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A comparison of *in situ* vs. *ex situ* filtration methods on the assessment of dissolved and particulate metals at hydrothermal vents



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ABSTRACT

The objective of this study was to assess the impact of the filtration method (*in situ* vs. *ex situ*) on the dissolved/particulate partitioning of 12 elements in hydrothermal samples collected from the Lucky Strike vent field (Mid-Atlantic Ridge; MAR). To do so, dissolved (< 0.45 μm) and particulate Mg, Li, Mn, U, V, As, Ba, Fe, Zn, Cd, Pb and Cu were measured using different techniques (HR-ICP-MS, ICP-AES and CCSA). Using *in situ* filtration as a baseline, we showed that *ex situ* filtration (on-board and on shore after freezing) resulted in an underestimation of the dissolved pool, which was counterbalanced by an overestimation of the particulate pool for almost all the elements studied. We also showed that on-board filtration was acceptable for the assessment of dissolved and particulate Mn, Mg, Li and U for which the measurement bias for the dissolved fraction did not exceed 3%. However, *in situ* filtration appeared necessary for the accurate assessment of the dissolved and particulate concentrations of V, As, Fe, Zn, Ba, Cd, Pb and Cu. In the case of Fe, on-board filtration underestimated the dissolved pool by up to 96%. Laboratory filtration (after freezing) resulted in a large bias in the dissolved and particulate concentrations, unambiguously discounting this filtration method for deep-sea chemical speciation studies. We discuss our results in light of the precipitation processes that can potentially affect the accuracy of *ex situ* filtration methods.

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1. Introduction

Assessing the behavior of trace metals is essential for understanding the link between metal composition and the distribution of deep-sea hydrothermal fauna (Sarradin et al., 2008). Some studies have suggested that local biological assemblages are partly controlled by geochemical conditions, including trace metal speciation along the hydrothermal fluid–seawater mixing gradient (Shank et al., 1998; Luther et al., 2001). The hydrothermal mixing gradient can be schematically split up into three areas: the “anoxic zone” (hot fluid), the “mixing zone”, characterized by steep chemical gradients (Johnson et al., 1986; Le Bris et al., 2003) when hot, reduced hydrothermal fluid mixes with cold, oxidized seawater, and the “oxic zone” (cold seawater).

Substantial efforts have been devoted to understanding the physico-chemical behavior of metal in these different areas.

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Previous studies assessing the dissolved metal input from hydrothermal vents have focused on the non-buoyant plume (Bennett et al., 2008), whereas others have evaluated total dissolvable metal levels in endmember hydrothermal fluids (Charlou et al., 2000). Still other studies have considered the chemical composition of particles (Feely et al., 1994; German et al., 2002) and their kinetics of formation (Rudnicki and Elderfield, 1993), focusing on the buoyant and/or the non-buoyant plume of high-temperature black smokers. In the mixing zone, secondary reactions of complexation between dissolved metal and organic metal-binding ligands may influence the chemical speciation of metal, and compete with sulfide precipitation (Sander et al., 2007; Toner et al., 2009; Yücel et al., 2011; Hawkes et al., 2013), potentially increasing the dissolved metal flux in the deep ocean (Sander and Koschinsky, 2011).

Metal behavior in the mixing zone is still poorly documented despite its significant impact on metal speciation, and data are still lacking in this specific environment (Von Damm et al., 1985; Field and Sherrell, 2000; Kádár et al., 2005; Sander et al., 2007; Sarradin et al., 2008; Sarradin et al., 2009). Data from the mixing zone show

Table 1

Dissolved and particulate concentrations measured in the 26 samples with their associated limits of detection (LOD). D refers to dissolved concentration (< 0.45 μm), P to particulate concentration. IS: *in situ* filtration, OB: on-board filtration (after retrieval) and LF: laboratory filtration (after freezing). Sample name is composed of the number of the dive (e.g. 502-01) and the number of the blood bag used for sampling (e.g. A1). Samples are classified according to the filtration method used (gray-scale) and by ascending Mn_T concentration.

Sample	T°C	pH	Mn		Mg		Li		U		V		As		Fe		Zn		Ba		Cd		Pb		Cu	
			μM		mM		μM		μM		μM		μM		μM		μM		μM		nM		nM		nM	
			D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P	D	P
			LOD	0.004 0.02	0.02 3	0.06 0.3	0.0001 0.0004	0.003 0.002	0.001 0.009	0.2 0.05	0.1 0.04	0.01 0.005	0.01 0.5	0.01 2	0.7 10											
505-04-A1-IS	4.6	7.6	0.12	<LOD	50.6	32	25.3	<LOD	0.014	<LOD	0.031	<LOD	0.03	<LOD	<LOD	<LOD	0.66	<LOD	0.11	<LOD	0.20	<LOD	<LOD	<LOD	0.8	<LOD
502-01-A1-IS	4.6	7.5	0.28	<LOD	49.4	37	24.8	<LOD	0.013	<LOD	0.028	<LOD	0.04	<LOD	<LOD	0.05	1.04	<LOD	0.16	0.01	0.13	<LOD	0.02	<LOD	2.0	<LOD
505-04-D2-IS	5.4	7.3	0.53	<LOD	48.6	42	25.4	<LOD	0.014	<LOD	0.028	<LOD	0.03	<LOD	0.23	0.06	1.23	<LOD	0.28	0.44	0.08	<LOD	0.05	<LOD	<LOD	<LOD
505-04-A3-IS	11	6.2	5.85	<LOD	49.4	29	31.6	<LOD	0.013	<LOD	0.028	<LOD	0.04	<LOD	3.77	<LOD	0.64	0.10	2.03	0.01	0.20	0.6	0.29	<LOD	<LOD	<LOD
505-04-B2-IS	13	6.1	5.88	<LOD	48.7	27	31.4	<LOD	0.013	<LOD	0.028	<LOD	0.04	<LOD	3.90	0.06	0.64	<LOD	2.02	0.01	0.05	<LOD	0.12	<LOD	0.8	16
505-04-E1-IS	19	6.1	7.86	<LOD	46.9	30	33.5	<LOD	0.012	<LOD	0.029	<LOD	0.04	<LOD	4.93	1.62	0.85	3.42	2.59	1.39	0.23	6.9	0.28	9	<LOD	111
505-04-C3-IS	23	5.7	12.33	<LOD	46.7	21	38.2	<LOD	0.010	<LOD	0.025	<LOD	0.03	<LOD	4.43	0.64	0.69	2.85	2.66	0.38	0.02	4.9	0.03	10	<LOD	48
502-01-B2-IS	34	4.4	14.12	<LOD	47.1	31	41.5	<LOD	0.010	<LOD	0.028	<LOD	0.04	<LOD	7.46	0.10	0.77	0.69	3.57	0.21	0.02	3.0	0.07	7	2.1	43
502-01-A2-OB	4.2		0.02	<LOD	50.3	36	26.7	<LOD	0.014	<LOD	0.031	<LOD	0.03	<LOD	<LOD	<LOD	0.75	<LOD	0.06	<LOD	0.18	<LOD	0.03	<LOD	1.7	<LOD
505-04-D3-OB	5.1	7.2	0.44	<LOD	50.8	40	26.9	<LOD	0.015	<LOD	0.029	<LOD	0.03	<LOD	<LOD	0.39	1.31	0.27	0.21	0.58	0.01	<LOD	0.02	<LOD	<LOD	12
505-04-A2-OB	5.1	7.3	0.61	<LOD	51.3	41	27.8	<LOD	0.014	<LOD	0.031	<LOD	0.04	<LOD	<LOD	0.31	0.31	0.10	0.28	<LOD	0.03	<LOD	0.02	<LOD	<LOD	<LOD
505-04-D1-OB	10	6.3	4.65	<LOD	52.0	56	32.0	<LOD	0.014	<LOD	0.027	<LOD	0.03	<LOD	2.69	0.44	0.11	0.28	1.66	0.28	0.13	<LOD	0.05	<LOD	<LOD	26
502-01-B1-OB	12	6.3	4.73	<LOD	50.7	36	31.8	<LOD	0.013	<LOD	0.024	<LOD	0.03	<LOD	0.40	<LOD	<LOD	0.84	1.26	0.01	0.02	0.8	0.02	<LOD	<LOD	12
505-04-B1-OB	17	6.2	7.81	<LOD	49.0	26	34.8	<LOD	0.012	<LOD	0.022	<LOD	0.04	<LOD	0.70	<LOD	<LOD	1.26	1.44	<LOD	0.02	1.0	0.02	<LOD	<LOD	14
505-04-E2-OB	22	5.9	9.94	0.06	50.1	42	39.6	<LOD	0.012	<LOD	0.023	0.004	0.04	0.03	0.77	11.9	<LOD	40.1	1.50	2.02	<LOD	77	<LOD	36	<LOD	701
505-04-C2-OB	24	5.7	12.55	<LOD	48.4	31	40.7	<LOD	0.011	<LOD	0.024	<LOD	0.03	<LOD	0.99	<LOD	<LOD	1.38	1.40	0.08	0.02	1.7	<LOD	2	<LOD	<LOD
502-01-B3-OB	47	5.7	16.08	<LOD	47.9	32	46.3	<LOD	0.010	<LOD	0.021	<LOD	0.03	<LOD	1.88	0.08	<LOD	2.22	2.36	0.02	0.03	1.9	0.03	4	<LOD	22
502-01-A2-LF	4.2		0.12	<LOD	50.3	33	26.7	<LOD	0.014	<LOD	0.032	<LOD	0.03	<LOD	<LOD	<LOD	0.61	0.14	0.06	<LOD	0.18	<LOD	0.03	<LOD	2.6	<LOD
505-04-D3-LF	5.1		0.46	<LOD	50.8	58	27.0	<LOD	0.014	<LOD	0.033	<LOD	0.03	<LOD	<LOD	0.39	0.81	1.54	0.21	0.49	0.05	<LOD	0.02	<LOD	0.8	15
505-04-A2-LF	5.1		0.69	<LOD	51.3	53	27.8	<LOD	0.014	<LOD	0.030	<LOD	0.03	<LOD	<LOD	0.26	0.16	0.20	0.28	<LOD	0.16	<LOD	<LOD	<LOD	2.2	<LOD
505-04-D1-LF	10		4.44	0.09	52.0	206	32.2	0.4	0.013	0.0005	0.028	0.003	0.04	<LOD	<LOD	3.54	<LOD	1.24	1.38	0.83	0.02	1.6	<LOD	2	4.6	94
502-01-B1-LF	12		4.78	0.04	50.7	53	30.8	<LOD	0.013	0.0006	0.026	0.003	0.03	<LOD	<LOD	3.97	0.25	1.35	1.46	0.45	0.01	1.4	0.12	6	<LOD	24
505-04-B1-LF	17		7.66	0.26	49.0	58	35.1	0.4	0.011	0.0013	0.029	0.003	0.04	0.02	<LOD	5.37	<LOD	1.30	1.52	1.11	0.10	1.3	0.02	2	<LOD	24
505-04-E2-LF	22		9.41	0.63	50.1	74	36.6	1.4	0.011	0.0015	0.028	0.008	0.03	0.13	<LOD	92.2	<LOD	140	1.30	4.94	0.01	261	<LOD	111	<LOD	2330
505-04-C2-LF	24		12.03	0.90	48.4	84	41.9	0.6	0.008	0.0029	0.028	0.004	0.03	0.03	<LOD	9.20	<LOD	1.53	1.89	1.51	0.01	1.7	<LOD	3	<LOD	17
502-01-B3-LF	47		15.45	0.59	47.9	55	45.2	0.4	0.009	0.0025	0.028	0.003	0.04	<LOD	<LOD	12.0	<LOD	2.12	1.78	2.82	0.05	2.8	0.02	4	<LOD	27

substantial variability, likely exacerbated by inappropriate sampling methods and an insufficient number of samples for this study area (Kádár et al., 2005). Despite remarkable improvement in the technical means for deep-sea exploration and research over the past 20 years, most scientists perform on-board filtration (typically 0.45 μm) after retrieval of deep-sea samples (Von Damm et al., 1985; Sander et al., 2007; Bennett et al., 2008; Sarradin et al., 2009; Yücel et al., 2011), despite being aware of the potential alteration of the chemical speciation due to dramatic changes in temperature and pressure and/or chemical equilibrium.

Commonly used in surface-water sampling (Gimpel et al., 2003), *in situ* filtration can reduce this chemical alteration, potentially caused by precipitation and/or adsorption of some dissolved elements. Obviously, direct *in situ* measurements would provide the best representative data of the fluid chemistry in deep sea environment (Chin et al., 1994; Luther et al., 2001; Vuillemin et al., 2009), but only a few trace metals can be measured this way. Hence, there is an urgent need to evaluate the fractionation biases of *in situ* vs. *ex situ* filtration methods and to quantify these biases for various elements.

Several specialized samplers have been designed and employed in hydrothermal vents to collect dissolved and particulate samples for *in situ* filtration for various types of analyses (Huber et al., 2003; Taylor et al., 2006; Preston et al., 2011; Ussler et al., 2013), including the analysis of dissolved and particulate Fe (Kádár et al., 2005; Sarradin et al., 2008; Breier et al., 2009, 2014). However, there have been no comparison of results between *in situ* and *ex situ* sample processing methods.

Here, we provide new data from the hydrothermal mixing zone to evaluate the impact of the filtration method (*in situ* vs. *ex situ*) on the dissolved-particulate partitioning of 12 elements (Mg, Li, Mn, U, V, As, Ba, Fe, Zn, Cd, Pb and Cu). Kádár et al. (2005) also

explored this comparative approach, but did not quantitatively assess the particulate phase because only sweeping electronic microscopy was used to determine the chemical composition of particles. Furthermore, the alteration of the dissolved phase due to *ex situ* filtration was not estimated. Our first objective was to quantify the biases in the assessment of the dissolved and particulate phases potentially induced by *ex situ* filtration methods using *in situ* filtration as a baseline. For each studied metal, we then determined whether it is imperative to filter fluids *in situ* or whether *ex situ* filtration can be acceptable. Our data could guide future studies by indicating the bias introduced by *ex situ* filtration on the chemical speciation of metals.

2. Materials and methods

2.1. Study area

This study was conducted during the MoMARSAT 2012 cruise, on the French oceanographic research vessel *Thalassa* with the ROV Victor 6000. The cruise focused on deep-sea EMSO-Azores observatory maintenance (SEAMON E/W, Tempo and BOREL buoy) located within the Lucky Strike hydrothermal field, on the Mid-Atlantic Ridge (MAR) (37°17'N) (Colaço et al., 2011). In the Lucky Strike field, vent sites are distributed around a lava lake at depths of between 1650 and 1750 m (Fouquet et al., 1995). The maximum temperature recorded for the endmember fluid at this location is 324 °C (Charlou et al., 2000). Water samples were collected on a vent close to the hydrothermal edifice Tour Eiffel (37°17.29'N, 32°16.45'W). Samples were a colorless mixture of mid-temperature fluid (~70 °C) and cold seawater, the first part of the mixing likely occurring in subsurface, within the permeable shallow crust.

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