Numerous trace elements are variable in ocean surface waters on time scales ranging down to days. Some metals (Pb, Fe, Al,...) (Boyle et al., 1986; Savoie et al., 1989; Young et al., 1991) are variable because they are delivered sporadically from the atmosphere, while other metals (Cd, Zn, ...) may vary rapidly due to pulses of vertical mixing, upwelling, and biological activity. The passage of ocean eddies and biological patchiness may also contribute to metal variability. To evaluate the biological consequences of Fe fertilization under conditions of "natural experiments" and eliminate aliasing as a factor in assessing the long-term evolution of the anthropogenic Pb emission experiment, we need to have measurements on the temporal variability of metals on time scales ranging down to a few days. We have developed a device which can collect 500 ml trace-metal-clean samples on a standard 3-m buoy surface mooring. Actual water samples have the advantage that multiple properties can be measured, drift and calibration is not at issue, and it is possible to archive samples for many years allowing for measurements of other properties in later years.
Mechanical and electronic design of the sampling units focused on the following goals and criteria:

- Trace-metal clean materials; easy to clean
- Sample bottle is well-flushed before sealing
- Simple mechanical operation
- Redundancy of electromechanical parts to minimize consequences of failure
- Withstands stresses of extended (6-12 month) deployment at any depth
- Easy to join in a variety of configurations
- Reliably deployed on standard moorings at no risk to mooring

The basic function of this instrument is to open and close (under program control) trace-metal clean sample bottles (initially filled with dilute acid) in an environment free from metal contaminants.

**Basic operating principle:** The instrument consists of a colony of independent sampling modules mounted onto a durable mooring unit. Each sample module is designed to function independently during deployment, so that failure of any one module does not prevent any other unit from functioning. For maximum flexibility, the units are capable of inter-module communication and external event-driven triggering. A timer-controlled DC motor opens and closes clean polyethylene bottles filled with dilute (1N) high purity HCl. The bottles are opened by simple rotary motion using an internal hex-shaft coupling to a sample holding cup matched to the bottle thread spacing. The low-density dilute acid within the bottles is replaced by denser seawater through passive density-driven flow. Mixing during this process
ensures that the bottle is effectively flushed with several volumes of seawater, with additional flushing from water motion relative to the sampler. Tests show that complete replacement occurs within a few minutes. The timer then reverses the motor, closing and sealing the bottle until recovery.

**Sample preservation:** Samples are preserved by diffusion of dilute acid retained in a diffusion chamber contained within the bottle. The diffusion chamber is constructed of a 5 ml volume high-purity fluorocarbon container which has five small pinholes in its cap and which is exhaustively hot-acid-leached before use. When the sample bottle is opened, the dilute 1N acid contained within it rapidly exchanges with the external seawater, being fully replaced within 5-10 minutes (flushing is verified for all samples by measuring their salt content). The acid in the diffusion chamber cannot exchange rapidly during this brief sampling interval because of restricted flow through the pinholes. But over a longer period of several days, the acid mixes out of the diffusion chamber and into the sample bottle, preserves the sample. Although the sample bottle is carefully cleaned by normal acid-leaching techniques before use, the storage of the 1N HCl in the bottle as it awaits triggering allows for further acid leaching right up to the moment of sample collection, allowing maximum freedom from bottle contamination (99% of any additional bottle contamination released during this period will be removed from the sample bottle when it is opened). It should be noted that this procedure results in a sample for “total metal” (if direct plasma analysis is used) or “total dissolvable metal” (if chemically extracted before analysis).

**Mechanical Design:** For trace metal cleanliness, the entire exterior of the unit in the vicinity is constructed from ultra-high molecular weight polyethylene (UHMW). The mooring attachment uses carbon-black UMHW so as to provide minimal interference with optical instrumentation on the mooring. The individual sample modules snap together in two dimensions; the most compact grouping places six units in a hexagonal array around a central polyethylene-encased stainless steel mooring pin, and stacks these arrays vertically on two levels. Each sample module has a sealed liquid-filled interior chamber which houses the motor, electronics, and batteries. The filling liquid is Fluorinert™, a non-conducting, non-flammable, relatively volatile fluid. A bellows on each unit allows for pressure compensation between the inside and outside, hence minimizing the potential for leakage of seawater into the interior. Because the electronics are viable at high pressures and operate in this nearly incompressible fluid, there is no need for a pressure case (the units have been deployed for short term deployments down to 5000 m), although batteries should be enclosed to prevent leakage of electrolyte upon depressurization. The 500 ml sample bottles contained within each module are opened by simple rotation. We have used polyethylene, polymethylpentene (PMP), and FEP fluropolymer bottles. Polyethylene is good for most purposes, but not for Al which is contaminated by the AlCl₃ catalyst used in polymerization. PMP has proven satisfactory for Al, Fe, and Pb, but is not yet tested for other metals, and teflon is good for everything tested to date (but is expensive). The bottles could be replaced by screw-cap bottles of other materials of similar geometry. The internal motor rotates a rod, sealed by with a silicone grease lubricated quad-ring within the smooth shaft main body, attached to a splined (hexagonal) shaft through a silicone grease lubricated quad-ring. The bottle holder has the same screw pitch as the bottle cap. The small size of each unit and its components allows the entire exterior portion of unit (or its component parts) to be cleaned and acid-leached to ensure trace metal cleanliness.
The unit’s component parts are small and easily machined with computer-controlled equipment found in a basic machine shop. This characteristic lowers the cost of constructing the sampler, and makes it possible for researchers to build (and modify) their own units.

**Electronics Design:** As part of the modular redundant design, each sampling unit has its own motor, electronics, and batteries. The electronics consist of a single 6-cm diameter circuit board containing an ultra-low power microcontroller (PIC 16LC84), real-time clock chip, and 25 other components. The electronic boards are left active all of the time because they draw only 60 microamps. A highly-geared 9V DC motor is attached to the board and turned on and off (forward and reverse) under program control. This motor consumes 50 milliamps, but is in use for only five minutes for each sample. Before deployment, each unit is programmed to sample at a preset time. This programming is accomplished on the fully assembled unit by wireless communication, using infrared transmission through the UMHW polyethylene. This feature also allows for inter-unit communication and external reprogramming. The C-cell alkaline batteries (rated to 7000 milliamp-hrs) battery life should exceed a year, and has been tested for up to six months. Alkaline batteries do not function at temperatures approaching the freezing point of seawater. At very cold sites, lithium batteries can be used. Dr. Kelly Falkner of OSU has deployed a MITESS device in the Bering Strait for one year using Li batteries. Motor rotation is detected with a magnetic sensor, which allows the microprocessor to monitor bottle opening and closing and verify that the sample has been taken and sealed at the proper time. These data are retained in non-volatile memory so that successful sample collection can be established even if power is lost after the sample is collected.

We have deployed MITESS units on the Bermuda Testbed Mooring (Dickey et al. 1997, 1998) continuously since spring 1995 and on the HALE/ALOHA mooring of Dave Karl since 1997. In the past two years, the samplers have been >95% electro-mechanically reliable (i.e., in a six month deployment, 23 or 24 samples are collected from 24 modules deployed; see figure). MITESS has proved to be durable and a reliable mooring citizen. It survived the passage of two hurricanes including a nearly direct hit by hurricane Felix in August 1995 and a catastrophic 4 km fall to the seafloor when a device above it failed in November 1995.

![Figure 6: Samples collected by MITESS at BT M mooring, 1995-1999.](image)

The reliability of the device for trace metal sample collection has been established in three ways: (1) by using it to collect samples providing "oceanographically consistent" profiles for Pb and Fe at profiles in the eastern and western North Atlantic and central North Pacific (HOT), (2) by comparison to surface water samples collected using our normal verified trace metal procedures. The vertical
profiles of Pb and Fe obtained in this way are consistent with profiles collected by known reliable trace metal sample collection methods (e.g. Bruland’s Go-Flo method and Schaule and Patterson’s “lander” method). Samples collected by this device agree with “total dissolvable” Pb and Fe samples collected by our normal surface sampling methods (pole sampling and underway sampler, e.g. Vink et al. (2000). Finally, we have programmed individual MITESS modules to collect samples at the same time. Often, these modules will be spaced 3-5 m apart, and any contamination introduced by the sampler environment or by handling after recovery should be random from one sample to the next. However, in all cases for Pb and in the vast majority of cases for Fe, duplicate samples agree within our analytical error. Hence we are confident in the ability of MITESS to document the true trace metal content of the ocean where it is deployed.

With five years of data from Bermuda and three years of data from Hawaii, what are we learning about oceanic trace metal variability? For the first time, we have observed time-resolved variability for Pb and Fe in the upper ocean. By time-resolved, we mean that sampling density is sufficient to document the events through (at least several data points). Variability is greater at Bermuda, as would be expected from more intense atmospheric sources and a more energetic eddy field. By averaging several years worth of data, we can establish statistically significant seasonal cycles for Pb and Fe, but the shorter-term variability is large so that any single year can be very different from the average. For example, from May 5, 1999 to June 13, 1999, Pb concentrations rose from 35 pmol/kg to 48 pmol/kg over three weeks, then fell back down again over the nest two weeks. There is less Pb variability at Hawaii and more year-to-year similarity; a clear annual cycle seen with a minimum of 27-35 pmol/kg in the summer and peaks of 35-50 pmol/kg in the winter. Fe is more variable than Pb at both sites.

References:


