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Deep-Sea Research I 49 (2002) 2103–2118

DEEP-SEA RESEARCH
PART I

www.elsevier.com/locate/dsr

Instruments and Methods

MITESS: a moored in situ trace element serial sampler for deep-sea moorings

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Received 1 August 2002; accepted 13 September 2002

Abstract

We have designed, constructed and tested a trace element clean sampling device for long term deployment (6 months or longer) on deep-sea moorings. The device collects unfiltered 500 ml samples by opening and closing a bottle originally filled with dilute acid (passively replaced by denser seawater). Each sample is collected by an independent module, so failure of a single unit does not affect others. Seven years of deployments have refined the sampler into a rugged and reliable device. The device also can be hung below a wire to collect water column samples. Automated trace element sampler (ATE), a spinoff from moored in situ trace element serial sampler, is a single-module device for allowing trace metal clean near-surface samples to be collected by personnel not trained in trace element sampling. ATE/VANE, another variation, allows the same personnel to collect upper water column profiles on conventional hydrowire. The systems have been tested by comparing samples collected for lead and iron with those collected by previously proven sampling techniques.

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Keywords: Automated seawater sampling; Trace metals; Moored sampler; Chemical time-series

1. Introduction

Biogeochemically active trace metals can vary rapidly in the upper ocean in response to atmospheric and oceanic processes. In order to investigate the mechanisms leading to trace metal variability and its biotic consequences, we need detailed data that document metal responses to variable fluxes from the atmosphere, physical processes within the ocean (mixed layer and

seasonal thermocline development, vertical mixing during storms, and mesoscale eddies), and biological activity. For example, Boyle et al. (1986, 1994) observed that Pb variability on the scale of weeks–months was larger than the signal due to decreased leaded gasoline utilization over a period of several years. Given the strong atmospheric variability expected for dust, elements such as aluminum and iron should also show strong short-term temporal variability (Jickells et al., 1994; Tersol et al., 1996). Finally, other elements are strongly depleted from surface waters by biological activity and enriched in deep waters by

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regeneration from sinking particles. These elements are likely to display a high degree of variability due to pulses of upwelling, mixing, and biological blooms. If we are to understand processes controlling these bioactive trace metals in the upper ocean, we must make high-frequency observations in order to resolve the true variability and its relation to atmospheric and oceanic forcing.

Moored In situ Trace Element Serial Sampler (MITESS) was developed to establish a capability for high-frequency, upper ocean time series sampling for trace metals. Previously, shipboard time-series cruises were the only means available for establishing the temporal variability of trace metals. Occupying a monthly time series station (such as Bermuda Atlantic Time Series Study (BATS) and Hawaiian Ocean Time Series (HOT) Karl and Michaels, 1996) is a difficult challenge, especially for a non-resident scientist. But even the monthly sampling frequency at these stations cannot resolve short-term responses to rain, dust storms, mixing events, mesoscale eddies and blooms. Clearly, the solution to the problem of short-term trace metal variability must involve moored instrumentation. Ideally, in situ sensors or analyzers would capture data continuously. Given the state of the art of trace metal analysis, that goal is still many years away. In the shorter term, it is more feasible to develop a device that will collect and preserve samples for later laboratory analysis. In the medium term, a sampling device will also be useful for testing and calibration of future in situ analyzers and sensors. In the long-term, the ability of a moored sampling system to retain an archived sample allows for the possibility of taking advantage of future analytical technology and concepts to reconstruct the temporal variability of properties that cannot be measured at the time the samples are collected.

We are aware of some other water-sampling devices developed for mooring use (e.g., RAS systems by McLane Research Laboratories, Falmouth, Massachusetts and described in McKinney et al., 1997). We chose to develop a sampling device independently because these other systems were not designed specifically for trace element

sampling. In particular, we believe that flushing of sample bottles before sealing is an important final defense in the collection of an uncontaminated sample. Ideally, we also would like to collect filtered samples, because some metals (e.g. Fe) have significant particulate concentrations (although others, such as Pb, do not). However, the additional complications introduced by filtration—especially filtration with flushing—were likely to make the goal of contamination-free sampling more difficult in the short term. Hence our aim was to obtain reliably contamination-free unfiltered samples. It should be noted that although MITESS was designed for trace element sampling, there is nothing to prevent it from being used for other types of measurements given appropriate sample bottles and preservation techniques.

Here, we describe the principles of operation of the MITESS sampling device and illustrate its utility with some data establishing the reliability of the instrument.

2. Design goals

The mechanical and electronic design of the sampling units was directed toward fulfilling the following goals: (1) trace-metal clean materials, easy to clean; (2) usable with a variety of sample bottles; (3) sample bottle is flushed before sealing; (4) simple mechanical operation; (5) partial-failure tolerance; (6) withstands stresses of extended deployment (6–12 mo) at any depth; (7) easy to join together into a variety of configurations; (8) reasonable cost, simple manufacture; and (9) deployable on standard deep-sea moorings at no risk to mooring.

We settled on a design that opens and closes sample bottles (originally filled with distilled water, replaced by seawater through density-driven flow) in a trace-metal clean environment. The device consists of a colony of independent sampling modules. Each sample module is designed to function independently during deployment, so failure of any one module does not prevent any other unit from functioning.

3. Operating principles

3.1. Basic operation

A timer-controlled DC motor opens 500 ml screw-cap bottles (filled with dilute high-purity acid) by simple rotary motion. The low-density dilute acid is replaced with 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 mooring motion and currents. Tests in the laboratory indicate that quiescent exchange is complete in about 5 min; mooring motion and currents are likely to make for more rapid exchange in the field. The timer then reverses the motor, closing and sealing the bottle.

A hollow cylindrical bottle holder is used to grip the bottle tightly. Because of variations between lots of bottles, the fit of the holder itself is loose, and made tight either by wrapping the bottles with ParafilmTM and DurasealTM or by inserting 1000 μ l plastic pipet tips (top half cut off) between the bottle and the cup holder to distort the bottle ensuring a tight fit.

3.2. Sample preservation

Mooring samples are preserved by diffusion of dilute acid (1 mol/l HCl, which is the same acid used to fill the 500 ml bottles for mooring deployments) out of a diffusion chamber inside of the bottle. This acid is analyzed beforehand to ensure that it will contribute a negligible blank. The diffusion chamber is a 5 ml PFA fluorocarbon vial with five pinholes in its cap. The vial is exhaustively leached in hydrochloric and nitric acid before use. When the bottle is opened, dilute 1 mol/l acid in the 500 ml bottle escapes and is replaced by seawater within several minutes. The acid in the 5 ml preservative chamber, however, cannot exchange rapidly because of the pinhole restrictions. After the sample bottle is closed, the acid diffuses into the sample bottle over a period of about a day and preserves the sample at pH 2.5. As a bonus, the acid that was contained within the bottle before sample collection accomplishes long-

term leaching of the bottle right up to the moment of sample collection, allowing additional insurance against bottle contamination after laboratory cleaning. Although a portion of any contamination leached into the bottle during storage may remain in the fluorocarbon chamber as well, 99% of any residual bottle contamination leached during deployment will be removed during sample collection. Because the sample bottles are always prepared in the laboratory to be free of contamination before deployment, the additional 99% leaching after full cleaning is a redundant precaution.

Other liquids may be used to fill the sample bottle. When we use MITESS to collect profiles at sea, we fill the bottles with slightly acidified distilled water (pH 3) and do not add a diffusion chamber (because samples can be acidified after collection). If a liquid that is heavier than seawater is used, the unit may be deployed upside down. Other preservatives (or no preservative) may be used.

3.3. Module mechanical design

For the sake of trace metal cleanliness, the entire exterior of the sampling modules and proximate parts of the mooring holder are constructed from ultra-high molecular weight polyethylene (UHMW). The sample modules are constructed from colorless (white) UHMW, whereas the mooring holder uses carbon-black UHMW (to avoid interfering with nearby optical instrumentation). Both types have been tested for metal cleanliness and found to be acceptable for many trace metals (e.g. Fe, Pb, Ni, Cu, Zn), particularly, at seawater pH. The individual sample modules fit together into two-dimensional arrays of any number of modules. The most compact grouping places six units around a central support rod, and stacks these in two levels, resulting in a cross-section appropriate for deep-sea moorings.

Each sample module has a sealed interior filled with FluorinertTM, a non-conducting fully fluorinated fluorocarbon (FC-77). One useful property of this somewhat expensive liquid (~\$30 per pound, hence we recycle it as fully as possible) is that it is volatile and evaporates quickly when

parts are removed from the liquid. A bellows on the lower portion of the device provides pressure compensation, hence there is no differential pressure gradient to drive seawater into the module. The inner chamber houses the motor, circuit board, and batteries (six alkaline C-cells are standard for above-freezing temperatures; more expensive lithium cells may be substituted for subzero conditions, K. Falkner pers. commun.). The electronic components and motor in this nearly incompressible fluid are not adversely affected by high pressures, hence there is no requirement for a pressure case. However, the alkaline C-cells contain small void spaces in their construction. Batteries that are to be deployed at depths greater than about 200 m should have small holes drilled between their tops and bottoms and these void spaces to allow the Fluorinert liquid to achieve complete pressure compensation without distorting the batteries.

The highly geared motor is mounted onto the circuit board. The circuit board (see below) controls the 9 V power to the motor (on/off and polarity). The motor rotor is attached to a splined (hexagonal) UHMW shaft which fits inside a separate bottle holder. The threaded bottle holder fits into the main body, with the same screw pitch as the bottle and cap being used. As the hex shaft rotates, the cup holder rotates with a net up or down motion, unscrewing the bottle open and screwing it shut again. We believe that this simple motion is likely to be more reliable than more complicated linkages.

An individual sample module and its components are illustrated in Figs. 1–3. Interlocking pins and a triangular footprint for each sample module allow units to be arranged in a variety of configurations. The small size of each module and its components allows the entire exterior portion (or its component parts) to be cleaned and acid-leached as appropriate to ensure trace metal cleanliness. Finally, the unit's component parts are small and easily machined by computer-controlled machine shop equipment.

Each module consists of the following components, from top to bottom (Figs. 1–3): (1) cap holder, (2) three cap holder support/spacer rods, (3) bottle holder, threaded on bottom, (4) main

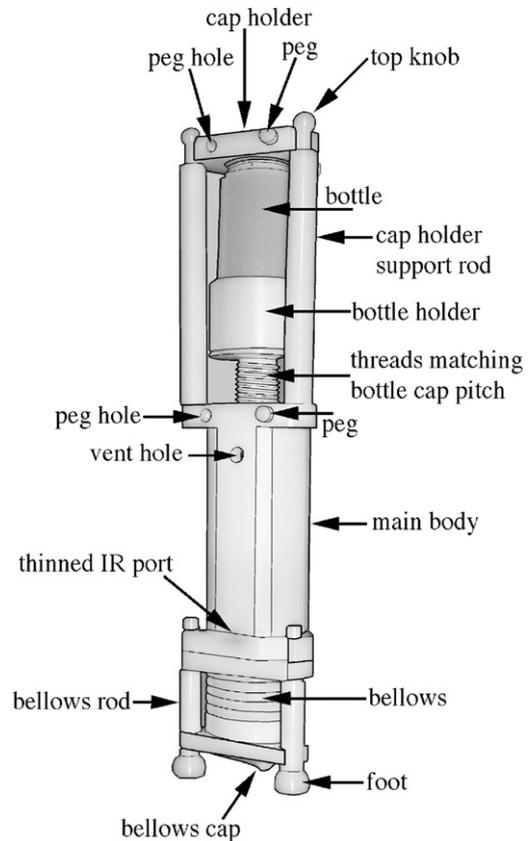


Fig. 1. MITESS sample module.

body, which holds: (5) board/motor assembly w/hex-shaft, (6) spot-welded battery packs, (7) Fluorinert filling liquid, (8) bellows unit w/3 bellows rods, and (9) cap for bellows unit.

The top cap holder fits into position on the top knobs of the cap holder support rods. The cap holder support rods are threaded tightly into the main body. The bottle holder is loosely threaded into the top of the main body. Six alkaline C-cell batteries are inserted into the main body as spot-welded battery packs, and two wires from the circuit board are soldered onto the battery pack. The hex-shaft inserts into a cylindrical central shaft within the main body. The unit is sealed at this end with two internal side-sealing “quad-rings” mounted onto a cylindrical portion of the hex shaft, fitting tightly against the cylindrical hole in the main body. Although properly aligned

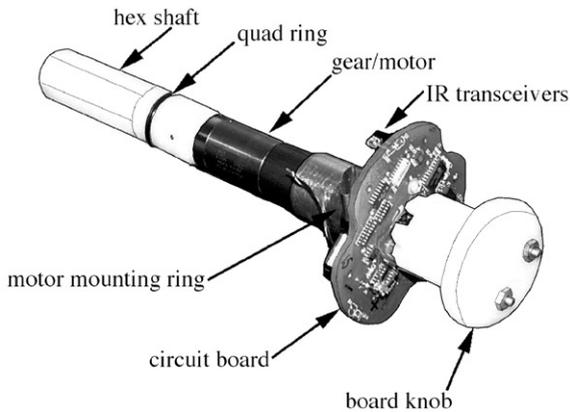


Fig. 2. Circuit board, gear/motor, and hex shaft assembly. Note that more recent versions use two quad rings on the hex shaft.

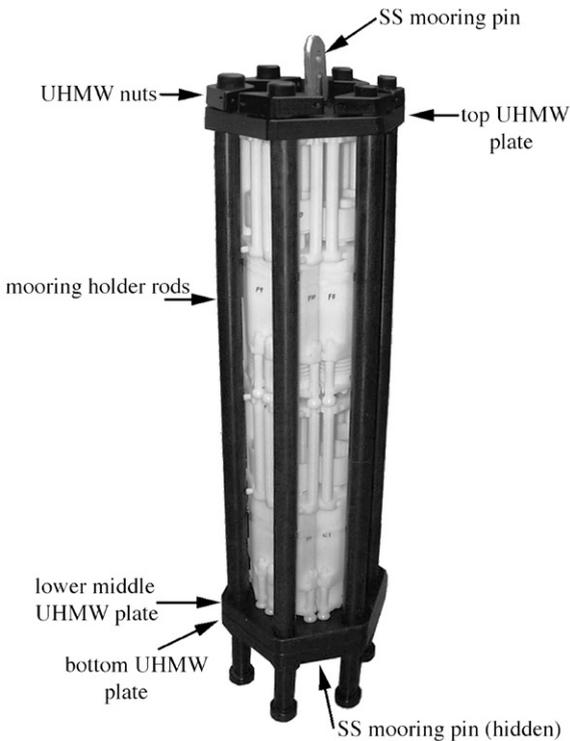


Fig. 3. Completely assembled MITESS: 12 modules in mooring holder.

asymmetrical side-sealing quad-rings provide an adequate seal, imprecise machining of the plastic may result in an imperfect seal of the quad-rings against the plastic. In order to ensure against

leaks, quad-rings are liberally greased with Dow/Corning silicone vacuum sealant. New quad-rings and o-rings are used for each mooring deployment. For profiling purposes, the quad- and o-rings are left in place throughout a cruise.

To assemble the device, the board/motor assembly is partially inserted into the main body. Fluorinert is poured into the battery chambers, then the board is inserted completely into the body. The bellows unit is fitted into the main body (sealed with side-fitting quad rings) and then filled with Fluorinert, eliminating all air space. The bellows cap, which contains one side-sealing quad-ring and a butt-seal outer o-ring for additional protection, is screwed into place while the bellows is pulled slightly upward, ensuring a slight positive initial pressure.

The mooring holder consists of: (1) plastic-enclosed central pin (1" type 316 stainless steel rod); (2) stainless-steel support plate (12.5" diameter) welded onto the lower section of the central pin; (3) three carbon-black UHMW end-plates to support and secure the module layers in place (one plate is held below the welded stainless steel support plate, a second plate lies on top of the welded support plate, and the third plate sits on the top of the sample modules); (4) six carbon-black UHMW exterior rods to hold the top and bottom plates together and protect modules during deck operations; and (5) six carbon-black UHMW nuts to secure the rods.

Each end of the stainless mooring pin has a hexagonal stainless steel plate (5.5" × 3.5" × 0.5") welded to the pin along a 2" cutout in the plate, with a 1" diameter hole for attachment to the mooring. This plate is inserted through a slot in the top and bottom, and then the center rod and plate are rotated to right angles. In this configuration, the mooring unit cannot come undone accidentally after assembly, even if the UHMW nuts were to loosen (or no more than five were to come completely off!). UHMW nut rotation is prevented by cable ties attached through holes between each nut. A stainless-steel plate is welded onto the lower portion of the mooring pin to provide support for the lower (middle) UHMW plate and to secure the lower layer of modules. The circular top knobs of the support rods fit into a

depression within the bottom of the bellows unit feet, allowing the units to stack into layers and fit inside holes in the top and middle mooring holder support plates. The fully assembled MITESS mooring assembly is shown in Fig. 3.

Between 1993 and 1997, the mechanical aspects of the sampler and mooring holder went through three prototypes and four test deployments, and the current design is final. The mooring holder has never failed or harmed the moorings in any way. Indeed, in two deployments, devices above MITESS failed and the whole mooring string below plunged to the bottom of the ocean. MITESS was recovered mechanically undamaged several months later in both cases.

3.4. Electronics design

As part of the redundant modular design, each sampling unit has its own motor, electronics, and batteries. The electronics consist of a single 6-cm diameter circuit board containing a microcontroller, a real-time clock chip (shown to be accurate within a few minutes over six months at subtropical temperatures), and 25 other components (Fig. 2). The microcontroller has a small non-volatile RAM cache to retain key operational data in the event of battery failure (if batteries fail, the time of failure also is stored). The board senses the number of motor shaft rotations in order to control the bottle movements. The circuit board draws very little power when the motor and IR communications are idle (60 μ A), so it remains on continuously. Given the 7000 mA h capacity of six C-cell batteries, the units should remain functional for more than six months, and have achieved this goal in field tests. At sub-zero temperatures, lithium batteries have functioned up to one year (K. Falkner, pers. commun.). The closure step includes three short pulses about 5 s apart after the bottle is restored to its initial position. These pulses tighten the bottle past the original closed setting. The pulses allow for some deformation of the sealing surfaces inbetween each pulse. This procedure results in a tightly sealed bottle.

Before deployment, each module is programmed to set: (a) the real time clock, (b) the opening time, and (c) the time the bottle is to remain open before

closing. The fully assembled unit is programmed by wireless communication through the sealed module. Infrared pulses are transmitted through a thinned portion of the UHMW body. This feature allows for programming via an external RS232 or RS422 serial device linked to an IR-transceiver wand. Because the sample units do not need to be opened, programming and interrogation can be done on fully assembled units in the lab or on the deck of the ship. The electronics board retains a non-volatile record of the timing of the basic operations of the sample module (Table 1): time of opening startup, time that full open is reached, time that closure begins, and time of full closure. These data can be retrieved upon recovery to verify that the sampler has functioned as desired. At shallow depths, the bubble in the top of the bottle is smaller for a sample than for the original filling solution, and at greater depths, the bubble is entirely absent, providing additional verification of sample collection. Finally, if the bottle does not open, the liquid inside a mooring-deployed unit has a pH of 0; if it is replaced by seawater and acidified by the internal diffusion vial, the pH is 2.5. For a profile-deployed unit, the salinity of the water verifies sample collection. With these means of verification, one can be certain that a sample was collected at the correct time.

Because the IR communication transceivers respond to bright light, a password sequence is required before control mode is enabled. Bright light and the consequent IR transceiver activity also cause excessive current draw, potentially depleting the batteries. Hence when MITESS is deployed, the externally facing IR ports are covered.

Because of rare occasional leakage of seawater or corrosive battery liquid into the modules, the circuit boards (and sometimes also the motors) must be considered partially expendable components and provision made for an adequate supply of backups.

3.5. Size, weight, and cost

The fully assembled mooring unit stands about 6' high with a 22" diameter. Including batteries and Flourinert, it weighs ~200 pounds in air.

Table 1
MITESS Communications and Programming

Communication with the modules is based upon simple one character commands: “y”es (four “y” commands must be sent to enable command mode), “o”pen (turn motor on to open bottle), “c”lose (turn motor on to close bottle), “s”top (stop motor), “r”eport (report on time, program, flags, and battery failure), “l”og (list time log for operation actions), “p”rogram (set to open at time indicated by next eight hexadecimal characters and remain open for time indicated by the final two hexadecimal characters), “t”ime (set clock to time indicated by next eight hexadecimal characters), “k”lear (clear flags, set to operate), “n”o (no more programming commands, i.e., go out of command mode). Upon being commanded to “r”eport, the module responds:

<i>Response:</i>	<i>Indicates:</i>
clock 16 63 25 C8	Current time (hexadecimal representation of number of 8 second intervals since beginning of 1904)
open 16 4E F7 D0	Time when sampler is programmed to open
flags 0F	Flags indicate operational status
resets 00	Resets indicate problems during operation
wait 71	Length of time for bottle to remain open
batt 00 00 00 01	Time at which low battery occurs
pmc 00	Program state (00=no commands;04=commands)

The “l”og command produces the activity report:

<i>Response:</i>	<i>Indicates:</i>
16 4E F7 D0	Time the motor began to open the bottle
16 4E F7 DD	Time the motor turned the bottle to full open
16 4E F8 4E	Time the motor began to close the bottle
16 4E F8 5C	Time the motor turned the bottle to full close.

Because the specific gravity of the plastic is 0.97 compared to the density of seawater (~ 1.03), the assembled device is nearly neutrally buoyant in seawater.

Although it is difficult to estimate how this device would be priced by a commercial entity, a reasonable guess at the non-profit price of construction for a 12-unit module with mooring holder, two IR wands, and six spare boards and motors would be approximately \$35,000 (2002 dollars).

Further information on the construction, assembly, and use of these samplers is available from the corresponding author upon request and at <http://boyle.mit.edu/~ed>.

4. Sample bottles

We deliberately designed MITESS to be flexible in choice of screw-cap bottles. No single bottle type is likely to be suitable for all purposes. Our initial work was dominated

by inexpensive high density NalgeneTM polyethylene bottles, which are suitable for Pb and Fe and many other trace metals, but which are not suitable or storage of seawater for Al analysis under acidic, room-temperature conditions (frozen unacidified samples appear to be minimally affected, Orians and Bruland, 1985). This contamination may result from AlCl₃ used as a polymerization catalyst (Ziegler–Natta reaction), but this information is treated as a trade secret by suppliers who will not reveal the process used for their polyethylene.

Because of Al contamination introduced by polyethylene, we have tested other bottle materials. Our first alternative was fluorocarbon (FEP bottles with ETFE caps). Although these bottles do not contaminate for Al and have been shown to be clean for most other trace elements, they are extremely expensive and would have to be reused to be a feasible alternative. Our first use of these bottles also showed that the caps do not seal as well as polyethylene under the light closure pressure

required pre-deployment, so some bottles leaked a small amount of acid during pre-deployment handling. This is an annoying problem but it is tractable. These same fluorocarbon bottles were found to be sealed tightly upon recovery (by the over-tightening motor pulses), and so they are suitable for reliable sample storage. Fluorocarbon also has the advantage of forming a strong positive meniscus, so the over-filled bottles were more easily opened than the more wettable polyethylene.

As an another alternative, we tested polymethylpentene (PMP) bottles. This material does not contaminate for Al (C.I. Measures, pers. comm.), and our data shows that this material does not contaminate for Pb and Fe (by comparison to samples collected in linear polyethylene bottles at the same time). Although PMP is several-fold more expensive than polyethylene, it is much less expensive than Teflon. PMP caps do not seal as well as polyethylene, and a higher level of force is required to open them. In order to minimize this problem, we prefer to use ETFE caps on PMP bottles.

Although the only other metal we have verified MITESS for (in addition to Pb, Fe, and Al) is Co (Saito and Moffett, 2002), our many years experience with trace metal contamination leads us to believe that MITESS would be appropriate for any trace element for which an appropriate sample bottle and preservation technique is available. We have no information indicating significant permeability of these plastic bottles for ionic and particulate trace metals and believe that only gases (including water vapor) exchange with seawater during extended deployment. Although we have not tested other bottle types, it is likely that any screw cap bottle of appropriate dimensions can be used with MITESS if it is suitable for the preservation of the property in question.

4.1. MITESS as a profiling sampler

MITESS can be deployed at the end of a hydrowire to collect trace metal clean samples in vertical profile. The modules are programmed to open at preset times, and the winch schedule is arranged to have the unit arrive at predetermined

depths at the appropriate times, waiting at each level for about 10 min to ensure complete flushing. Only very dilute (\sim pH 3) acid is put inside the bottles for these profiles and no interior Teflon diffusion chamber is included, because the samples can be acidified manually on the ship after removing subsamples for filtration [note that shipboard filtration under class 100 conditions is possible on these samples because the water does not remain in the bottles long enough for adsorption to be a concern].

When MITESS is deployed as a profiler, $a \geq 200$ lb weight is hung about two meters below the unit and the top is attached to the hydrowire with a secure shackle. The unit can be lowered and raised at 50 m min^{-1} . It might be thought that contamination from the weight and hydrowire could be a problem when working in this fashion, but we have encountered no problems sampling for lead (hydrowire below) or iron (hydrowire above and below). Unless the unit is deployed in a flat calm with no wind or surface currents, the device normally is being dragged through the water creating a strong lateral flow as the hydrowire forms a catenary. Water that has seen the hydrowire or hydrowire is being swept away laterally and the modules only see clean water being swept in from upstream.

Although other trace-metal clean systems are capable of collecting vertical profile samples (e.g. General Oceanics Go-Flo on Kevlar[®] cable or trace metal clean rosettes), they require careful attention to maintain them in a clean state; only trace metal experts can ensure reliable use. A comparative advantage of MITESS as a sampler is that it can go on any wire and requires only minimal cleaning, other than for the sample bottle itself which is prepared in a clean laboratory. Because the bottles are sealed at all times (other than while open during deployment), MITESS can be deployed successfully by individuals who are not trained in trace metal contamination control at sea. We have used MITESS as a vertical profiling device for more than 20 stations on seven cruises in the past four years. On cruises Endeavor 328 (September 1999) and Endeavor 367 (March 2002), MITESS was used to collect 330 samples down to 5000 m depth at 17 stations. A 12-sample

profile to 1000 m can be collected in ~ 4 h, and a 12-sample profile down to ~ 5000 m can be collected in ~ 6 h. Hence MITESS is a practical alternative profile sampler with some significant benefits.

4.2. Automated trace element: MITESS module deployed as a surface sampler

When routine time-series stations such as BATS and HOT are occupied, they would be more valuable if they could collect trace-metal samples. But it cannot always be arranged to have a trace metal specialist on board. In order to allow for surface sampling without requiring trace metal expertise, we modified a single module unit from MITESS into a device dubbed automated trace element sampler (ATE). ATE is a slightly modified single MITESS module with coated weights hanging below and 10 m of plastic-coated steel cable harness above. The user programs the unit to open 10 mins from the start of the sampling. ATE is then tossed over the side of the ship and hangs far enough below the hull to avoid paint and rust contamination from the ship. At the end of the sampling, ATE is returned to the surface and the sealed bottle is stored until return to a clean lab. ATE is easily deployable with only a little training. Because the sample bottle remains sealed at all times when it is not collecting a sample, a trace-metal trained individual is not required to operate ATE. ATE has been deployed at 10 m at recent HOT, BATS, and the Cariaco Basin time series stations during the past several years.

4.3. ATE/VANE: weather-vaning MITESS module deployed on a wire to obtain shallow water profiles

A minor modification of ATE is to mount a single module on a weather-vaning device that is free to swivel around a wire and orients itself so the that ATE module end is upstream of the current. Because of wind drift (or even induced ship motion by a brief turn of the ship's screws), the orientation of the ATE/VANE avoids sampling water that has contacted the hydrowire. Several of these devices may be hung on a wire at a time. This version is more time-efficient than a

12-unit MITESS cast for collection of a small number of samples.

5. Testing and deployment

The first complete instrument was field-tested in Bermuda in October 1993 by hanging it below a hydrowire to obtain a water column profile for Pb in the upper 600 m (see, Wu and Boyle (1997) for Pb data from that deployment). This test was successful, but experience from this effort led us to consider how the instrument could be made simpler to construct and more reliable in the field. Accordingly, a second generation design (both hardware and electronics) was deployed on Tommy Dickey's ALTAMOOR surface mooring near Bermuda beginning in the Spring of 1995 (ALTA-MOOR was subsequently renamed as Bermuda Testbed Mooring, BTM (Dickey et al., 1997, 1998)). Most problems with the design and deployment were solved by the end of 1997; in the two 3–4 month Bermuda deployments in 1998, 47 successful samples were obtained from 48 bottles. As the reliability increased, we devoted some samples to duplicate sample collection to confirm the reliability of the samples (see later). MITESS also has been deployed at Dave Karl's HALE-ALOHA mooring near Hawaii, from May 1997–2000. Use of the instrument has been completely routine during the past three years, with no problems other than those associated with the choice of bottles. Following standard procedure, most modules collect samples. Although the loss of a few samples from leaks or battery failures is unfortunate, the fact that a single failure does not prevent other samples to be collected has proven to be a successful design feature.

Turnaround of a profiling unit is relatively fast, but recycling of a mooring deployment takes several days. Because the profiling unit is not fouled and the batteries are good for 5–10 samples, we simply have to disassemble the mooring unit, remove filled sample bottles and replace with new ones, and reassemble the mooring unit. This procedure can be completed in a few hours. Excluding time at sea, a typical recovery/redeployment

cycle for two 12-module upper ocean mooring deployments in the field requires two individuals working full time for about 3 days. The largest portion of the time is spent on cleaning up fouling replacing o-rings. This work includes complete disassembly of the mooring unit and modules, cleaning off the fouling, downloading operational logs from the previous deployment, greasing quad-rings, inserting the battery packs into the modules and soldering leads, loading the sample bottles, programming the modules, and assembling the pieces into the mooring assembly.

The mooring recycling time estimate above does not include laboratory preparation prior to the turnaround: (1) sample bottle preparation (approx. one person for 4 days, including preparation of 2.5 l of high purity 6 mol/l HCl acid plus 14 l of high purity water and testing it for metal contamination), (2) battery pack spot welding (approx. one person for one day), and other preparation (approx. one person for 2 days). Nor does it include post-deployment effort: (3) transferring samples into clean containers (approx. one person for one day), and (4) sample analysis (depends on what is being measured—for Pb, Fe and Al, probably requiring approx. 3 weeks using by current methods). Preparation of bottles for profile samples is streamlined because they are filled with distilled water with a few drops of pure HCl, and battery packs are used for multiple samples.

5.1. Fouling and related issues

The degree of fouling encountered during 3–6 month deployments has ranged from mild to severe, even in oligotrophic regions such as BATS and HOT. At no time did fouling become so severe as to impede proper operation of the sampler (opening and closing). We saw no evidence for obvious biological fouling of the samples collected (i.e., no strands of seaweed or barnacles inside the bottles). At the end of each deployment, the sampler is initially cleaned with a high-pressure water sprayer, which removes most of the fouling. The units are then disassembled and cleaned with

detergent and a scrub brush in the lab before redeployment.

Does fouling have an adverse affect on the trace metal integrity of the samples? This question can be resolved by comparison of MITESS samples to samples collected by other means and by duplicate sampling. We collect a water sample by our normal shipboard methods (“pole sampling”; underway water sampler, Vink et al., 2000; or ATE) on each recovery cruise, hence giving a point of comparison for the last sample collected on the previous deployment and the first sample of the next deployment. In addition, ATE samples at BATS and HOT give occasional mid-deployment checks. We have also collected duplicate samples with MITESS (individual modules programmed to collect samples at the same time). The premise for this duplicate sampling is that contamination from fouling is likely to depend on the fouling situation very close to each bottle, and that units separated by up to 3 m will not encounter the same degree of contamination. Pb and Fe analyses of duplicate samples collected from BTM MITESS in 1998–1999 are shown in Table 2. A few samples where parafilm strips (from an over-long parafilm “skirt” on the cap) were seen in the bottle were excluded from this comparison. As can be seen, out of 22 individual bottles, only one bottle is contaminated for Pb (as compared to its lower duplicate sample)

Table 2
Duplicate samples collected by MITESS at BTM, ~40–50 m depth

Date	MITESS		MITESS	
	1	2	1	2
	Pb (pmol/kg)		Fe (nmol/kg)	
November 18, 1998	44.4	35.9	1.35	1.39
February 4, 1999	257.9	45.6	1.17	2.25
April 20, 1999	36.1	35.8	1.22	1.09
May 1, 1999	47.8	48.8	2.29	1.98
May 30, 1999	48.3	48.9	0.62	0.72
July 5, 1999	48.6	48.8	2.23	1.90
July 30, 1999	37.7	37.4	1.85	1.75
September 3, 1999	29.2	30.0	2.15	0.64
October 1, 1999	29.5	30.5	1.71	1.49
October 8, 1999	32.1	32.4	2.02	2.31
November 2, 1999	31.9	31.2	3.02	2.95

Table 3
Comparison of MITESS with other proximate samples at HALE/ALOHA (Hawaii)

MITESS		ATE		Pole	
Date	Pb (pmol/kg)	Date	Pb (pmol/kg)	Date	Pb (pmol/kg)
29-May-97	31	20-May-97	30	20-May-97	25
3-Jul-97	29	11-Jul-97	35		
17-Jul-97	36				
6-Aug-98	30	9-Aug-98	27		
23-Sep-98	25				

and only two bottles are contaminated for Fe. This is a reasonable success rate for samplings of contamination-prone elements such as Pb and Fe in the ocean. MITESS samples at Hawaii (where the sampler is usually within the mixed layer) compare well with temporally proximate ATE and ship samples for Pb (Table 3). For comparison, Johnson et al. (1997) note that 11% of their iron samples were rejected as contaminated. With samples spaced sufficiently close in time and with a significant number of duplicate samples, one can use “oceanographic consistency” to identify and reject occasional contaminated samples.

Growth on the lower threads of the sample bottle caps, which might be wetted by an overflowing sample as it is opened, is a fouling issue that is eliminated by vigilance during bottle opening back in the laboratory. Because the bottle is opened and closed underwater, it returns almost completely filled with liquid (some degassing usually produces a small bubble). It is difficult to open the bottles without having water leak down the threads (this problem is more severe for more wettable polyethylene bottles compared to Teflon bottles which tend to form a strong positive meniscus). If this liquid were to contact algal growth and drip into the sample as the cap is removed, the sample could be contaminated. Two steps are taken to prevent this from being a problem. First, upon development the lower threads are protected from fouling before opening by a parafilm wrapping, so that fouling of the lower threads cannot occur until after the sample is taken. Second, a procedure was devised to wick up the liquid flowing down the threads (as the cap

is slowly opened) with acid-leached filter paper. This procedure prevents excess liquid from dripping back into the sample bottle. In order to eliminate concerns about contamination during subsequent openings, the sample is immediately transferred into a clean container. The success of this technique in avoiding contamination is proven by a comparison between water inside the acidification vials with the bulk liquid in the bottle. We immediately removed the 5 ml internal teflon acidifying vial after transferring the sample out of the bottle. During the time since sample collection this vial will have equilibrated with the sample inside of the bottle. Because of the restricted flow, any contamination introduced during bottle opening will not appear inside the vial. Analyses of eight vial/bottle pairs for Fe showed that usually there was no significant difference between vials and bottles (6 pairs), one marginally significant pair where the bottle was slightly higher, and one pair where the bottle was clearly contaminated. Hence contamination during bottle opening can be avoided, and analysis of the liquid in the vial can be used to eliminate this problem entirely for a small sub-sample.

5.2. Shipping issues

Shipping complications arise from the use of trace metal clean 1 mol/l HCl as the bottle filler during sample deployment. One mol/l HCl is classified as hazardous material and requires special handling by a certified agent before it can be air freighted. We prepare the clean 1 N acid within the 500 ml bottles in the laboratory. We

tightly close the caps, wrap the caps with parafilm, and then pack the bottles inside 3 sets of plastic bags. These bags are then sent to a certified handler who packs them according to current regulations and forwards them to the freight agent. Also, as shipped, the cap closures are too tight for the bottle to be opened by the sample modules. So before the bottles are used for deployments, the caps must be loosened so that they are just sufficiently tight to prevent leaks (this procedure just requires a small fraction of a turn and does not expose the bottle to contaminated air).

6. Some illustrative MITESS data

Three examples of successful use of MITESS will be shown in this paper to demonstrate the validity of this sample collection method. Other data will be discussed in later papers focused on specific scientific issues. The Pb and Fe analyses discussed here were made using isotope dilution ICPMS methods (Wu and Boyle, 1998).

6.1. Pb in Bermuda, 1996

Between the end of March and the end of October, 16 MITESS samples were collected at 53 m. In addition, two surface samples were collected with ATE (Fig. 4). These samples were analyzed for Pb (Fe was not analyzed for this group of samples because the acid used to preserve the samples had a high iron blank). Through early

June, lead concentrations at the surface and 53 m are the same, averaging 51.3 ± 2.5 (1σ) pmol/kg. Then, Pb concentrations at 53 m begin to drop, reaching a low of 38 pmol/kg in mid-August, while surface water concentrations rise slightly to 53 pmol/kg. From early September through late October, Pb concentrations at 53 m rise abruptly to 67 pmol/kg at the point where autumn erosion of the seasonal thermocline has deepened the mixed layer down to the level of MITESS (the timing of this event is constrained by UCSB temperature recorder data).

These results can be understood from the perspective of a simple model of the development of the seasonal mixed layer. As Boyle et al. (1986) pointed out, the shoaling of the mixed layer from 200 m in late March to ~ 20 m in late August has a profound effect on the lead concentrations of surface water. Elements released from soluble aerosols during this period are trapped in the thin mixed layer in late summer. Considering this process in isolation from the variability of atmospheric deposition, surface concentrations are expected to reach a maximum in late summer and then decrease as the mixed layer deepens. At 53 m, however, after the 53 m level becomes part of the stratified seasonal thermocline, the flux of lead from the atmosphere is cut off (save for a diffusive flux), allowing in situ biological scavenging to remove lead. The average scavenging residence time of lead in the upper Atlantic is about two years (Bacon et al., 1976); hence in a period of 4 months, we expect lead concentrations

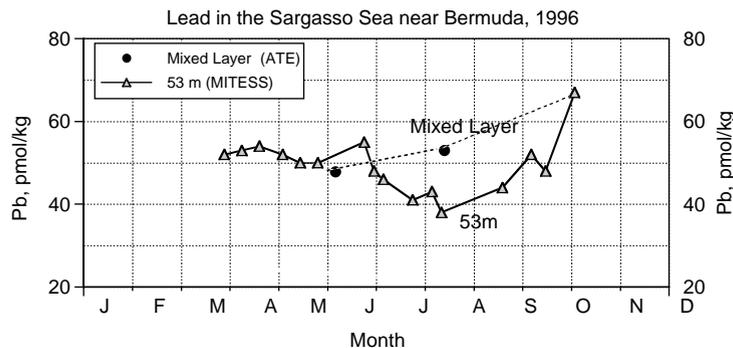


Fig. 4. Lead data from BTM (Bermuda) mooring in 1996.

to fall about 15%. In the fall, as the high Pb surface mixed layer deepens and reconnects to 53 m, the concentration at depth will rise abruptly. The more gradual observed transition is due to vertical diffusion, which begins mixing Pb down to 53 m before the mixed layer reaches this depth in the fall.

This is a highly idealized view of the processes that can affect Pb variability. Eddies, variable atmospheric inputs, and time- and depth-dependent scavenging can alter this idealized view, and subsequent years with more detailed data will reveal some of these complications. However, the MITESS Pb data from 1996 illustrate how a high-density trace element time series can be used to evaluate models for the behavior of trace metals in the upper ocean.

6.2. *Pb decreases in the Central North Pacific Ocean: 1977–1997*

Schaule and Patterson (1981) obtained the first valid Pb data in the central North Pacific from samples collected in 1977. A sample collected near Hawaii (24°19'N, 154°29'W) had 64 pmol/kg; the average of this sample and four others between that site and 33°03'N, 140°29'W was 65 pmol/kg with a range 60–72 pmol/kg. Between May 29, 1997 and May 18, 1998, we analyzed 26 samples for Pb obtained with MITESS, ATE, and ship-board “pole” samples at the HALE/ALOHA mooring site (22.5°N, 158.2°W). The average Pb concentration of these samples is 30.5 pmol/kg with a standard deviation of 3.1. The variability of Pb is much less than observed near Bermuda (see above and Boyle et al., 1986, 1994). The minimal variability of Pb at this site and at those of Schaule and Patterson suggests that a comparison of our 1997–1998 data with their surface data is appropriate. We conclude that Pb concentrations in the central North Pacific have decreased by ~50% during this 20 year interval because of the phasing out of leaded gasoline (mainly by Japan, Canada, and the United States). This factor of two decrease can be contrasted to the factor of four decrease observed in the western North Atlantic from 1979 to 1997 (Wu and Boyle, 1997). The proportionately larger decline in the Atlantic can be

attributed to US dominance of global leaded gasoline emissions and transport of US lead emissions with the westerlies. Interestingly, the concentrations of Pb in the central North Pacific and the western North Atlantic at present are similar, suggesting that Pb emission sources from Asia may now be higher than those from North America (given the larger area of the North Pacific relative to the North Atlantic). This deduction seems consistent with the survey of 1989 Pb emissions by Pacyna et al. (1995).

6.3. *Pb and Fe profiles on the Bermuda Rise, 1998*

In June, 1998, MITESS was used in profiling mode to reoccupy a station northeast of Bermuda on the Bermuda Rise (33°40'N, 57°37'W, 4479 m water depth) where “vane” samplers (Boyle et al., 1986) had been used in August, 1984. For the samples collected on the 1998 occupation, Fe was analyzed on samples filtered through 0.4 m Nuclepore™ filters. Fig. 5a compares the lead profile from 1984 and 1998. Lead concentrations in the upper water column are decreasing in response to the phasing out of leaded gasoline and ventilation of the thermocline by lower-lead waters, as also seen nearer Bermuda (Wu and Boyle, 1997). Fig. 5b compares the 0.4 μm filtered iron profile (Wu et al., 2001) at this central Sargasso Sea site with the iron profile obtained from a Go-Flo cast at a site 1365 km away near the western edge of the Sargasso Sea (36°17'N 72°17'W). Although the MITESS Fe data is lower in the upper water column, this difference can be attributed to horizontal gradients within the Sargasso Sea. We do not have T and S data from the Wu and Luther station (WL), but data is available from nearby station AII109 Station 10 (Lat 37°27'N, 71°57'W, 237 km away from WL, Fig. 6). The upper water columns down to ~1500 m diverge significantly, but converge below that depth. Similar differences in the Fe data are evident; convergence of the deepwater data is the correct basis for comparison between the Fe data from these two sites. The similarity of the MITESS deepwater

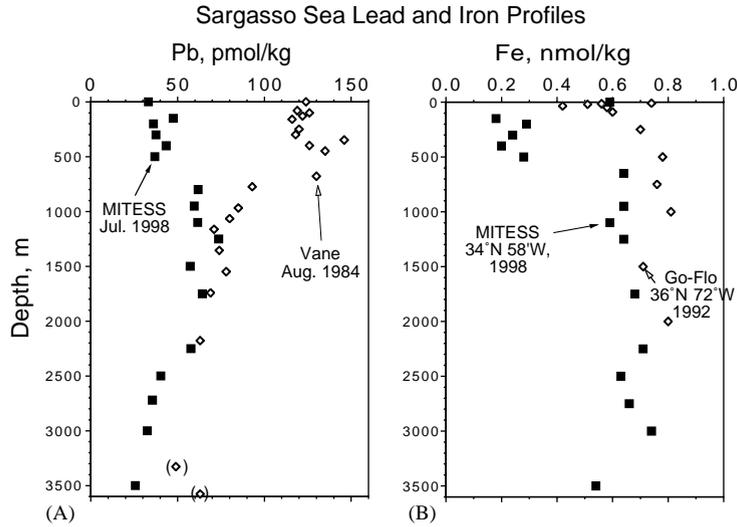


Fig. 5. Profile data for: (a) Total Pb, and (b) 0.4 μm filtered Fe from the Bermuda Rise, July, 1998, compared to Pb at the site in 1984 and Fe data from the edge of the western Sargasso Sea in 1992 (WL, Wu and Luther, 1994). Fe filtration was done on board in a class-100 environment. Note the two “vane” samples below 3000 m are marked with parentheses because this sampler had a tendency to seize at high pressures and the data may reflect shallower post-trip water. We doubt that such a large reduction in deep waters is likely.

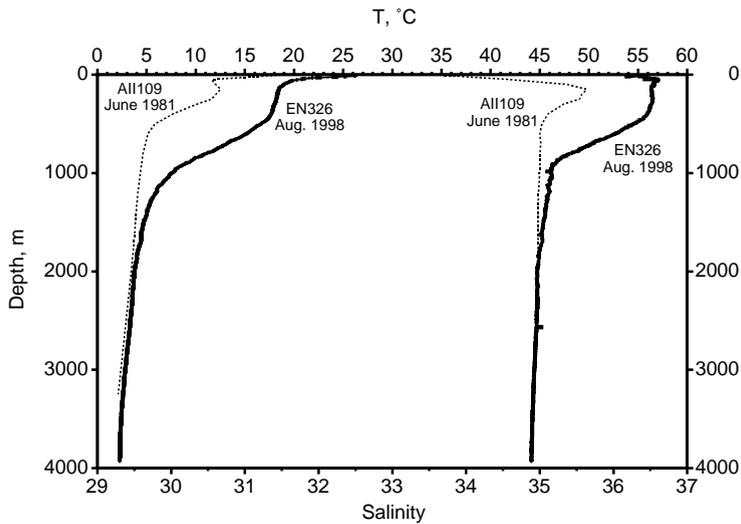


Fig. 6. Temperature and salinity data from Bermuda Rise station EN326, (July, 1996) and AII109 Station 10 (1981; near the WL western edge of the Sargasso Sea station).

data with other North Atlantic Fe data (e.g. see, Johnson et al., 1997) demonstrates that MITESS collects samples that are not contaminated for iron.

7. Conclusion

MITESS and its offspring ATE and ATE/VANE are now proven methods for collecting

trace metal clean water samples. MITESS can be used to collect time-series samples from a deep sea mooring over periods of at least 6 months, during profiling through the water column with a winch on board a ship, or from the surface during a simple rope-and-weight lowering.

Acknowledgements

Rick Kayser and Barry Grant have been invaluable in refining the sampler into a routine and reliable tool. Mike Prichard contributed with design consultation and CAD work. We also would like to thank people who helped in the field deployments during the testing phase: Mike Prichard, Jess Adkins, Yu-Harn Chen, and Jingfeng Wu. We are grateful to Tommy Dickey (OCE-9627281) and Dave Karl (OCE96-01850 and OCE96-17409) for accommodating our sampler on their moorings, and to John Kemp, Terry Houlihan, Louis Tupas, Dave Sigurdson, and Derek Manov for their roles in maintaining the moorings and their instrumentation. We thank the Bermuda Station for Biological Research and Chris Measures of the University of Hawaii for the use of their laboratories during mooring turnarounds, the personnel of BATS and HOT for deploying the ATE sampler during their monthly stations, and Jingfeng Wu and Rick Kayser for their Pb and Fe data illustrating the successful uses of MITESS. We also thank Lloyd Keigwin for allowing us to collect the Bermuda Rise profile on his cruise (Oceanus 326 and the officers and crews of the R/V *Endeavor*, R/V *Oceanus*, R/V *Moana Wave*, and R/V *Weatherbird II*. Development of MITESS was supported by ONR (NOO014-90-J-1759) and deployment by NSF (OCE-9711814).

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