Sampling and analysis of the sea surface microlayer for dissolved and particulate trace elements

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Abstract

The air-sea interface, or sea surface microlayer (1-1,000 μm), is a unique environment with different physical, chemical, and biological properties compared to the underlying water column. It is an important, yet often ignored component in the biogeochemical cycling of trace elements in the marine environment due to the lack of trace element clean sampling and analysis methods. A novel technique, a hollow cylinder of ultra-pure SiO_2 (quartz glass) with a plastic handle, was developed to sample the microlayer for trace elements. This research also developed and optimized clean trace element techniques to accurately measure nine trace metals (Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) in the dissolved and particulate fractions of the microlayer and underlying water column. Preliminary data from a study in the Western Mediterranean Sea involving a mesocosm (*in situ* all plastic bag) showed consistent measurements in the trace element concentrations over the course of several days. Microlayer samples that were collected outside the mesocosm showed increased dissolved and particulate trace element concentrations resulting from a wet deposition event.

1. Introduction

The sea surface microlayer is a thin layer at the boundary between the ocean and the atmosphere, covering approximately 71 % of Earth's surface. The microlayer is a unique environment; its biological, chemical, and physical properties are very different from the underlying water column (Hardy, 1982, Cunliffe et al., 2013). The microlayer is dynamic in nature due to the numerous non-equilibrium processes such as irradiance, temperature fluctuation, salinity gradients, and wind and wave actions that influence its biogeochemical properties (Harvey, 1966). However, the microlayer is mechanically more stable than the water column below due to the surface tension created between water molecules and the high concentrations of surface-active organic compounds; creating a more rigid film-like layer over the surface of the ocean (Hardy, 1982; Wurl et al., 2009).

All material that enters the ocean from the atmosphere must pass through the microlayer (e.g. gas exchange, wet and dry deposition, Liss, 1975). These materials can then be altered through biological, chemical, and photochemical processes occurring in the microlayer before entering the ocean through dissolution, sinking and/or physical mixing. All material that leaves the ocean

to the atmosphere must also pass through the microlayer through bursting bubbles, evaporation, and wind generated aerosols (Blanchard, 1964). Finally, material from the underlying water interacts with the microlayer by bubble floatation and physical mixing, making this interface a very dynamic microenvironment.

While there have been recent advances in understanding the organic and biological content of the microlayer (e.g. Cunliffe et al., 2013), trace elements in the microlayer have received much less attention. Within the last ten years of microlayer research, only about 5% of the published articles ($n = 70$) involve trace elements. A major factor in this lack of research is the difficulty in cleanly sampling the microlayer for trace elements. The sampling techniques that have been used to sample the microlayer for trace elements (glass plate, rotating drum) can be difficult to clean initially and to keep clean during use. One of our goals was to develop a method that is inexpensive and easy to use while minimizing contamination during sampling of the microlayer.

Specifically, this paper describes the development of a microlayer sampling technique that is then used to study dissolved and particulate Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the microlayer. Some of these trace metals are micronutrients for biological activity (Mn, Fe, Co, Ni, Cu, Zn, Cd) while others are tracers of natural or anthropogenic deposition to the ocean (Al, Mn, Pb). All these metals are associated with aerosols and are therefore important for biogeochemical cycles in the open ocean. The trace elements studied in this research are also “key” trace elements for the international GEOTRACES program (<http://www.geotraces.org>).

2. Experimental

2.1. General information

All sample handling and analysis was done under Class-100 clean room conditions using “trace metal clean” techniques (e.g. Bruland et al., 1979). All equipment used for collection of seawater samples was acid-cleaned prior to use in the field. All acids used in sample analysis were prepared by sub-boiling distillation of the respective acid using a quartz glass still and ultra-high purity (UHP) deionized water ($>18 \text{ M}\Omega\cdot\text{cm}$).

2.2. Sea surface microlayer collection

The sea surface microlayer was sampled using a hollow quartz tube (length: 45 cm, diameter: 10 cm, surface area: 2,400 cm²; Technical Glass Products, Inc.) fitted with a polyethylene handle (Figure 1). A hollow tube was chosen over the more traditional glass plate because it is structurally more sound and less likely to break during transport to and from the field. Fused silica quartz was used in place of glass because it has lower trace element content. The polyethylene handle was fitted to the top of the tube using an indentation blown into the upper part of the cylinder. The handle eliminates the need to use a clamp or rope to deploy the sampler, and minimizes the risk of contamination since only the quartz tube comes in contact with the water.

The quartz tube is used for microlayer sampling in the same way as the glass plate method. Briefly, (1) the tube is dipped vertically into the water column until most of the surface area is submerged, (2) the tube is removed vertically from the water column at a slow rate (5 – 10 cm/s), and (3) the tube is held over a receiving bottle for the microlayer sample to drip off (Harvey and Burzell, 1972; Figure 2). The process is repeated until the desired volume of microlayer sample is acquired. A squeegee can be used to wipe the microlayer sample from the tube's outer surface however we did not use this technique in the present study because we were unable to avoid trace element contamination using either a silicone rubber or a Teflon squeegee.

The sampler was cleaned rigorously in the lab prior to use. It was transported to the field double-bagged in an acid-washed polyethylene pipette jar (60 cm, Scienceware) to prevent contamination during transport. The first three dips of the tube into the water column were discarded in order to condition the tube prior to collection.

2.3. Underlying water column collection

Samples of the bulk water underlying the microlayer were collected by submerging a capped sample bottle to approximately 30 cm depth wearing shoulder-length polyethylene gloves. After submerging the bottle, the cap is removed below the surface to allow the bottle to fill. The bottle is then re-capped before bringing the bottle out of the water. The bottle is first rinsed three times with underlying water using this procedure. The purpose of this technique is to avoid contaminating the underlying water samples with microlayer water that may be enriched in trace elements.

2.4 Sample filtration

Within an hour of collection, all samples (microlayer and water column) were filtered (150 to 200 mL) through 47mm 0.4 μm polycarbonate track-etched membrane filters by vacuum filtration using a polysulfone filtration apparatus (Pall). The seawater samples were acidified with 6 M quartz distilled HCl (q-HCl) to a final concentration of 0.024 M q-HCl and the filters were frozen until analysis.

2.5. Sample analysis

2.5.1. Dissolved trace element analysis

Dissolved trace elements were pre-concentrated by extraction using a cation exchange column prior to analysis by high resolution inductively-coupled plasma mass spectroscopy (HR-ICP-MS). The high salt content of seawater precludes direct analysis of the samples using ICP-MS. The concentrations of dissolved trace metals in the oceans can also be very low, often near the detection limits of the ICP-MS instrument. Using column extraction, the salinity matrix is eliminated and the trace metals are concentrated by a factor of 12.

A detailed description of the method can be found in Milne et al. (2010). Briefly, 12 mL of each acidified seawater sample is spiked with a mixed element standard of the following isotopes: ^{57}Fe , ^{62}Ni , ^{65}Cu , ^{68}Zn , ^{111}Cd , and ^{207}Pb ; all greatly enriched over natural abundance. Standard additions of a mixed Al, Mn, and Co solution were added to individual 12mL sub-samples of the same sample. The samples were UV oxidized for 1.5 hours prior to extraction to oxidize Co and Cu binding ligands. The samples were then buffered offline to a pH of 6.4 ± 0.2 using NH_4Ac (final acetate concentration of 0.14 M). The samples were extracted using a $\sim 200 \mu\text{L}$ column of Toyopearl AF-Chelate-650M resin. After pumping the sample through the column, the resin was rinsed with 1mL of UHP water to rinse out the remaining seawater. The trace elements were then eluted from the column with 1mL of 1.0 M q- HNO_3 . The samples were analyzed using a Thermo Scientific Element 2 (E2) HR-ICP-MS. The concentrations of Fe, Ni, Cu, Zn, Cd, and Pb were calculated using a standard isotope dilution equation and the concentrations of Al, Mn, and Co were calculated using the slopes of the standard additions curves.

2.5.2. Particulate trace element analysis

The filters were analyzed for “labile” and “refractory” particulate trace elements. The labile fraction treatment was designed to quantify trace metals that can potentially be released from the suspended particulate matter and become bioavailable (Koçak et al., 2007). The refractory fraction would include trace metals in the mineral matrix of the suspended matter and all other unreactive phases.

The filters were leached using a weak acid and reducing agent scheme proposed by Berger et al. (2008) to solubilize the labile fraction. The filters were folded and placed into 15 mL centrifuge tubes and 5 mL of 4.4 M q-HAc with 0.02 M hydroxylamine hydrochloride (HH) was added to each tube to submerge the filter. The centrifuge tubes were then heated for 10 minutes in a 90°C water bath. The heating step was proposed to solubilize biogenic trace metals by denaturing intracellular proteins associated with phytoplankton (Berger et al., 2008). The samples were then left at room temperature for 12-16 hours (overnight). Finally, the samples were centrifuged and the acetic acid leach was decanted into a subsample bottle. To rinse the filter, one 5 mL aliquot of UHP water was added to the tube, centrifuged again, and then decanted into the subsample bottle. The samples were then diluted 5 times (final acetate concentration of 0.44 M) and analyzed using the E2 HR-ICP-MS. The trace metal concentrations were calculated based on the slopes of external calibration standards prepared in the same leaching solution matrix.

After the filters were leached, the remaining particulate matter was digested using microwave digestion to dissolve the refractory fraction (Ho et al., 2011; Upadhyay et al., 2009). Briefly, the filters were placed in 20 mL microwavable Teflon tubes (CEM) and 3.8 mL of concentrated (15.8 M) q-HNO₃ and 0.2 mL of concentrated (8.8 M) *Optima* H₂O₂ (4 mL total volume) were added to the Teflon tubes to submerge the filters. The samples sat overnight (12-16 hours) to minimize the pressure from CO₂ and NO fumes that would be generated during microwave digestion (Upadhyay et al., 2009). The filters were then digested in a MARS Xpress microwave oven (CEM) at 180°C for 20 minutes with a 10 minute ramp from room temperature to 180°C. After digestion, the samples were poured into 15 mL Teflon jars. The microwave tubes were rinsed three times with 2 mL of UHP water and each rinse aliquot was added to the 15 mL Teflon jars with the samples. The 15 mL Teflon jars were then placed on a hot plate at 80°C and the samples were dried down overnight (12-16 hours). Once dry, the final residue was re-dissolved in 0.32 M q-HNO₃ for analysis. The samples were analyzed using the E2 HR-ICP-MS.

The trace metal concentrations were calculated based on the slopes of external calibration standards prepared in the same acid matrix.

2.6. Analysis of certified reference materials

In order to determine the accuracy of the dissolved trace element analysis, surface (~10 m, SAFe-S1) and deep (1000 m, SAFe-D2) seawater samples from the SAFe inter-comparison project (Johnson et al., 2007) were analyzed with every set of extractions. To determine the accuracy and precision of the refractory particulate digestion, the sediment standard reference material NIST-2704 (Buffalo River Sediment) was analyzed in triplicate. In addition, Arizona Test Dust (ATD, <3 µm, Powder Technologies) was analyzed in triplicate to compare to other laboratories involved in an inter-comparison project (Morton et al., 2013).

2.7. Microlayer and subsurface water sampling

Sea surface microlayer and underlying water column samples were collected *in situ* from the Bay of Villefranche. The sampling location (43.69611°N, 7.31639°E) is characterized by a semi-enclosed embayment with a steeply descending slope to the seafloor (~ 100 m). The circulation within the bay is mainly influenced by the Liguro-provençal current which flows counterclockwise along the French Riviera (Millot, 1999). This current continuously flushes the bay with offshore water, making the bay oligotrophic. Sample collection took place in the middle of the bay off of a platform made of plastic cubes on October 18 and 21, 2011. Microlayer and water column samples were taken from inside an all plastic mesocosm on these two days as well. The mesocosm (described in detail in Guieu et al., 2010) was set up in the bay for preliminary tests for the Mediterranean Sea Acidification in a Changing Climate (MedSeA) campaigns that occurred in summer 2012 and winter 2013 (Gazeau et al., *submitted*). The mesocosm had a plastic roof to eliminate any atmospheric deposition from entering.

3. Results

3.1. Sea surface microlayer thickness

Samplers such as the bursting bubble method can produce very thin sea surface microlayer samples (0.5 to 1 µm, MacIntyre, 1968) whereas the screen method collects relatively thicker microlayer samples (100 to 540 µm, Garrett, 1965). The range in microlayer thickness is

therefore operationally defined as 1 to 1,000 μm due to the wide range collected with the difference sampling techniques (Hardy, 1982). The thickness of the microlayer collected with a glass plate is based on the volume collected and the surface area of the plate. The thickness sampled (δ) is calculated using the following equation:

$$\delta = \frac{V}{An} \quad (1)$$

where V is the sample volume, A is the surface area of the sampling device, and n is the number of dips to acquire the sample volume (Zhengbin et al., 2006).

The average microlayer thickness from the quartz tube sampler was $40 \pm 4 \mu\text{m}$ (range 31 to 48 μm ; $n=115$). This value agrees well with the actual thickness of the microlayer determined by microelectrode in Zhang et al. (2003). On average, each dip of the quartz tube recovered approximately 10 mL of microlayer sample. The variability was related to the speed with which the quartz tube sampler was pulled through the microlayer.

3.2. Blank measurements associated with the quartz tube sampler

While the fused quartz glass tube was expected to introduce lower levels of trace element contamination, it was still thoroughly tested before use. After vigorous acid washing using 0.5M q-HCl and thorough rinsing with UHP water, 100 mL of a low concentration acidified (0.024M HCl, pH ~1.8) surface seawater sample was slowly poured over the surface of the quartz tube and collected for analysis. The concentrations of each trace element added to the seawater sample from the quartz tube are summarized in Table 1. Concentrations for most elements showed good agreement with the seawater that had not come into contact with the quartz tube. Only Zn and Cd concentrations showed significant increases; $0.179 (\pm 0.074) \text{ nM}$ and $0.0025 (\pm 0.0004) \text{ nM}$, respectively. However, this test should over-estimate the leaching of trace metals from the quartz tube since the seawater was acidified to pH ~ 1.8 whereas *in situ* seawater normally ranges between 8.0 and 8.2. The lower pH is expected to leach higher amounts of trace elements from the quartz tube compared to what might be expected from actual field use of the sampler. Overall, the quartz tube contributed relatively minor concentrations of trace metals considering the concentrations (~nM) that might be expected in the microlayer in coastal waters and therefore were not subtracted from sample concentrations.

3.3. Dissolved trace elements

3.3.1. Blank measurements and limit of detection

Blank measurements for the extraction and analysis of the microlayer and underlying water samples were performed in the same fashion as described in Milne et al. (2010). The measurement is the sum of the buffer blank and the blank signal associated with the extraction manifold, the elution acid, and the ICP-MS analysis. Briefly, the ammonium acetate buffer blank (4 aliquots, 600 μ L) was spiked with the I.D. spike (100 μ L). Standard additions were performed on three of the aliquots to determine Al, Mn, and Co concentrations. All aliquots were acidified to 1.0 M q-HNO₃ with concentrated q-HNO₃ and UHP water for an equal volume of each volume (1 mL). A similar set of blanks were performed replacing the buffer with UHP water. These UHP blanks were then subtracted from the buffer signal to acquire just the contribution associated with the NH₄Ac. The second blank was acquired from an elution cycle over the extraction column using the 1.0 M q-HNO₃ elution acid. The eluent was spiked with the I.D. spike afterwards. Table 2 shows the average blank determined during a typical set of extractions. This blank was subtracted from all samples. Table 2 also shows the limit of detection based on three times the standard deviation of this blank measurement.

3.3.2. Analysis of Consensus Reference Seawater

The accuracy of the seawater extraction method was shown by extracting the SAFe S and SAFe D2 seawater CRMs with every set of extractions. The results are summarized in Table 3. The average concentrations of each element were calculated for approximately 20 separate sets of extractions. Overall, there is good agreement between the concentrations determined in this study and the consensus values. For the SAFe S CRM, Co was not quantified since our limit of detection was higher than the consensus value. The Cd concentrations were higher than the consensus value by approximately 2 pM. At such low concentrations, it is hard to interpret why our concentrations were slightly higher than the consensus values, or whether the difference was statistically significant. For the SAFe D2 CRM, Ni was consistently lower in concentration compared to the consensus value but was still within 10% RSD.

3.4. Particulate trace elements

3.4.1. Blank measurements and limit of the detection

Blank measurements for the analysis of the suspended particulate matter samples were performed by leaching and digesting unused acid-washed filters using the methods described in section 2.5.2. Table 4 shows the average blanks for both the labile and refractory fractions. These blanks were subtracted from the samples. Table 4 also shows the limits of detection for the labile and refractory fractions based on three times the standard deviation of the blank measurements.

3.4.2. Analysis of Certified and Consensus Reference Materials

There is currently no suspended particulate matter standard reference material, especially for the labile fraction, and therefore no way to conclusively demonstrate the accuracy or selectivity of the leaching treatment. However, certain trace elements can serve to demonstrate that very small amounts of refractory trace elements were solubilized using the labile fraction leaching procedure. Elements such as Ti and Zr are often associated with refractory particulate phases, especially when atmospheric dust (aluminosilicates in particular) is the source material (Yigiterhan et al., 2011) and are not associated with Fe and Mn oxides that often form on the surfaces of particles in seawater (Jenne, 1968; Tessler et al., 1979). Therefore, both elements can be used to show that the leaching scheme does not solubilize significant amounts of the refractory trace elements. For all Bay of Villefranche samples that were leached for this particular experiment, the average fractional solubilities of Ti and Zr ($n = 8$) were 0.34% and 0.008%, respectively. For comparison, the average solubilities of Mn and Fe for the same set of samples were 50% and 8.3%, respectively.

The accuracy of the refractory digestion method was shown by digesting NIST-2704 SRM (Buffalo River Sediment). The results are summarized in Table 5. Overall, there is good agreement between the trace element concentrations measured in this study and the certified values. The average Fe concentration was slightly higher than the consensus value and the average Cu and Zn concentrations were slightly lower than the consensus value, however, all three were within $\pm 15\%$ RSD of the certified concentrations. Digestions of Arizona Test Dust (ATD) were also conducted using this method to help build a database to create a consensus reference material for the trace elements of interest (Shelley et al., *in press*). These results are also shown in Table 5.

3.5. Application of the microlayer sampling method – Bay of Villefranche

The dissolved and particulate (labile and refractory) concentrations of Al, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the sea surface microlayer and underlying water column are presented in Table 6 and Figure 3 (excluding Ni). In our experience, Ni data from the Element 2 ICP-MS are occasionally unreliable. Without replicate samples from the mesocosm experiment, we cannot resolve the apparent discrepancies in the dissolved and particulate Ni data. The Ni data are reported in Table 6, but will not be discussed. Concentrations are shown for two days inside the mesocosm and outside the mesocosm. With the exception of Al and Fe, the elements are predominantly found in the dissolved fraction for all samples. Al and Fe are predominantly in the refractory particulate fraction, indicating that they are associated with mineral dust particles.

The total trace element concentrations inside the mesocosm did not change significantly for most metals over the two sampling days. Al, Mn, Fe, Co, Cd, and Pb showed no significant increase or decrease from Oct. 18 to Oct. 21 in the microlayer. With the exception of Co, the same elements did not show a significant increase or decrease from Oct. 18 to Oct. 21 in the water column. Co, Cu, and Zn showed more of a change ($\sim \pm 2$ times) in the microlayer and water column between the two sampling days.

When the total concentration is broken down into dissolved and particulate fractions, some patterns emerge. For example, Figure 3b (top panel) shows the dissolved and particulate concentrations of Fe in the microlayer and water column of the mesocosm on the two sampling dates. The dissolved Fe concentrations increased both in the microlayer and water column between Oct. 18 and Oct. 21 while the particulate Fe concentrations decreased. The fact that there are only slight differences between the two days, especially in the enriched particle concentration found in the microlayer, suggests that the conditions inside the mesocosm were relatively stable.

Outside the mesocosm, the total trace element concentrations did change significantly for most metals over the two sampling days (Table 6, Figure 3). Al, Mn, Fe, Co, Cu, Zn, and Pb showed a factor of 2-7 increase in concentration from Oct. 18 to Oct. 21 in the microlayer. Al, Fe, Co, Cu, Zn, and Pb showed more modest increases (~ 2) in concentration from Oct. 18 to Oct. 21 in the

water column. The only element that showed no difference between the two days in both the microlayer and water column was Cd.

Again, breaking down the total concentration into dissolved and particulate fractions further shows this pattern of increased concentrations on the second sampling day. For example, Figure 3b (bottom panel) shows the dissolved and particulate concentrations of Fe in the microlayer and water column outside the mesocosm on the two sampling dates. The dissolved and particulate Fe concentrations dramatically increased (factor of 6 for both) in the microlayer between Oct 18 and Oct 21. The dissolved and particulate Fe concentrations also increased (factor of 2 for both) in the water column between Oct. 18 and Oct. 21. The large increase could be coming from an atmospheric deposition event. It rained Oct. 19, which could easily introduce both dissolved and particulate Fe to the water column. The fact that the microlayer concentrations were much higher than the water column again suggests that particles in the microlayer had a retention time on the order of 1-2 days in this case. The wind speeds during and after the rain event were 3 to 4 m s⁻¹ so little mixing of the microlayer would have occurred.

In the microlayer outside the mesocosm, dissolved Fe, Cu, and Zn increased by factors of 3-5, while dissolved Al and Pb increased by factors of 2-3. The refractory particulate Al, Mn, Fe, Co, Cu, and Pb increased by up to a factor of 23, while the increases in particulate Zn, and Cd were less pronounced but still significant. These higher dissolved and particulate concentrations in the microlayer after the rain event were reflected in elevated enrichment factors (relative to the underlying water column) for dissolved Al, Fe, Cu, and Zn and very high enrichment factors for particulate Al, Mn, Fe, Co, Cu, Zn, Cd, and Pb (discussed below).

Wet deposition events have been shown in other studies to dramatically alter the microlayer. Lim et al. (2007) reported load factors (concentrations after wet deposition compared to concentrations before) up to 43 for dissolved polycyclic aromatic hydrocarbons (PAHs) and up to 337 for particulate PAHs. Wurl and Obbard (2005) found elevated concentrations of various persistent organic pollutants (POPs) up to 50 times in the microlayer compared to the underlying water column.

Perhaps because of the plastic cover over the mesocosm, the rain event did not have a significant impact on the concentrations and enrichment factors for dissolved or particulate trace elements

with the possible exceptions of dissolved Zn, and particulate Cu, and Zn. Until we have had an opportunity to conduct more sampling with these mesocosms, we do not want to speculate too much on the processes that resulted in modest increases and decreases in the mesocosm concentrations from Oct. 18 to Oct. 21. In general, it was encouraging that concentrations of dissolved and particulate trace elements in the microlayer and underlying water in the mesocosm did not vary too much from day to day.

Microlayer data are often reported in terms of enrichment compared to the underlying water column in the literature (eg. Antonowicz and Trojanowski, 2010; Cuong et al., 2008; Duce et al., 1972). Table 7 shows the enrichment factors for the nine elements of interest in the dissolved and total particulate (labile + refractory) fractions in the microlayer. Enrichment factors (EF) are calculated by the following equation:

$$EF = \frac{[M]_{SML}}{[M]_{UWC}} \quad (2)$$

where $[M]_{SML}$ is the concentration of a particular trace metal in the sea surface microlayer and $[M]_{UWC}$ is the concentration of that same trace metal in the underlying water column.

The total particulate enrichment factors for all elements showed enrichment in the microlayer ($EF > 1$) on all days both inside and outside the mesocosm, demonstrating that particles were consistently enriched in the microlayer. Other studies have shown consistent enrichment in the microlayer for particulate trace elements as well (Brügmann et al., 1992; Cuong et al., 2008; Hardy et al., 1990). However, there is a large range in enrichment factors for the dissolved fraction. Elements such as Al and Fe showed slight depletion in the microlayer ($EF < 1$) for both days inside the mesocosm and October 18, 2011 outside the mesocosm yet showed enrichment on October 21, 2011 outside the mesocosm after the rain event. Elements such as Cd and Pb showed slight enrichments in the microlayer for all days both inside and outside of the mesocosm.

4. Conclusions

The sea surface microlayer is an important yet often ignored component in the biogeochemical cycling of trace elements in the marine environment. The main reason for this is the difficulty in cleanly sampling and analyzing the microlayer. This research developed and optimized trace

element clean techniques to accurately measure nine dissolved and particulate trace elements in the microlayer. The quartz tube sampler can easily be transported to and from the field and can be used to sample the microlayer from any floating platform or small boat. Finally, *in situ* samples taken during a preliminary study illustrate the dynamic and complex nature of the sea surface microlayer. Now that the microlayer can be sampled for trace elements relatively easily, more experiments are needed to start to understand the processes and mechanisms occurring within this critical environment.

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Figure Captions

Figure 1: The hollow quartz tube and all plastic handle microlayer sampling device.

Figure 2: (a.) Immersion, (b.) withdrawal, and (c.) collection of microlayer samples using the hollow quartz tube.

Figures 3a and 3b: Dissolved (red), labile particulate (black), and refractory particulate (light blue) Al (a.) and Fe (b.) concentrations of the sea surface microlayer (SML) and underlying water column (UWC) in the Bay of Villefranche inside the mesocosm (top panels) and outside the mesocosm (bottom panels). Samples are from October 18 and 21, 2011. All concentrations are in nM.

Figures 3c and 3d: Dissolved (red), labile particulate (black), and refractory particulate (light blue) Mn (c.) and Co (d.) concentrations of the sea surface microlayer (SML) and underlying water column (UWC) in the Bay of Villefranche inside the mesocosm (top panels) and outside the mesocosm (bottom panels). Samples are from October 18 and 21, 2011. All concentrations are in nM.

Figures 3e and 3f: Dissolved (red), labile particulate (black), and refractory particulate (light blue) Cu (e.) and Zn (f.) concentrations of the sea surface microlayer (SML) and underlying water column (UWC) in the Bay of Villefranche inside the mesocosm (top panels) and outside the mesocosm (bottom panels). Samples are from October 18 and 21, 2011. All concentrations are in nM.

Figures 3g and 3h: Dissolved (red), labile particulate (black), and refractory particulate (light blue) Cd (g.) and Pb (h.) concentrations of the sea surface microlayer (SML) and underlying water column (UWC) in the Bay of Villefranche inside the mesocosm (top panels) and outside the mesocosm (bottom panels). Samples are from October 18 and 21, 2011. All concentrations are in nM.

Table 1: Contamination check after pouring acidified surface seawater over quartz tube. All average concentrations (± 1 S.D.) are in nM (n = 3).

	Al	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Surface SW	0.977 (0.028)	0.995 (0.086)	0.269 (0.031)	0.0035 (0.0003)	1.97 (0.05)	0.53 (0.04)	0.210 (0.030)	0.0019 (0.0003)	0.044 (0.0003)
Quartz Tube	1.20 (0.75)	1.11 (0.12)	0.283 (0.003)	0.0039 (0.0007)	1.96 (0.01)	0.58 (0.17)	0.389 (0.068)	0.0044 (0.0002)	0.041 (0.002)

Table 2: Trace element blanks and limit of detection associated with dissolved fraction extraction and analysis. All average concentrations (± 1 S.D.) are in nM (n = 5).

	Al	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Mean blank	3.10 (0.18)	0.035 (0.002)	0.083 (0.011)	0.010 (0.003)	0.032 (0.002)	0.018 (0.004)	0.172 (0.014)	0.0065 (0.0006)	0.0013 (0.0001)
Limit of Detection (3 S.D.)	0.538	0.006	0.033	0.009	0.006	0.012	0.042	0.002	0.0003

Table 3: Validation results of dissolved fraction seawater reference material SAFe S1 and D2. All average concentrations (± 1 S.D.) are in nM (n = 50).

	Al	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
SAFe S1	1.77 (0.17)	0.80 (0.10)	0.099 (0.009)	<0.009 ^a	2.22 (0.19)	0.51 (0.04)	0.069 (0.006)	0.0031 (0.0003)	0.044 (0.002)
SAFe S1 consensus values	1.71 (0.10)	0.81 (0.06)	0.095 (0.008)	0.0049 (0.0012)	2.34 (0.09)	0.53 (0.05)	0.071 (0.010)	0.0011 (0.0003)	0.049 (0.002)
SAFe D2	1.17 (0.06)	0.35 (0.08)	0.908 (0.094)	0.0435 (0.0031)	7.89 (0.44)	2.25 (0.23)	7.17 (0.43)	1.040 (0.069)	0.026 (0.002)
SAFe D2 consensus values	1.06 (0.09)	0.36 (0.05)	0.956 (0.024)	0.0468 (0.0030)	8.85 (0.26)	2.34 (0.15)	7.62 (0.26)	1.011 (0.024)	0.028 (0.002)

^a Value less than detection limit.

Table 4: Trace element blanks and limit of detection associated with the particulate fraction leaching (labile) and digestion (refractory). All average concentrations (± 1 S.D.) are in nM (n = 5).

	Al	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Labile blank	1.69 (0.05)	0.012 (0.002)	0.119 (0.031)	0.0016 (0.0004)	0.009 (0.002)	0.056 (0.009)	0.165 (0.006)	0.0011 (0.0001)	0.0010 (0.0001)
Labile LOD (3 S.D.)	0.158	0.006	0.094	0.0013	0.005	0.028	0.018	0.0004	0.0003
Refractory blank	3.62 (0.15)	0.062 (0.003)	1.42 (0.26)	0.012 (0.001)	1.30 (0.05)	0.058 (0.011)	0.236 (0.022)	0.0021 (0.0002)	0.0026 (0.0008)
Refractory LOD (3 S.D.)	0.454	0.008	0.783	0.003	0.151	0.034	0.065	0.0006	0.0024

Table 5: Validation results of particulate fraction sediment reference material 2704 and values for Arizona Test Dust (ATD). Al and Fe average concentrations (± 1 S.D.) are in Wt. % and Mn, Co, Ni, Cu, Zn, Cd, and Pb average concentrations (± 1 S.D.) are in $\mu\text{g g}^{-1}$ (n = 3).

	Al	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
BRS2704	6.24 (0.21)	598 (6)	4.27 (0.35)	12.6 (0.6)	40.3 (5.2)	80.9 (11.6)	362 (26)	3.55 (0.10)	158 (8)
BRS2704 consensus value	6.11 (0.16)	555 (19)	4.11 (0.10)	14.0 (0.6)	44.1 (3.0)	98.6 (5.0)	438 (12)	3.45 (0.22)	161 (17)
ATD (this study)	7.24 (0.12)	759 (14)	3.36 (0.68)	14.0 (0.7)	19.2 (6.0)	29.3 (8.2)	117 (13)	0.485 (0.091)	33.8 (1.1)
ATD (Shelley) ^a	6.96 (1.87)	764 (12)	3.36 (0.60)						
ATD (Murray) ^a	6.91 (1.21)	728 (10)	3.23 (0.52)						

^aShelley et al. *in press*.

Table 6: Dissolved, labile particulate, and refractory particulate concentrations of trace elements in the sea surface microlayer (SML) and underlying water column (UWC) in the Bay of Villefranche. All concentrations are in nM.

Mesocosm	Date	Sample	Al	Mn	Fe	Co	Ni ^a	Cu	Zn	Cd	Pb
Dissolved											
Inside	10/18/2011	SML	36.1	7.16	3.32	0.262	3.31	4.93	7.88	0.077	0.383
		UWC	46.6	7.52	3.95	0.242	3.29	4.48	5.83	0.064	0.300
	10/21/2011	SML	40.0	7.34	4.87	0.283	6.70	5.97	10.2	0.080	0.410
		UWC	50.4	6.98	6.01	0.173	3.19	11.1	16.7	0.066	0.370
Outside	10/18/2011	SML	27.4	5.67	3.45	0.168	3.16	3.90	4.93	0.070	0.208
		UWC	45.2	6.14	4.33	0.162	3.23	3.72	4.97	0.063	0.168
	10/21/2011	SML	73.9	7.11	19.4	0.219	3.40	16.8	15.3	0.076	0.456
		UWC	50.3	6.69	6.75	0.265	6.63	5.33	8.67	0.068	0.366
Labile											
Inside	10/18/2011	SML	6.69	0.307	5.55	0.0058	0.052	0.230	1.01	0.0039	0.0325
		UWC	1.04	0.085	1.02	<0.0013 ^b	0.008	0.095	0.221	0.0006	0.0034
	10/21/2011	SML	7.37	0.314	7.11	0.0078	0.047	0.358	1.37	0.0010	0.0252
		UWC	1.40	0.139	2.05	0.0017	1.06	0.074	0.192	0.0012	0.0085
Outside	10/18/2011	SML	2.33	0.153	1.98	0.0022	0.019	0.179	0.272	0.0009	0.0073
		UWC	1.70	0.173	2.17	<0.0013 ^b	0.009	0.088	0.170	<0.0004 ^a	0.0073
	10/21/2011	SML	7.24	0.524	13.6	0.0065	0.010	1.06	0.844	0.0010	0.0788
		UWC	3.56	0.330	7.17	0.0021	0.016	0.370	0.418	0.0006	0.0262
Refractory											
Inside	10/18/2011	SML	187	0.511	75.5	0.019	1.01	0.205	1.13	0.0087	0.0129
		UWC	30.0	0.076	19.5	0.006	0.318	0.813	0.848	0.0018	<0.0024 ^b
	10/21/2011	SML	240	0.542	67.2	0.026	2.33	2.11	2.04	0.0036	0.0240
		UWC	44.3	0.054	12.1	0.006	0.467	0.083	0.365	0.0013	<0.0024 ^b
Outside	10/18/2011	SML	122	0.163	38.8	0.008	0.962	0.239	0.774	0.0038	0.0081
		UWC	106	0.104	29.8	0.008	0.333	0.230	0.709	0.0024	0.0050
	10/21/2011	SML	976	1.33	225	0.070	1.29	5.45	2.75	0.0074	0.0921
		UWC	209	0.169	46.0	0.012	0.548	0.327	0.871	0.0008	0.0090

^a Ni data may be unreliable. See text for explanation.

^b Value less than detection limit.

Table 7: Enrichment factors of dissolved and total particulate (labile + refractory) in the Bay of Villefranche.

Mesocosm	Date	Al	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Dissolved										
Inside	10/18/2011	0.78	0.95	0.84	1.08	1.01	1.10	1.35	1.22	1.27
	10/21/2011	0.79	1.05	0.81	1.63	2.10	0.54	0.62	1.21	1.11
Outside	10/18/2011	0.61	0.92	0.80	1.04	0.98	1.05	0.99	1.11	1.24
	10/21/2011	1.47	1.06	2.88	0.83	0.51	3.15	1.77	1.10	1.25
Total Particulate										
Inside	10/18/2011	6.24	5.08	3.95	4.13	3.26	0.48	2.00	5.25	13.4
	10/21/2011	13.5	4.44	5.25	4.39	1.56	15.7	6.12	1.84	5.79
Outside	10/18/2011	1.15	1.14	1.28	1.28	2.87	1.31	1.19	1.96	1.25
	10/21/2011	4.63	3.72	4.49	5.43	2.30	9.34	2.79	6.00	4.86

Figure 1

Figure 2

Figure 3