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# 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 (1–1000 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 analytical 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 difficultly 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

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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 MΩ∗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: 2400 $cm^2$; Technical Glass Products, Inc.) fitted with a polyethylene handle (Fig. 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; Fig. 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 47 mm 0.4 μm

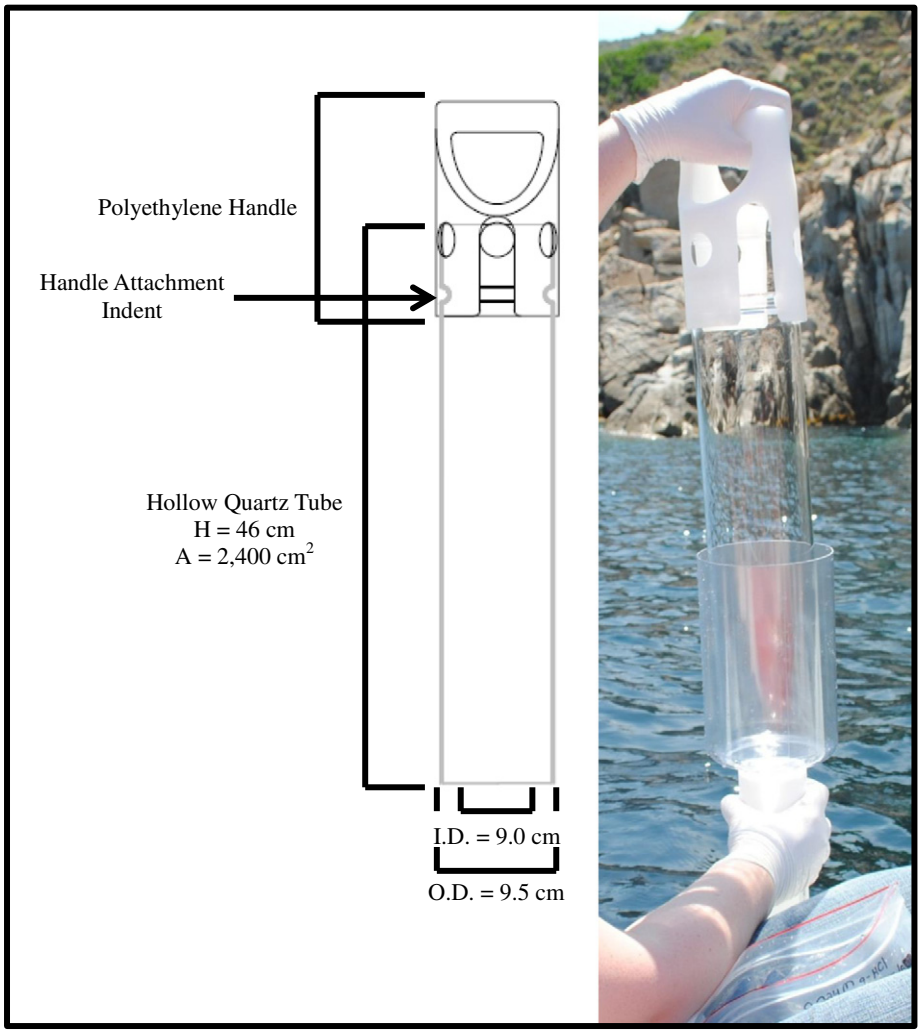


**Fig. 1.** The hollow quartz tube and all plastic handle microlayer sampling device.