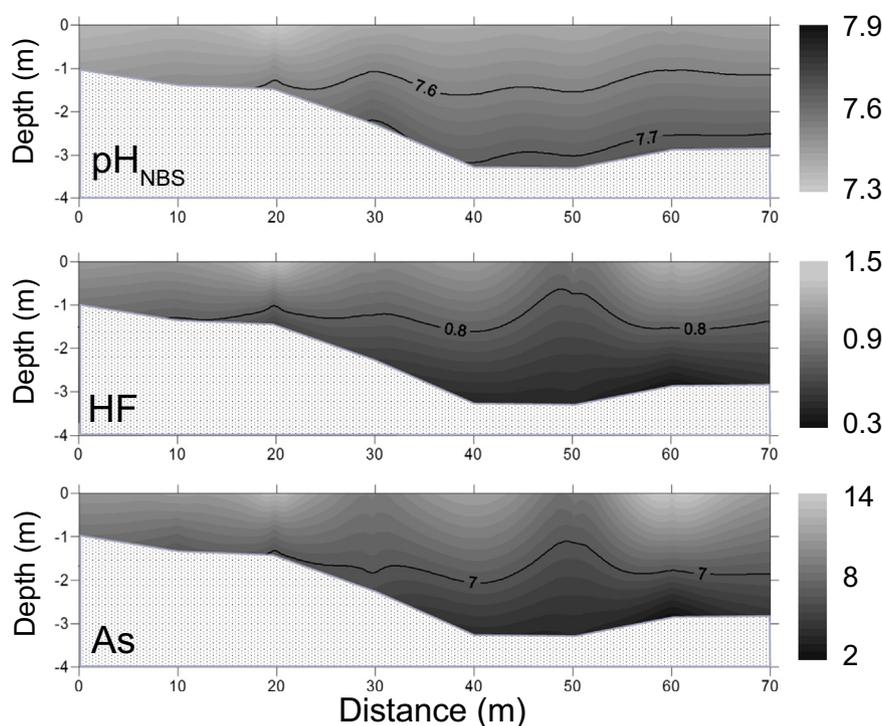


Fig. 3. Cross sections of: (a) seawater pH_{NBS} ; (b) the hydrothermal fluid (HF); (c) arsenic content (As) through the center of the study area in Fig. 1. The direction of the section from left to right is from the shore towards open water and parallel to and in between transects T2 and T3 in Fig. 1c.

that hydrothermal activity within Tutum Bay commenced around that time.

Measurements that were made in September 2016 and May 2017, revealed that at least 4500 m² of coral reef area in Tutum Bay are exposed to seawater with a pH well below modern values. Based on the distribution of hydrothermal activity Most likely, however, it is likely that all corals in Tutum Bay are exposed to low pH. The large amount of CO₂ emitted by the four main vents and the hundreds of smaller seeps all around Tutum Bay maintain the seawater mass at a mean pH_{T} of 7.68 ± 0.14 from the surface to approximately 6 m depth. In agreement with previous data reported from other tropical and sub-tropical CO₂ vents, seawater pH was frequently measured below the values predicted for the future (i.e., $\text{pH}_{\text{T}} < 7.8$). Indeed, 38 % of data recorded by SeaFET probes were between 7.7 and 7.9, which correspond to a Ω_{arag} of 2 to 3, and 56 % were below 7.7. This large variability is expected for an area with CO₂ venting (e.g., Kerrison et al., 2011), where values may unexpectedly change (see also Supplementary Figs. S2, S3). For instance, Smith et al. (2016) investigated the heterotrophic ability of the coral *Galaxea fascicularis* living at averaged pH_{T} of ca 7.8 at the Upa Upasina reef in PNG. During 7 days of pH acquisition the Authors showed that pH at the study site varied with extreme variations and intense sudden changes down to pH 6.8 and up to 8.1 (see also Fabricius et al., 2014). Hence, study sites should not be described by their average pH value. The pH should be measured continuously to account for pH variation in order to document the frequency of the organismal exposition (i.e. dose-effect). In Tutum Bay, seawater pH minima and maxima values were in the same range as other similar CO₂ systems although it seemed that the change in pH was smoother (i.e., spikes were almost absent). There, the pH variation seemed more dependent on the tidal cycle than to other environmental drivers such as wind or seawater current changes. Interestingly, only 6% of the total seawater pH measurements in Tutum Bay were above 7.9 pH_{T} units. Therefore, corals in Tutum Bay rarely benefited from recovery periods at what could be considered “normal” conditions (see St 12–14 in Supplementary Fig. S1). Those should be two advantages when comparing to other CO₂ vent sites, because in Tutum Bay the dose-effect of

acidification is closer to values expected for the future. To the best of our knowledge only the CO₂ vents in Shikine (Japan) have pH values constantly lower than 7.9 pH_{T} units (Agostini et al., 2018).

4.2. Hydrothermal fluids and chemical composition of seawater in Tutum Bay

Trace element enrichment is a typical feature in most hydrothermal systems (e.g., Dando et al., 1999; Aiuppa et al., 2006; Villanueva-Estrada et al., 2013) and surprisingly, only a few studies that used such settings for studies of a more biological nature have measured trace elements (e.g., Boatta et al., 2013; Chan et al., 2014; Hung et al., 2018). Most studies limited their measurements to the main gas composition (i.e., CO₂, H₂S, CH₄, N₂, O₂), although determining the seawater trace element composition should be fundamental to assessing the real suitability of a vent system for the study of OA effects on marine organisms.

In Tutum Bay, the four vents, in addition to a number of minor vents and hundreds of seeps, constantly emit a huge amount of gas and fluids at a discharge rate as high as 400 L min⁻¹ (Pichler et al., 1999a). The gas discharge is composed of > 95 % CO₂ with minor CH₄, N₂ and O₂ (Pichler et al., 1999a). The most important point, however, was the complete absence of H₂S and consequently there should be no detrimental effect from the gas phase other than a decrease in seawater pH. However, similar to most hydrothermal systems and CO₂ vent areas in shallow water, ambient seawater in Tutum Bay was enriched in some trace elements, particularly in As and Si. We found that vent water contained up to 928 $\mu\text{g L}^{-1}$ of As, and 97.6 mg L⁻¹ of Si, values that did not differ from those of previous studies in Tutum Bay (e.g., Pichler et al., 1999a; Price and Pichler, 2005; Price et al., 2013). Relative to seawater Si was enriched in the hydrothermal fluids by a factor of 2400 and As was enriched by a factor of 650. Hence the abundance (or percentage) of hydrothermal fluid (HF) in Tutum Bay seawater was calculated based on the concentration of Si, rather than As, which allowed for a better arithmetic separation between individual samples during calculating of the contour maps. Another important consideration for the use of Si was that the Si/As ratio in Tutum Bay seawater was

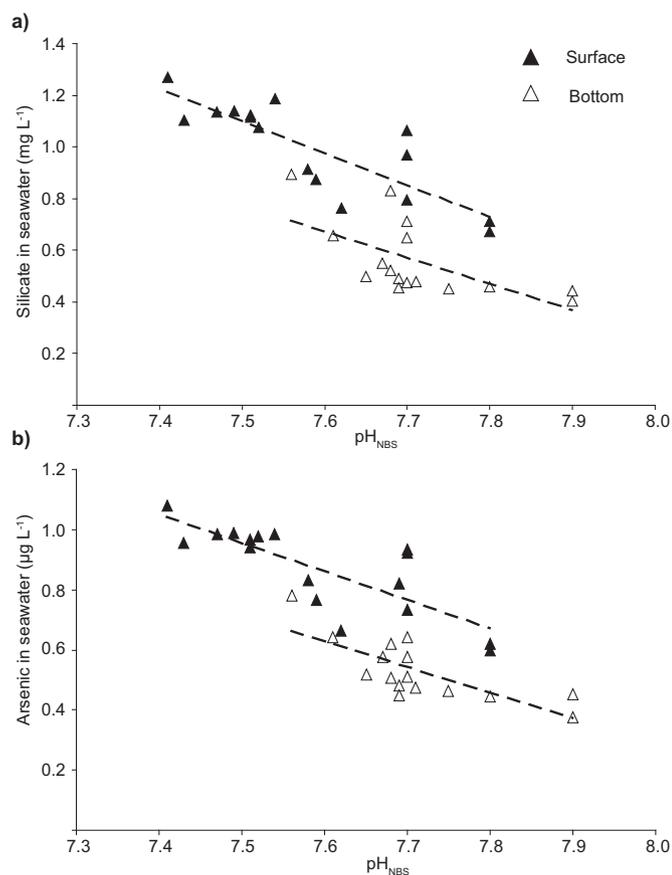


Fig. 4. Relationships between silica (Si) content, arsenic (As) content and seawater pH measured along transect T2 in the study area (Fig. 1), which was sampled during three consecutive days. **a)** Linear relationships were: $y = -1.2426x + 10.42$ ($r^2 = 0.695$) and $y = -1.0298x + 8.5026$ ($r^2 = 0.405$) for surface and for bottom samples, respectively. **b)** Linear relationships were: $y = -9.5192x + 80.954$ ($r^2 = 0.639$) and $y = -8.6073x + 71.7$ ($r^2 = 0.586$) for surface and for bottom samples, respectively.

approximately 28 and that in the hydrothermal fluid was approximately 105. Hence, the Si concentrations in seawater were proportionally 27 % higher than what they should be if the Si/As ratio would be the same in hydrothermal fluid and seawater. There are only two possible explanations for this observation that proportionally: (1) Si was added or (2) As was removed from Tutum Bay seawater between the time of hydrothermal discharge and the time of sampling. The addition of Si from a source other than the hydrothermal fluid is inconceivable since Si concentrations in seawater around Ambitle Island and the region are inherently low (Pichler et al., 1999a; Treguer et al., 1995) indicating that there are no additional Si sources, such as dust or dissolution of Si bearing phases. The second explanation that As was removed between the time of hydrothermal discharge and the sampling time was more likely and would be consistent with previous observations. Pichler et al. (1999b) concluded that As removal due to sorption by ferrihydrite (Fh) was an effective mechanism to decrease the input of hydrothermal As and to remove As from Tutum Bay seawater. Upon mixing with seawater As(III) oxidizes to As(V) and is adsorbed (ca. 98.6 %, Price and Pichler, 2005) by the abundant Fh that precipitates when the hydrothermal fluids mix with ambient seawater (Pichler et al., 1999b). While Fh can also adsorb and incorporate Si during precipitation (e.g., Berquo et al., 2007; Swedlund et al., 2010), adsorption is much larger for As. This assumption was confirmed by comparing the Si/As ratios in the hydrothermal fluid to the Si/As ratios in Fh. The average Si/As ratio in Fh ($n = 7$) precipitated from Tutum Bay hydrothermal fluids is

approximately 1.5 (Pichler and Veizer, 1999), while the Si/As ratio in the hydrothermal fluid itself is 99.5. In the absence of Si incorporating organisms, such as abundant diatoms or radiolarians (e.g., Harper and Knoll, 1975), incorporation into Fh should be the only sink for Si in Tutum Bay. The maximum amount of Si removed from the hydrothermal fluid through adsorption by Fh is 0.3 mg L^{-1} (or 0.31 %), which was determined by calculating the possible amount of Fh precipitation in Tutum Bay based on the hydrothermal fluid Fe concentration. The concentration of Fe in the hydrothermal fluid is approximately 1.5 mg L^{-1} (Pichler et al., 1999a) and the Fe/Si ratio in Fh is approximately 5 (Pichler and Veizer, 1999), hence only 0.3 mg L^{-1} Si are removed from the hydrothermal fluid during the precipitation of Fh in Tutum Bay. Compared to the Si concentration in the hydrothermal fluid this amount is negligible, i.e., 0.31 %.

Although seawater in Tutum Bay was already reported to be to some extent enriched (or depleted) in some trace elements (Price et al., 2013), we were also interested to determine their concentrations at our study site. Since only minimal amounts of Si (0.4 %) were removed between discharges and sampling (see above) it was permissible to use its concentrations in Tutum Bay seawater to calculate the abundance of several trace elements introduced via hydrothermal activity. Based on the same analysis as for As, the relative enrichments presented in Table 2 should be regarded as maximum values, since it is likely that similar to As, some amounts could have been removed from Tutum Bay seawater in the time span between discharge and sampling, as indicated by elevated concentrations in Fh and aragonite (Pichler and Veizer, 1999; Pichler and Veizer, 2004). As a result, only Mn, Cs, Fe and Zn were slightly more concentrated in Tutum Bay when compared to the reference seawater (Table 2). These values, although elevated, are in the same range concentrations usually measured in most coastal coral reefs. For instance, for manganese and iron, maximal concentrations around respectively $0.1 \text{ } \mu\text{g L}^{-1}$ and $0.2 \text{ } \mu\text{g L}^{-1}$ have been already measured in different reefs (Bergquist and Boyle, 2006; Morley et al., 1997; Obata et al., 2008), which remain comparable to what has been measured for these two elements in the present study. For zinc, concentrations can reach $0.4 \text{ } \mu\text{g L}^{-1}$ in the coral reefs of Aqaba (Ruiz-Pino et al., 1991), which is only 4 times lower than what has been measured in Tutum Bay. Most of the concentrations found in the study area are within the range of values reported in coastal reefs worldwide (Table 3). Indeed, only manganese (Mn) and especially arsenic (As) were in larger concentrations than in other coastal coral reefs, though it is difficult to generalize since these two metals are rarely measured.

In Tutum Bay, As and Si concentrations are higher in surface seawater than at the bottom, where the corals are. Arsenic in bottom seawater in Tutum Bay were around $5.9 \pm 1.7 \text{ } \mu\text{g L}^{-1}$ (Supplementary Table 2), a value that is > 40 % lower than the allowed concentration of As in drinking water (WHO, 2011). That amount is furthermore diminished due to adsorption of As by Fh, which is abundant in Tutum Bay (Pichler and Veizer, 1999; Pichler et al., 1999b). In conclusion, because of its tremendous affinity to Fh, As is almost completely removed from the hydrothermal fluid and scarcely present in seawater. The low concentrations of hydrothermal fluid in the bottom water are not surprising given the physicochemical conditions of the fluid discharge. The vent fluids have a salinity of about 3 ‰ (compared to 34 ‰ for seawater), which combined with their discharge temperature of > 90 °C, makes them relatively buoyant. As a result, the hydrothermal fluid rises to the surface, where it then dissipates.

On the other hand, arsenic concentrations, even if higher, were far below the Criterion Continuous Concentration (CCC) of $36 \text{ } \mu\text{g L}^{-1}$ given for marine organisms by the National Recommended Water Quality Criteria of the U.S. Environmental Protection Agency, which represents the highest concentration of metals in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable harm.

Table 3
Seawater main trace element concentrations found in Tutum Bay and around coral reefs throughout the world.

Region	Elements ($\mu\text{g L}^{-1}$)							
	As	Mn	Fe	Co	Ni	Cu	Zn	Pb
Tutum Bay – PNG	2.8-	1.6-	15.0-	0.03-	1.8-	0.2-	0.3-	0.1-
<i>This study</i>	15.1	11.2	46.6	0.04	1.8	0.3	1.0	0.1
Gulf of Thailand	–	–	–	0.01-	0.26-	0.46-	0.30-	–
<i>Censi et al., 2006</i>				0.40	4.20	2.08	1.73	
New-Caledonia	–	0.13-	0.08-	0.01-	0.13-	0.02-	–	–
<i>Moreton et al., 2009</i>		2.53	2.65	0.13	7.10	1.63		
Northern Red Sea	–	–	9.10-	0.21-	2.33-	2.08-	7.18-	0.37-
<i>Ali et al., 2011</i>			28.35	0.52	5.80	5.23	15.21	0.80
Bay of Bengal	–	0.72-	0.78-	0.03-	0.02-	0.44-	0.10-	0.11-
<i>Srichandan et al., 2016</i>		7.34	13.71	0.19	3.56	1.98	3.55	1.39
<i>Rejomon et al., 2008, 2010</i>								
Singapore coast	0.335-	–	–	–	0.282-	0.228-	0.974-	0.009-
<i>Cuong et al., 2008</i>	2.035				0.784	1.163	3.662	0.062
Australian east coast	0.394-	–	0.142-	0.005-	0.009-	0.151-	0.018-	< 0.002-
<i>Munksgaard and Parry, 2001</i>	1.350		34.10	0.068	0.552	1.04	2.19	0.057
<i>Haynes and Johnson, 2000</i>								
West India	–	–	–	0.20-	0.99-	4.02-	10.79-	1.01-
<i>Krishnan et al., 2007</i>				0.43	1.51	11.26	64.39	3.64
South Korea	–	–	–	–	–	0.17-	0.25-	0.03-
<i>Lee et al., 1998</i>						1.23	4.91	0.09
National Recommended Drinking Water Standards	36	–	1000	–	8.2	3.1	81	8.1
<i>US EPA, 2018</i>								

4.3. Effects of arsenic and trace elements on corals and other marine benthic organisms

Trace elements are naturally present in seawater and in general they are bioconcentrated in marine invertebrates by one order of magnitude (Eisler, 1981; Simkiss and Taylor, 1989). Some trace elements, such as iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) are essential and beneficial for the organism's metabolism (Rainbow, 2002). Others, such as cadmium (Cd), lead (Pb) and arsenic (As) seemingly do not have any biological function and can be toxic (Rainbow, 2002).

Elevated concentrations of trace metals are well known to negatively affect coral health (e.g., Bastidas and García, 1999; Bielmyer et al., 2010; Chen et al., 2010; Edinger et al., 1998; Fabricius, 2005; Ferrier-Pagès et al., 2001; Guzmán and Jiménez, 1992; Mitchelmore et al., 2007). For example, at slightly elevated cobalt concentrations of $0.2 \mu\text{g L}^{-1}$, a decrease of 28 % in growth rates was observed for the two adult scleractinian coral species (Biscéré et al., 2015). Yet, some studies highlighted that the fertilization success or the early life stages of corals were not so sensitive to higher metal concentrations with relatively high NOEC (No Observed Effect Concentration). Thus, while no effect of Co was observed, the most toxic metal was copper (Cu) with a NOEC around $10 \mu\text{g L}^{-1}$. The sensitivity to Zn was highly species-specific, where the first effect appeared around $10 \mu\text{g L}^{-1}$ Zn for *Acropora tenuis*, nevertheless these two concentrations were much higher than the one calculated for Tutum Bay (Reichelt-Brushett and Harrison, 2005; Reichelt-Brushett and Hudspeth, 2016). Otherwise, metals at moderate concentration can also play an essential metabolic role. At Mn and Ni concentrations similar to those we calculated for Tutum Bay, Biscéré et al. (2017 and 2018a,b) observed an enhancement of the calcification rates of *Acropora muricata* and *Pocillopora damicornis* and a stimulation of the photosynthetic parameters of *Stylophora pistillata*.

The case of arsenic is more complicated because of the lack of studies dealing with its effect in coral reef ecosystems and especially for corals themselves. Benson and Summons (1981) showed that species living with endosymbionts such as the large *Tridacna* or *Hippopus* clams accumulated more As than other species, but As would be stocked in non-toxic organic form (trimethylarsoniumlactate and its derivatives). In addition, Pilon (1974) demonstrated the ability of *Pocillopora damicornis* to reduce arsenate (As V) to arsenite (As III) and suggested that this form, although toxic as well, could be more easily excreted. Also,

Ruiz-Chancho et al. (2013) found that As(III) was biosynthesized by *Cycolpe neritea* to the non-toxic tetramethylarsonium ion. Not once were As values in Tutum Bay above $10 \mu\text{g L}^{-1}$, a value considered safe for human consumption (WHO, 2011). Thus, although arsenic concentrations in surface seawater in Tutum Bay were found to be slightly elevated and despite some affinity for As to incorporate into aragonite (Pichler and Veizer, 2004), no As was detected in Tutum Bay corals (Pichler et al., 2000). Assuming that a chronic exposition to moderate concentrations could in some ways affect coral metabolism, the toxic effect would compound the effect of pH, rather than counteracting it. Although it was not within the scope of our study to assess the effect of As on coral abundance at Tutum Bay, and further investigations and experiments will be needed, it was evident that abundance and diversity of coral species in Tutum Bay were not affected. Indeed, we observed quite similar diversity and coral abundances in both Tutum Bay and at the reference site (see Supplementary Fig. S5).

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2018.11.003>.

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Authors' contributions

R.R.-M. and T.P. led the project planning and study design. T.P., T.B. and R.R.-M. wrote the article in collaboration with all other authors. M.Z. processed and analyzed the environmental data. T.P. processed and analyzed the trace element data. All authors read, improved and approved the manuscript.

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