Dissolved and particulate organic carbon in hydrothermal plumes from the East Pacific Rise, 9°50'N

Sarah A. Bennett a,*, Peter J. Statham a, Darryl R.H. Green b, Nadine Le Bris c, Jill M. McDermott d,1, Florencia Prado d, Olivier J. Rouxel e,f, Karen Von Damm d,2, Christopher R. German e

a School of Ocean and Earth Science, National Oceanography Centre, Southampton SO14 3ZH, UK
b National Environment Research Council, National Oceanography Centre, Southampton SO14 3ZH, UK
c Université Pierre et Marie Curie—Paris 6, CNRS UPMC TRE3350 LECOB, 66650 Banyuls-sur-Mer, France
d University of New Hampshire, Durham, NH 03824, USA
e Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
f Université Européenne de Bretagne, European Institute for Marine Studies IUEM, Technopôle Brest-Iroise, 29280 Plouzané, France

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ABSTRACT

Chemoautotrophic production in seafloor hydrothermal systems has the potential to provide an important source of organic carbon that is exported to the surrounding deep-ocean. While hydrothermal plumes may export carbon, entrained from chimney walls and biologically rich diffuse flow areas, away from sites of venting they also have the potential to provide an environment for in-situ carbon fixation. In this study, we have followed the fate of dissolved and particulate organic carbon (DOC and POC) as it is dispersed through and settles beneath a hydrothermal plume system at 9°50’N on the East Pacific Rise. Concentrations of both DOC and POC are elevated in buoyant plume samples that were collected directly above sites of active venting using both DSV Alvin and a CTD-rosette. Similar levels of POC enrichment are also observed in the dispersing non-buoyant plume. ~500 m downstream from the vent-site. Further, sediment-trap samples collected beneath the same dispersing plume system, show evidence for a close coupling between organic carbon and Fe oxyhydroxide fluxes. We propose, therefore, a process that concentrates POC into hydrothermal plumes as they disperse through the deep-ocean. This is most probably the result of some combination of preferential adsorption of organic carbon onto Fe-oxyhydroxides and/or microbial activity that preferentially concentrates organic carbon in association with Fe-oxyhydroxides (e.g. through the microbial oxidation of Fe(II) and Fe sulfides). This potential for biological production and consumption within hydrothermal plumes highlights the importance of a multidisciplinary approach to understanding the role of the carbon cycle in deep-sea hydrothermal systems as well as the role that hydrothermal systems may play in regulating global deep-ocean carbon budgets.

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1. Introduction

Hydrothermal circulation is an important source and sink of elements to the ocean (Elderfield and Schultz, 1996; German and Von Damm, 2004). In particular, hydrothermally sourced iron (Fe), stabilised by organic complexes within dispersing plumes may be important to global ocean budgets (Bennett et al., 2008; Toner et al., 2009; Tagliabue et al., 2010; Wu et al., 2011). In a typical basalt hosted hydrothermal field, end-member fluids are enriched in Fe(II) but depleted in organic carbon (Von Damm, 1995a; Lang et al., 2006). Therefore, any elevated concentrations of organic carbon present within a hydrothermal plume must be entrained from adjacent areas of diffuse flow and chimney walls (Cowen et al., 1986; Winn et al., 1986; Lang et al., 2006) and/or produced in-situ within the plumes themselves (Roth and Dymond, 1989; McCollom, 2000; Lam et al., 2004).

Hydrothermal plumes are dynamic, 3-dimensional biologically active zones in the deep-sea and biological communities within the hydrothermal system rely on chemoautotrophic primary production fueled by hydrothermal fluids (McCollom, 2000). As hot, chemically reduced fluids mix with oxygenated seawater, complex redox disequilibria are established that provide chemical energy for microbial metabolism. Areas of diffuse flow and chimney walls are well known for their rich biomass and symbiotic bacteria, with elevated concentrations of dissolved and particulate organic carbon.
in the surrounding waters (Rau and Hedges, 1979; Karl et al., 1980; Comita et al., 1984; Lang et al., 2006). Free living microbes within hydrothermal plumes are also an important, but often overlooked, primary producer (Cowen et al., 1999; Lam et al., 2008; Dick and Bradley, 2010; German et al., 2010; Sylvan et al., in review). Both symbiotic and non-symbiotic microbes play an important role in chemical cycling in these environments.

Early plume studies detected elevated microbial biomass at plume depths both near- and far-field, entrained from bottom waters near the vents (Cowen et al., 1986; Winn et al., 1986; Straube et al., 1990). This was followed by the demonstration of chemosynthetic carbon fixation and biological removal of organic matter in the hydrothermal plume (Roth and Dymond, 1989). Bacteria and viruses have been detected within hydrothermal plumes (Juniper et al., 1998; Ortmann and Suttle, 2005; German et al., 2010), along with zooplankton directly above the plume, apparently grazing off the hydrothermal constituents (Burd and Thomson, 1994; Vereshchaka and Vinogradov, 1999; Cowen et al., 2001).

The microbial community within the hydrothermal plume has been inferred to include methane (Cowen et al., 2002), ammonia (Lam et al., 2004; Lam et al., 2008), hydrogen and sulfide oxidizers (Jannasch and Mottl, 1985; Sunamura et al., 2004), as well as microbes that utilize Mn and Fe (Cowen et al., 1998; Dick et al., 2009). Sulfide and hydrogen oxidation is considered to be important in the buoyant or early non-buoyant plume, whereas methanotrophy and ammonia oxidation are more likely to be important in non-buoyant plumes (Lam et al., 2008). The plume environment is biologically and chemically rich and is able to host both auto- and hetero-trophic communities, yet bulk dissolved and particulate organic carbon (POC and DOC) analyses are lacking for this setting. Initial vent end-member carbon measurements made by Lang et al. (2006), suggested that the flux of carbon from hydrothermal vents to the open ocean is minor compared to most oceanic source and sink terms. However, the dynamic plume environment has been suggested to be a source of ‘new’ organic carbon to the deep-ocean (Karl et al., 1984).

This study focuses on bulk organic carbon variations, both particulate and dissolved, directly above a hydrothermal source, its evolution through a dispersing plume and its presence within sinking particles settling beneath the buoyant plume.

2. Sample collection, processing and analysis

All samples for this study were collected during 2006 from the well-characterized basalt hosted vent system at 9°50′N, East Pacific Rise (EPR), which is one of the best characterized vent systems worldwide. Samples were collected from four separate research cruises of the area (Table 1) during the months immediately following a volcanic eruption event that occurred in winter 2005–2006 (Tolstoy et al., 2006; Cowen et al., 2007). Within the axial summit collapse trough (ASC), five sites of high-temperature hydrothermal activity remained actively venting after the eruption: Biovent, Bio9, P vent, Ty and Io (Fig. 1). There were also microbial mats covering basaltic substrates and areas of diffuse flow, occupied by patches of Tevnia and Alvinella. The majority of the Riftia and vent mussels present prior to the eruption had been destroyed. It is unlikely that the volcanic eruption affected our samples to a major extent, even though increased microbial activity and generation of biomass within diffuse flow areas have been reported in previous eruptions at mid-ocean ridges (Haymon et al., 1993; Juniper et al., 1995; Juniper et al., 1998; Huber et al., 2003). The samples collected in this study were obtained at least 6 months following the eruption event, and even though microbial mats were still largely visible in the surrounding diffuse vents, chemosynthetic megafauna already appeared to dominate the biomass of vent biological assemblages, with Tevnia dominating. This stage in the colonization of vent systems was reported by Shank et al. (1998), 10 months post the 1991 eruption at 9°50′N EPR.

Table 1
Details of cruise number and dates during which the samples for this study were collected.

<table>
<thead>
<tr>
<th>Cruise number</th>
<th>Dates</th>
<th>Sample collection</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT15-6</td>
<td>June 2006–July 2006</td>
<td>Sediment trap deployment</td>
</tr>
<tr>
<td>AT15-12</td>
<td>October 2006–November 2006</td>
<td>Sediment trap recovery</td>
</tr>
<tr>
<td>AT15-13</td>
<td>November 2006–December 2006</td>
<td>Vent fluid collection</td>
</tr>
<tr>
<td>AT15-14</td>
<td>December 2006–January 2007</td>
<td>Plume samples</td>
</tr>
</tbody>
</table>

Fig. 1. Locations of CTD stations 83 and 91 relative to the positions of the Ty, Io, Bio9, P vent and Biovent vent sites at 9°50′N EPR.
2.1. Vent fluid samples

End-member vent fluid samples were collected with titanium ‘majors’ bottles using DSV Alvin as reported in Von Damm (2000). High-temperature vent fluid samples were collected from four smoker orifices; Bio9, P vent, Biovent and Ty, with titanium major sampler pairs using the DSV Alvin. Bottles were triggered when the Alvin high-temperature probe or inductively coupled link temperature probes, both calibrated to a NIST traceable standard, stabilised at a maximum temperature.

Shipboard sample treatments were as reported in Von Damm et al. (1995b, 2000). On the day of sampling, high-temperature vent fluid samples were processed shipboard for H2S (5% precision, standardised to Dilut-it® standard solutions) by iodometric starch titration. The remaining vent fluid samples were acidified with 0.5–1.0 ml of concentrated 3x quartz distilled HCl, and stored in high-density polyethylene (HDPE) bottles. Any remaining precipitates were rinsed out of the bottles during the sample draw and saved in HDPE bottles.

At the University of New Hampshire (UNH), USA, high-temperature vent fluid samples were filtered through 0.45 µm nucleopore filters in a laminar flow bench. The acidified, filtered fluid fraction samples were stored at room temperature in HDPE bottles, while the filters and filtered particles were saved in separate HDPE bottles. Fluid fractions were analyzed for Fe and Mn (both 1% precision, standardised to Ricca Chemical Company AA standards) by flame atomic absorption spectroscopy (FAAS). Fe and Mn end-members were calculated for a high-temperature vent by performing a least-squares regression of an individual chemical species versus Mg and assuming a linear relationship passing through the ambient bottom seawater composition, and extrapolated to 0 mmol/kg Mg. Reported Fe and Mn end-members were calculated using only data derived from filtered samples (dissolved fraction). As such, this does not take into account the precipitated or suspended fractions (but does include colloidal material), and so will under-estimate the true end-member values.

Detailed studies on the vent fluid evolution and chemical evolution following the winter 2005–2006 eruptions are beyond the scope of this paper and will be reported in detail elsewhere (Von Damm et al., unpublished data). In this study, we will use end-member vent-fluid Fe/Mn ratios to help calculate the relative dilution factors that can be ascribed to buoyant plume samples collected directly above each vent-site and H2S concentrations to determine the potential for microbial sulfide oxidation.

2.2. Plume samples

Near-field buoyant plume samples were collected from above four high-temperature vent sites; Bio9, P vent, Biovent and Ty, using 1 L externally sprung Niskin bottles placed in the basket attached to DSV Alvin. A total of eight samples was collected, with two samples from each site obtained sequentially as DSV Alvin flew a few meters above the active chimneys. The distance of DSV Alvin above the vent orifice was sub-sampled into acid-cleaned HDPE bottles and acidified to pH 1.6 using HNO3 (Fisher Scientific, stored in glass) to pH 2 and stored at 4 °C for analysis in our shore laboratories. All GF/F filters were folded in combusted foil and frozen, with volumes of seawater filtered recorded for subsequent calculations of particulate material concentrations per litre of ocean/plume water.

Analyses of total dissolved Fe and Mn (TdFe and TdMn) in the near-field plume samples collected directly above the vent orifices were carried out at the National Oceanography Center, Southampton (NOCs), UK. A 4% solution of each sample in 0.4 M HNO3 was analyzed using a Perkin Elmer Optima 4300DV ICP-OES that was calibrated against matrix-matched standard solutions that bracketed the concentration ranges of the sample solutions. Standard solutions were prepared using single element 1000 µg L−1 standards (Specpure, Spex) of Fe and Mn. A 4% IAPSO seawater standard was also run, even though it contained very low Fe and Mn concentrations, to check for contamination. The limit of detection of the technique was 6.5 nM for Fe and 1.3 nM for Mn, determined by repeated analysis of the seawater matrix blank (3σ, n = 10). While these detection limit values are high compared to open-ocean trace metal concentrations, they are much lower than the concentrations reported for the near-vent hydrothermal plume samples investigated here (µM concentrations).

Determination of DOC was carried out on a coupled high-temperature combustion total organic carbon-nitrogen chemiluminescence detection (HTC TOC–NCD) system at NOCS. The measurements were performed using a Shimadzu TOC 5000A total carbon analyzer coupled with a Sievers NCD 255 nitrogen chemiluminescence detector (Pan et al., 2005). A procedural blank of MQ water, gave an analytical precision of ±0.8 µM (1σ, n = 3) and the accuracy of the technique was determined from the
analysis of a certified reference material. The standard deviation of each sample was obtained from 3 to 5 injections of the same sample into the instrument.

Determination of POC was carried out at the Plymouth Marine Laboratory, UK. The GF/F filters were unfolded, removed from the foil and placed in small polystyrene containers. The filters were then treated with sulfuric acid under vacuum for 24 h to remove the inorganic carbonates (Verardo et al., 1990). The filters were dried at 60 °C for 24 h, quartered and packaged in pre-combusted aluminum foil (Hilton et al., 1986). The samples were then analyzed on a Thermo Finnigan Flash EA1112 Elemental analyzer using acetonitrile as a calibration standard. Filter blanks were used for blank correcting all samples. The analytical precision, determined from analysis of the filter blanks, was 0.55 μg (1σ, n=6).

2.3. Sediment trap samples

Sediment trap samples analyzed for this study were collected using a McLane 21-position time-series trap deployed at the Bio9 vent-site at 9°50.29′N, 140°17.49′W and at a depth of 2505 m, 3 m above the seafloor. This ‘R1’ trap was deployed during AT15-6 from the RV Atlantis and repositioned during Alvin submersible dive 4262 on 30th June, 2006. The sediment trap was positioned ~25 m laterally away from the Bio9 vent-site with the intention that the trap would then be sufficiently close to underlie (hence, collect particles settling from) both the buoyant and non-buoyant portions of the hydrothermal plume dispersing away from this vent-site. The R1 trap then collected samples continuously, with each sample representing a 14.8-day cycle (to coincide with spring/neap tidal cycles in the overlying water column) until its recovery during Alvin dive 4262 (3rd November, 2006, RV Atlantis AT15-12). Further information on this deployment will be reported in German et al. (manuscript in preparation, 2011).

Prior to deployment, each 250 mL polyethylene sample cup was filled with dimethyl sulfoxide (DMSO) and buffered to pH 9.0 ± 0.5. This preservative prevents any biological activity continuing within the sample-cups, post-collection, while retaining sample integrity for mineralogical, bulk geochemical, and molecular microbiological investigations (Comtet et al., 2000). Upon trap recovery, each sample cup was capped and refrigerated at 4 °C for return to the laboratory and shore-based analysis.

All subsequent sample processing was conducted at Woods Hole Oceanographic Institution using standard methods established for deep-ocean sediment trap analyses (Honjo et al., 1995). Samples were sieved to retain coarse fragments and the remaining < 1 mm fraction passed through a 10-port rotating wet sediment splitter. Total dry mass for mass flux calculations was determined from three of the sample splits. Dried subsamples (5–10 mg) were analyzed for particulate inorganic carbon and POC using a CHN analyzer, and Al, Fe, Mn and V, after acid digestion, using ICP–OES and ICP–MS. A number of geo-reference standards (BHVO-1 and IFG) were analyzed along with the samples to confirm analytical accuracy, which was better than 5% for all elements reported.

3. Results

3.1. Vent fluid samples

The end-member temperature, Fe, Mn and H2S concentrations for each high-temperature vent are listed in Table 2. The end-member concentrations for vent-fluids were sampled over several days. End-member regressions were calculated from major ion analyses for 2–6 discrete samples.

3.2. Plume samples

The POC and DOC concentrations in the near-field vent samples together with their respective TdFe and TdMn concentrations, Fe/Mn ratios, maximum temperature and calculated percent end-member fluid in these samples (see later) are listed in Table 2. The POC concentrations ranged from 0.87 to 3.81 μM and the DOC concentrations ranged from 37.9 to 47.1 μM. The averaged temperature, pH and free sulfide recorded by the in-situ probes for these samples and height of DSV Alvin above the seafloor during each sampling event are shown in Table 3. The CTD depth profiles of POC concentrations, DOC concentrations, potential temperature anomalies and particle anomalies are shown in Fig. 2 and the depth vs density plots for these two CTD casts are shown in Fig. 3. Potential temperature and particle anomalies were determined as described in Baker (1998). The POC concentrations in the plume ranged from 0.07 to 0.46 μM compared to an average ‘background’ value of 0.16 ± 0.05 μM measured above and below the plume. DOC concentrations were approximately one order of magnitude greater than POC concentrations and ranged from 35.3 to 43.2 μM in these samples compared to ‘background’ values of 38.2 ± 0.9 μM above and below plume-height. The upper and lower background limits are shown on Fig. 2.

Table 2

<table>
<thead>
<tr>
<th>Vent fluids</th>
<th>Near-field buoyant plume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>[Fe] (μM)</td>
</tr>
<tr>
<td>Biovent</td>
<td>321</td>
</tr>
<tr>
<td>Bio9</td>
<td>382</td>
</tr>
<tr>
<td>P vent</td>
<td>355</td>
</tr>
<tr>
<td>Ty</td>
<td>386</td>
</tr>
<tr>
<td>Background</td>
<td>–</td>
</tr>
</tbody>
</table>

[Fe] and [Mn] are the concentrations of Fe and Mn with subscript ‘Td’ indicating ‘total dissolvable’. Reported vent fluid concentrations have been corrected to allow for seawater entrainment (Section 2.1). [POC] is the concentration of particulate organic carbon and [DOC] is the concentration of dissolved organic carbon. The Fe/Mn ratio was calculated using the concentrations of total dissolvable Fe and Mn measured in the near-field buoyant plume samples. The % end-member fluid represents the dilution of the vent fluids with the surrounding seawater and was calculated using Mn as a conservative tracer (see Section 4.1 for further details).

* One of the Niskin bottles fired at Ty, was not shaken prior to sample collection.
3.3. Sediment trap samples

The sediment trap flux data for elements pertinent to this study are shown in Table 4 and Fig. 4. A more complete discussion of post-eruption EPR sediment trap fluxes will be presented in German et al. (manuscript in preparation, 2011). For this study, we have calculated the relative abundance of hydrothermally sourced Fe-oxyhydroxide material, [Fe-oxy]hyd, in each of the sediment trap samples, using a protocol previously described for hydrothermal sediments, sediment trap samples and hydrothermal plume particles (German et al., 1997; German et al., 2002; Bennett et al., 2009). This method exploits the scavenging

<table>
<thead>
<tr>
<th>Site</th>
<th>Dive number</th>
<th>Time</th>
<th>Height above seafloor (m)</th>
<th>Average temp (°C)</th>
<th>pH</th>
<th>Free H₂S (μM)</th>
<th>% end-member fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>BioVent</td>
<td>4295</td>
<td>20:52:25–20:52:40</td>
<td>7.5</td>
<td>5.0</td>
<td>6.9</td>
<td>22</td>
<td>0.9</td>
</tr>
<tr>
<td>Bio9</td>
<td>4292</td>
<td>20:04:16–20:04:34</td>
<td>7.0</td>
<td>7.7</td>
<td>7.0</td>
<td>26</td>
<td>1.5</td>
</tr>
<tr>
<td>P Vent</td>
<td>4292</td>
<td>20:47:34–20:47:49</td>
<td>4.1</td>
<td>7.2</td>
<td>7.0</td>
<td>26</td>
<td>1.3</td>
</tr>
<tr>
<td>Ty</td>
<td>4294</td>
<td>21:07:51–21:08:11</td>
<td>4.2</td>
<td>4.7</td>
<td>7.6</td>
<td>9</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Data were averaged over 15 s at the maximum temperature anomaly. The height of DSV Alvin above the seafloor was recorded with an altimeter attached to the bow of the submersible. The % end-member fluid was calculated using the average temperature measured in the plume and the maximum temperature measured in each end-member (Table 2), subtracting the background temperature from each value.
properties of Fe oxyhydroxides for oxyanions (e.g. vanadium (V)) within the water column, resulting in V:Fe ratios which vary systematically with the composition of the ambient seawater (Feely et al., 1998). By knowing the concentration of vanadium that is derived from hydrothermal Fe-oxyhydroxide scavenging, we can calculate the concentration of \([\text{Fe-oxy}]_{\text{hyd}}\). The chemical constituents within the trap will be sourced from both eolian inputs sinking through the water column and hydrothermal inputs dispersed laterally within the hydrothermal plume. Therefore, we must first determine how much of the vanadium in the trap samples was sourced from the hydrothermal system as opposed to eolian inputs.

In order to correct for these continental eolian inputs, we have used sediment data reported in Kyte et al. (1993) to provide us with detrital vanadium:aluminum ratios and assumed that total Al content within the sediment traps is a result of such inputs (German et al., 1997). From this, we can calculate the predicted detrital concentration of vanadium in each sample using

\[
[V]_{\text{det}} = \frac{[\text{Al}]_{\text{trap}} 	imes (V)/[\text{Al}]_{\text{eolian}}}{(1)}
\]

where \([V]_{\text{det}}\) is the predicted detrital concentration of vanadium in a sediment trap sample, \([\text{Al}]_{\text{trap}}\) is the measured aluminum concentration in a sample and \([V]/[\text{Al}]_{\text{eolian}}\) is the average V:Al ratio in the upper 0–1 m of sediment as reported by Kyte et al. (1993) and shown in Table 4. The excess of vanadium in each sample is assumed to be hydrothermal plume fall out, \([V]_{\text{hyd}}\).

---

**Table 4**

Sediment trap data.

<table>
<thead>
<tr>
<th>Days elapsed</th>
<th>Mass mg/m²/day</th>
<th>Fe mg/m²/day</th>
<th>C org mg/m²/day</th>
<th>Al mg/m²/day</th>
<th>V µg/m²/day</th>
<th>([\text{Fe-oxy}]_{\text{hyd}}) mg/m²/day</th>
<th>RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>81.0</td>
<td>14.4</td>
<td>1.8</td>
<td>1.09</td>
<td>5.07</td>
<td>12.7</td>
<td>12.3</td>
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<tr>
<td>12</td>
<td>79.6</td>
<td>16.2</td>
<td>1.6</td>
<td>1.44</td>
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<tr>
<td>18</td>
<td>16.9</td>
<td>2.6</td>
<td>2.3</td>
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<td>1.28</td>
<td>0.30</td>
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<tr>
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<tr>
<td>30</td>
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<td>0.80</td>
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<tr>
<td>54</td>
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<td>3.8</td>
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<td>1.96</td>
<td>0.49</td>
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<td>10.3</td>
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<td>0.43</td>
<td>3.64</td>
<td>1.08</td>
<td>10.0</td>
</tr>
<tr>
<td>N. Pac. clay</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>98.5 mg/g</td>
<td>152 µg/g</td>
</tr>
</tbody>
</table>

Average 0–1 m from LL44-GPC3 (Kyte et al., 1993)

Fe, organic carbon (C org), Al and V flux data are shown for bulk compositions within the trap samples. These data were used to calculate the Fe-oxyhydroxide hydrothermal component (\([\text{Fe-oxy}]_{\text{hyd}}\)), as described in the text (Section 3.3), along with a propagated relative standard deviation (RSD).
such that

\[ |V_{\text{hyd}}| = |V_{\text{trap}}| - |V_{\text{det}}| \quad (2) \]

where \( |V_{\text{trap}}| \) is the measured vanadium concentration in the sediment trap sample. The uptake of \( V \) by Fe oxyhydroxides along the EPR has a \( V/Fe \) ratio of 0.0028 (Feely et al., 1998), therefore, the hydrothermal Fe oxyhydroxide component \( (|Fe-ox|_{\text{hyd}}) \) of the sediment trap samples can be calculated using

\[ |Fe-ox|_{\text{hyd}} = 1/0.0028 \times |V|_{\text{hyd}} \quad (3) \]

The results of these calculations are shown in Table 4.

4. Discussion

4.1. Dilution of near-field plume samples

Within the short time frame of buoyant plume rise (~1 h), from emission at the vent orifice to emplacement at non-buoyant plume height (Baker et al., 1995), dissolved Mn can be treated as a conservative tracer. By contrast, Fe does not show conservative behavior over this time frame, due to the formation of polymetallic sulfide precipitates within the first few seconds of venting and the rapid oxidation of Fe(II) to form Fe oxyhydroxide precipitates. Both of these particulate Fe species can fall out of a plume during buoyant plume rise. By contrast, Mn oxidation is much slower and dissolved reduced Mn species can be considered to be quantitatively transported to and emplaced within non-buoyant hydrothermal plumes.

Using the vent fluid data collected in November 2006 (Table 2), we can investigate the evolution of near-field plumes and calculate the percent dilution for each near-field buoyant plume sample using

\[ \% \text{ end-member fluid} = \frac{|Mn|_{\text{BP}}}{|Mn|_{\text{BP}} + |Mn|_{\text{PE}} \times 100} \quad (4) \]

where \( |Mn|_{\text{BP}} \) is the Mn concentration measured in the near-field buoyant plume samples and \( |Mn|_{\text{PE}} \) is the corresponding vent fluid end-member Mn concentration. Dilution factors calculated by this method fall in the range of 125- to 1000-fold dilution with ambient seawater (i.e. the samples contain just 0.1–0.8% end-member vent fluid, Table 2), demonstrating that the dilution that is associated with turbulent mixing within the first few meters of buoyant plume rise. Except for Ty, duplicate near-field buoyant plume samples taken successively at each site exhibit very similar Fe/Mn ratios, demonstrating that each plume was rather homogeneous.

Dilution factors calculated from in-situ temperature measurements ranged from 0.8% to 1.5%. These values were calculated as for Mn but using the average temperature measured within the plume and the maximum temperature measured within the vent fluid at each site (and subtracting background temperature of 2 °C from each value) (Table 3). These lower dilution ratios reflect minimum dilution conditions experienced in the core of the plume, as illustrated by steep peaks simultaneously recorded for all three parameters (temperature, pH and sulfide) while DSV Alvin flew a few meters above the high-temperature chimneys. In comparison, Niskin sample contents have integrated several mixing fractions from the turbulent plume, with larger seawater dilution.

4.2. Buoyant plume rise and dispersal

As buoyant plumes rise up into the water column, further dilution continues. At CTD 83, directly above the EPR 950-N vents, strong particle anomalies coupled with positive temperature anomalies were detected from just above the seafloor up to 2460 m. Importantly, the density profile for this station (Fig. 3) also reveals an instability in the water column coincident with the positive temperature anomalies from the seafloor up to 2460 m, confirming that we had intercepted a buoyant (rising) hydrothermal plume at these depths (Lupton, 1995). During this same cast, a lowered-acoustic Doppler current profiler (L-ADCP) attached to the CTD rosette, measured a current velocity at 2400 m depth of 8.6 cm s\(^{-1}\) along heading 199°. Because the depth of the ASCT is only ~20 m, this rising plume would not have been constrained by the local topography but, rather, should have been dispersed away from the ridge axis along the prevailing current direction.

At CTD 91, occupied ~500 m southwest of the 950°N vents (i.e. in the projected down-plume direction), particle anomalies were observed at a typical non-buoyant plume height of between 2350 and 2275 m, 150–225 m above the seafloor. At these depths, no density anomalies were observed indicating that the plume was no longer buoyant (Fig. 3). Further, the L-ADCP measured a current velocity at plume-height of 5.8 cm s\(^{-1}\) on a heading of 233°, consistent with the 950°N high-temperature vents being the source for this plume.

4.3. DOC and POC in the near-field plume

POC concentrations in our near-field plume samples exhibit elevated concentrations over background, ranging from 0.87 to 3.81 μM with highest concentrations at the Ty and P vents (Table 2). The DOC concentrations in these same near-field plume samples ranged from 37.9 to 47.1 μM, a range that spans the local value for background seawater (38.2 ± 0.9 μM), but also reflects enrichments of up to ~20% at three of the sites investigated. The analysis of POC and DOC is operationally defined as the separation of particles through a combination of GF/F glass fiber filter (0.7 μm nominal pore size). A direct consequence is that the majority of any DOC fraction measured is often dominated by microorganisms, including microbial biomass and larvae (Mullineaux et al., 2010), whereas DOC sources commonly include extracellular release from bacteria, grazer mediated release and excretion, release via cell lysis (from viruses and bacteria), solubilization of particles and bacterial transformation and release (Carlson, 2002). DOC sinks include biotic consumption (e.g. by heterotrophic bacteria) and abiotic sorption onto particles.

Winn et al. (1986) estimated living carbon concentrations within a hydrothermal plume by using ATP measurements as an indicator of microbial biomass, and reported particulate living carbon concentrations of 1.2 μM at 20 m above a vent-chimney and 0.3 μM at 50 m off-bottom at hydrothermal sites along the Juan de Fuca Ridge. These concentrations are similar to the total POC measured in our near field plume samples collected from DSV Alvin as well as in the buoyant and non-buoyant plume samples collected during CTD casts 83 and 91 (POC ≤ 0.46 μM; Fig. 2).

We do not believe that EPR 950°N vent fluids can be the source for the POC and DOC enrichments in our near-field plume samples, because the required end-member DOC and POC concentrations would be unreasonably high. Typically, thermal degradation of organic matter is to be expected at the high-temperatures associated with typical ‘black smoker’ venting. For example, at the Main Endeavor field, and at Axial Volcano, on the Juan de Fuca Ridge, average DOC concentrations in end-member fluids are 15 and 17 μM, respectively (Lang et al., 2006). By contrast, if our Alvin-collected Niskin samples (average DOC concentration of 42.5 μM) have experienced a 125- to 1000-fold dilution with seawater (Table 2), the required end-member vent-fluid DOC concentration would fall in the range 5.3–42.5 mM, some three orders of magnitude higher than previously measured at the Juan de Fuca Ridge vents.
A more plausible source for the DOC and POC in our near field plume samples is from entrainment of diffuse flow and chemosynthetic life on the chimney walls into the base of the buoyant plume (Cowen et al., 1986; Karl et al., 1988; Bailly-Bechet et al., 2008). At the time of sampling, the high-temperature chimney walls were covered with Alvinella colonies and it is expected that hydrodynamic constraints will favor the entrainment of organic material from the chimney walls or alvinellid colonies (Bailly-Bechet et al., 2008). In addition, diffuse systems typically host the most abundant chemosynthetic communities associated with seafloor hydrothermal venting and during our dive program, areas of high biomass were observed in the areas surrounding the vents at 9°50'N EPR. Within these environmental niches, DOC concentrations have been observed to reach values (39–69 μM) that are nearly double background deep-ocean values (Lang et al., 2006) and are closer to those measured in the most productive waters associated with the equatorial Pacific upwelling region, where DOC concentrations reach 67 μM (Carlson and Ducklow, 1995).

Elevated POC concentrations (of up to 18.3 μM) have also been observed in warm (20 °C) diffuse-flow fluids at 21 °N, EPR (Comita et al., 1984). In that study, DOC concentrations were 53–71 μM, similar to the range reported by Lang et al. (2006), who concluded that the high DOC concentrations present in diffuse flow vent fluids were a result of high microbial activity sustained by energy produced from the oxidation of sulfur species and H₂ (McCollom and Shock, 1997; Sarradin et al., 1999). Thus, while entrainment of pre-formed DOC and POC into our plume samples could explain the data reported here, we cannot preclude the possibility that on-going microbial productivity within the buoyant and non-buoyant plume might also play an important role in producing biomass ± organic ligands ± exopolymers.

Certainly, in-situ production of microbial biomass has the potential, energetically, to occur within plumes themselves, due to the redox disequilibria set up between the chemically reduced vent fluids and oxygenated seawater (McCollom, 2000; Lam et al., 2008; Dick et al., 2009). Of course, any in-situ production within the buoyant plume samples obtained using Alvin, prior to their collection, is likely to be minimal because the samples were taken from turbulent rising plumes just a few meters above each vent orifice. In-situ production could have occurred subsequently, however, within the closed Niskin bottles, during the ascent of Alvin but prior to being filtered aboard the ship. This would be expected to result in the production of biomass (increasing POC) as well as the production and consumption of DOC. Within the early stages of buoyant plume rise, microbial activity is most likely the result of hydrogen and sulfide oxidation (Lam et al., 2008), with the oxidation of elemental sulfur and sulfide precipitates providing the biggest biomass potential (McCollom, 2000). Hydrogen sulfide in the vent fluids ranged from 8.6 to 28.7 mM and the free sulfide concentrations measured in-situ as DSV Alvin flew through the plume were high compared to background seawater (Table 3). It is also important to remember that free sulfide represents only part of the total sulfide transported by hydrothermal plumes. Since aqueous and polymeric iron sulfides in equilibrium with H₂S and HS⁻ may contribute more than 60% of the total ‘dissolved’ sulfide pool (Luther et al., 2001; Le Bris et al., 2003) the total amount of reduced sulfur that was trapped within each Niskin bottle, and hence available for microbial oxidation following each sampling event, was most probably still larger than the values reported in Table 3.

Previously, McCollom (2000) carried out a theoretical study to quantify the component of biomass production within hydrothermal plumes that can be directly attributed to inorganic chemical reactions. He determined that approximately 50 mg of biomass could potentially be produced per kg of vent fluid (from EPR 21°N OBS vent) as the fluid dilutes 1000-fold with the surrounding seawater in the rising plume. This is equivalent to 23 mg of C per kg of fluid (when 2.2 g biomass contains 1 g of C (Battley, 1998)) or ~1.9 mM C. In a diluted buoyant plume, this would only result in a 1.9 μM increase in POC concentrations over background which, for EPR 9 50’N (background = 0.16 ± 0.05 μM), would imply maximum predicted POC values within our Alvin-collected near-field samples of ~2.1 μM. Intriguingly, that value compares extremely well with the POC concentrations that we did measure in our Niskin samples, processed aboard ship, which fall in the range 0.87–3.81 μM (Table 2).

4.4. DOC and POC in the dispersing plume

As hydrothermal plumes rise and become progressively more dilute, they can be tracked readily using in situ optical sensors that respond to the high concentrations of suspended particulate matter within those plumes (Baker et al., 1995). In this study, such a phenomenon is most readily apparent in cast CTD 91 where a particle-rich lens of water at 2275–2350 m depth provides clear evidence for a dispersing non-buoyant hydrothermal plume (Fig. 2). What is particularly notable at this station is that the profile of measured POC concentrations directly mimics this turbidity profile, indicating that highest values of POC occur toward the core of the dispersing non-buoyant plume (Fig. 2). Further, the maximum POC concentrations observed at CTD 91 are directly comparable to the highest buoyant plume concentrations observed at CTD 83, situated immediately above the seafloor. Given that we should expect plume samples at CTD 91 to have undergone at least one order of magnitude further dilution, relative to samples from the deep water column at CTD 83 (Lupton, 1995), this indicates that there must have been some further process resulting in the addition of POC to the dispersing non-buoyant plume. The close correlation observed between particle anomalies and POC data, suggests that an additional source of POC to the plume may result from passive scavenging of dissolved organic carbon onto plume particles and/or from a microbial community active within the dispersing plume.

Adsorption of organic carbon onto plume particles should result in a shift in the size fractionation of the total organic carbon present, increasing the POC fraction and decreasing the DOC fraction. Likewise, a hetero- or mixotrophic microbial community would consume DOC (decreasing that concentration) while increasing its biomass (leading to increased POC concentrations). In either case, one would expect any increase in POC to coincide with a complementary decrease in DOC concentrations. In our plume samples—and within the precision of our measurements—none of the DOC concentrations measured at plume height differ significantly from background. Nevertheless, across the depth-range for the non-buoyant plume at CTD 91, as defined from in-situ turbidity signals, there does appear to be a concave curvature in the profile of DOC that mirrors the concave curvatures observed in both the POC profile and the in-situ turbidity sensor profile. This could be consistent with scavenging and/or biological consumption of DOC from the dispersing non-buoyant plume (Fig. 2). At the core of the plume, however, maximum POC concentrations are ~0.4 μM representing an increase of just ~0.2 μM over background. By contrast, DOC concentrations appear to decrease from ~39 to ~37 μM over the same depth range—a deficit of ~2 μM. If this much larger decrease were due to uptake of DOC onto into particulate matter at plume-height, the apparent net deficit would need to be explained by some additional removal process—e.g. in the form of settling plume particulates.

Evidence that such a mechanism is plausible can be gained from a consideration of fluxes to sediment traps underlying the EPR 9 50’N plume (Fig. 4). In those sediment traps, particulate organic carbon fluxes during the period immediately prior to our Alvin and CTD-rosette based sampling appear to relate more closely to the
calculated Fe oxyhydroxide (FeOOH) fluxes than to total mass-flux or total Fe flux (Fig. 4, Table 4). Since this Fe oxyhydroxide fraction represents just 1–2% of the total mass flux, this would appear to be consistent with a more specific \(C_{**}\text{Fe}^{2+}\) transport process than just surface-independent particle scavenging or adsorption. Such removal of organic carbon in association with Fe-oxyhydroxide species could occur as a direct result of the preferential adsorption of organic carbon onto Fe oxyhydroxide mineral surfaces (Balistrieri and Murray, 1987; Gschwend and Schwarzenbach, 1992), and/or through microbial oxidation of Fe(II) and Fe sulfides that preferentially concentrates organic carbon with Fe oxyhydroxides. While detailed microscopic, biogeochemical and mineralogical analyses on similar trap samples have recently demonstrated that Fe(III) oxyhydroxide aggregates occur in the presence of exopolymeric organic carbon (i.e. organic substances excreted from microbial species (Toner et al., 2009)), it remains to be determined whether this is as a result of biotic or purely abiotic geochemical processes. Investigating the relative importance of the two remains an important topic for continuing deep-sea hydrothermal biogeochemical research.

5. Summary

In this study, we have investigated dissolved and particulate organic carbon concentrations within an evolving hydrothermal plume. We conclude that organic carbon is entrained into buoyant plumes from chimney walls and adjacent areas of biologically rich diffuse flow but that there may be further addition of organic carbon during plume dispersal. Within and beneath hydrothermal plumes, we observe a relationship between POC and plume particulate matter—particularly Fe-oxyhydroxide phases. These close associations may result from scavenging of DOC from the surrounding plume-waters and/or in-situ microbial productivity (e.g. from active microbial oxidation of Fe(II) and Fe sulfides within the plume). The study of organic carbon cycling within hydrothermal plume environments is complicated by this potential for biological production and consumption. Consequently, we recommend that future studies should include a multidisciplinary approach to understand carbon cycling in deep-sea hydrothermal systems that encompasses the system as a whole, including dispersing hydrothermal plumes.

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References


