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# Rapid and noncontaminating sampling system for trace elements in global ocean surveys

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## Abstract

A system for the rapid and noncontaminating sampling of trace elements with volumes of up to 36 L per depth and including the dissolved and particulate phases has been developed for ocean sections that are a crucial part of programs such as International GEOTRACES. The system uses commercially available components, including an aluminum Seabird Carousel with all titanium pressure housings for electronics and sensors to eliminate zinc sacrificial anodes and holding twenty-four 12 L GO-FLO bottles, and a 7500 m, 14 mm Vectran conducting cable (passing over an A-frame with nonmetallic sheave) spooled onto a traction winch. The GO-FLO bottles are stored and processed in a clean lab built into a 20′ ISO container. To minimize contamination, the GO-FLO bottles are triggered when the carousel is moving upward into clean water at 3 m $\text{min}^{-1}$. Analyses of salinity and nutrients in bottle samples from the stopped versus moving carousel show no detectable smearing, whereas the contamination-prone trace elements show the samples are uncontaminated when compared with other clean sampling methods. Based on the use of this system on three major cruises, the launch-sample-recover time for the carousel (2 bottles triggered per depth) is 1 h per 1000 m, and dissolved and particulate sampling time averages 6 h per hydrocast. Thus, the system described here meets all the requirements for ocean basin sampling for trace elements: rapid, good hydrographic fidelity, and noncontaminating.

It is widely recognized that trace elements and their isotopes (TEIs) can function as nutrients, contaminants, and tracers or proxies of various oceanographic processes. Results from the Geochemical Ocean Sections Study (GEOSECS) of the 1970s led to much of this recognition (e.g., Broecker and Peng 1982), however only a few TEIs were determined during this early program. The development of clean sampling protocols and new, highly sensitive analytical methods, combined with advances in modeling tools that can link and synthesize large data sets, have revolutionized our ability to now study the marine biogeochemical cycling of trace elements and isotopes on a global scale; we can now go well beyond what GEOSECS started. Indeed, the new GEOTRACES program (Henderson et al. 2007; www.GEOTRACES.org) is seeking to do just this—examine the global distributions of trace elements and isotopes in the world's oceans and reveal the processes that affect/control them. However to do this on the scale of an ocean basin, sampling equipment and protocols that can quickly take representative (i.e., corresponding to the hydrography) and uncontaminated samples for the full water column on ocean basin sections are essential. Given that many countries and scientists will be undertaking the GEOTRACES' surveys, cost and reliability are additional considerations. The "traditional" method of taking samples for TEIs (e.g., Bruland et al. 1979) used individual GO-FLO bottles hung on a Kevlar cable and triggered with plastic messengers; while successful, it is clearly too slow for global surveys. Early attempts at speeding up sampling for selected TEIs used coated stainless steel rosettes and conducting metal or Kevlar cables (e.g., Hunter et al. 1996; Löscher et al. 1998). More recently, the all titanium and conducting Kevlar cable system called "TITAN" was specially built and deployed for the GEOTRACES program and takes uncontaminated samples for all TEIs tested to date (De Baar et al. 2008).

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This article describes a trace element sampling system based on that developed for the CLIVAR-$CO_2$ Repeat Hydrography Program (Measures et al. 2008) for the upper 1000 m. The US GEOTRACES carousel can sample the full water column (to depths of 7500 m) with 24 12-L bottles per cast for dissolved and particulate (filtered) TEIs. It also uses commercially available components and hydrographic sensors (pressure, conductivity, temperature, oxygen, beam transmittance, and fluorescence) housed in titanium pressure cases to completely eliminate the need for zinc sacrificial anodes and therefore potential sample contamination (except perhaps for Ti). The carousel is lowered through the water with conducting Vectran cable with an extruded polyester outer jacket. The sampling system is flushed on the descent through the water column and samples are acquired while the carousel is being slowly raised into clean water. Thus, the focus of this paper is on the hydrographic fidelity of the samples (i.e., what depth?) as well as an assessment of their cleanliness (i.e., degree of any contamination). Because of the wide scope of assessing the performance of this sampling system, only results for dissolved (<0.2 or 0.4 µm) constituents are considered, whereas data for particulate TEIs are examined in Planquette and Sherrell (in press). Results for dissolved TEIs not included in this analysis are found in other articles in this volume.

## Materials and procedures

### Sampling system—carousel, winch and cable, and A-frame

The sampling carousel itself is the prototype for what is now a "standard" item (Model 32G) from Seabird Electronics. The frame is one-piece, welded aluminum with a polyurethane electrostatic coating and a titanium lifting bail. The GO-FLO sampling bottles rest on titanium retaining pins fitted to pivoting Delrin blocks (with titanium bolts) that allow the GO-FLO bottles to be tilted in/out for installation and removal (Fig. 1). This minimizes damage to the GO-FLO mounting blocks (Measures et al. 2008). The pressure housings on the electronic release system that fires the bottles, the main 911 plus CTD unit, and SBE 43 oxygen, dual temperature, and dual conductivity sensors are titanium. The Seapoint fluorometer has a rigid polyurethane housing and the WET Labs C-Star 25 cm transmissometer has an anodized aluminum housing with its Zn anode removed. The titanium and aluminum con-

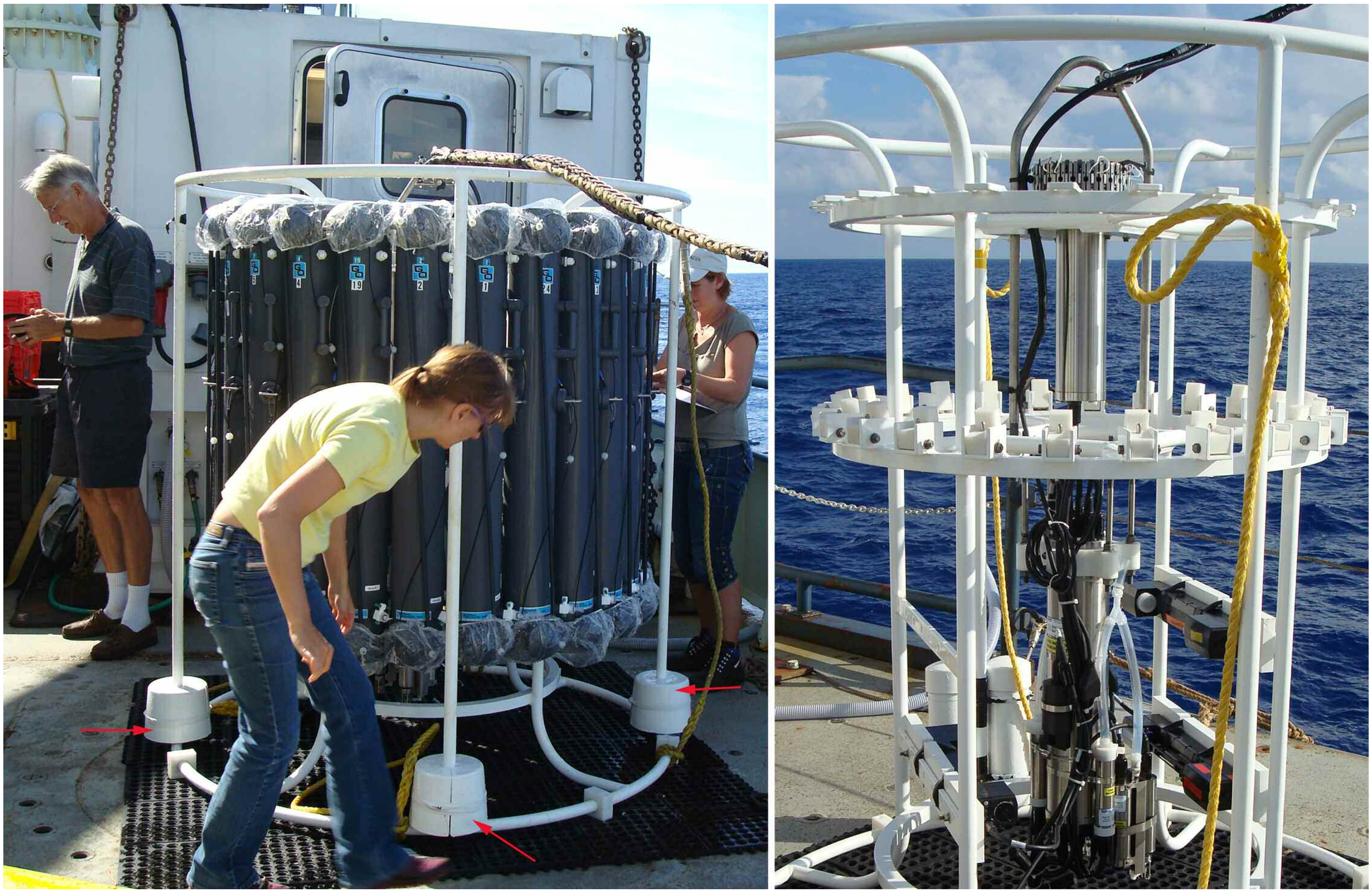

**Fig. 1.** US GEOTRACES carousel with GO-FLO bottles mounted and additional weights marked with red arrows, and close-up of sensor system and GO-FLO mounting blocks.

struction of the system eliminates the need for sacrificial zinc anodes to prevent galvanic corrosion, a potential source of contamination. One modification to the Seabird carousel system is the addition of four 35 kg epoxy-encased lead weights (140 kg total) to the bottom of the vertical tubes on the carousel (Fig. 1) to make sure the conducting cable remains taut during lowering through the water column. These weights are made just like those on the CLIVAR rosette (Measures et al. 2008), except the lead shot/epoxy resin mixture is cast in a 7 L polyethylene bucket with a PVC pipe (3.2 cm OD) glued at the bottom in the center of the bucket. Before adding the epoxy and lead shot, the pipe and bucket are coated with silicone grease to ease removal after the mixture cures. After curing, the weight is cut in half length-wise, the cut surfaces recoated with epoxy resin, painted with 4 coats of white epoxy paint, and the matching halves placed around the vertical tubes of the carousel (arrows in Fig. 1). Each of the weights is then kept together with all 316 stainless steel, worm drive clamps (McMaster-Carr #5682K25). Besides these weights, a minor modification is the addition of 18 cm loops of 1 mm monofilament line below each trigger on the electronic release unit (Seabird Carousel manual, p. 22: www.seabird.com/pdf_documents/manuals/32_018.pdf). Up to three triggering lanyards from the GO-FLO bottles can be placed over one of these loops, and the loop then put over the release trigger, allowing 2-3 bottles to be fired simultaneously.

Twenty-four 12 L GO-FLO bottles (General Oceanics, Model 108012T) are mounted to the carousel. They are Teflon-coated by the manufacturer, all o-rings are Viton, the air bleed valve is replaced with a Swagelok Nylon fitting with o-ring (NY-600-1-OR) to allow direct air-pressurization (a Teflon plug, Swagelok T-600-P, is used to cap this fitting), and the normal sample drain valve replaced with a 3/8″ Teflon plug valve (Chemfluor/Cole Parmer # 06392-31). An ca. 25 cm piece of acid-cleaned 3/8″ FEP Teflon tubing with one end cut at a 60° angle is attached to the inside of the plug valve so that the beveled end fits against the opposite side bottom of the bottle. This facilitates draining the entire sampler content and the collection of any particles that might sink below the level of the drain valve during sampling.

New GO-FLO bottles are completely disassembled (including o-rings) and the o-ring grooves are wiped cleaned with 2-propanol and Kimwipes to remove remaining oil/grease and contaminants from manufacturing. The bottles are reassembled, filled with DI water and dilute Micro detergent, and allowed to soak for 24 h (Note: the Teflon drain valve is briefly opened to fill it with detergent solution). The bottles are then rinsed with DI water until all detergent is removed. Next, the bottles and valves are rinsed with 2-propanol to remove any organic contaminants (ca. 500 mL per bottle), then rinsed again with DI water. A final 24 h soak uses 0.3 M HCl; care should be taken to not expose the flexible nylon rods that hold the outer retaining rings to the HCl solution since they would become brittle and crack. After the HCl soak the GO-FLOs are thoroughly DI rinsed. They are then ready for use after proper conditioning with seawater (see below) and are not recleaned with this 3-step process unless major repairs occur or severe contamination is encountered. When not being sampled, the Teflon sampling valves on the GO-FLOs are plugged at the outlet to prevent contamination with a 3/8,″ 2.5 cm Bev-a-Line IV tube (Cole Parmer, # S-06490-39) with one end melted shut. Lanyards for triggering the GO-FLO bottles are made of 1 mm monofilament line with stainless steel nicropress sleeves that are painted with white epoxy paint to minimize corrosion and contamination.

The winch is a Dynacon Oceanographic unit (Bryan, Texas USA) with overhead electro-active level wind and cast nylon sheave (60 cm diameter), and line monitoring (length out/in, speed, tension). The winch drum is spooled with 7800 m of 14 mm conducting Vectran cable (braided) with four 18 gauge conductors and extruded polyester outer jacket (Cortland Cables). A Focal Technologies slip ring (Model 180) connects the paired cable conductors to a Seabird Deck Unit (11plus) and computer with Seabird Seasoft software. From the winch the Vectran cable runs through a Dynacon P19 style cast nylon sheave (71 cm diameter) mounted to an Allied Systems (Sherwood, Oregon USA), electrically driven, hydraulic A-frame. Both the winch and A-frame have remote controls so that a single operator can run the complete deployment system, although an operator for each is typically used.

### Clean van

The clean laboratory "van" is an ISO-sized 20 ft aluminum container built to US UNOLS standards (http://www.unols.org/committees/rvoc/vanspec.html) by Silhouette Steel (British Columbia, Canada). The van is divided into two rooms, a small anteroom for storage and sample bottle transfers, and the larger, positive pressure clean room for GO-FLO sampling and sample handling. The inner walls are covered in polypropylene sheeting over the standard aluminum walls, and the floor is Altro rolled vinyl with a total of 5 floor drains. The 5′ anteroom contains a closet within which is the heating/cooling system (HVAC; two Cruisair 16,000 BTU marine air conditioner units with seawater heat exchange) and air compressor for pressurizing the GO-FLO bottles (Gast Model 1HAB-11T-M100X, with dual water trap/5 µm filters and single stage regulator set at 41.4 kPa). The anteroom also has polyethylene storage racks holding up to 8 spare GO-FLO samplers that are not for sampling.

The remaining portion of the van is the clean sampling area that has the same polyethylene racks holding 12 GO-FLOs per side (Fig. 2); the doorway between the anteroom and clean room has top to bottom clear vinyl strips to minimize return airflow (i.e., the clean room is positive pressure and at least 14.2 CMS [cubic meters per second] of HEPA-filtered air exits through the vinyl stripped doorway). The end of the clean lab (Fig. 2) has a counter with sink (ship's water), DI system (Barnstead B-Pure high capacity unit plumbed

**Fig. 2.** Inside clean area of lab van and close-ups of GO-FLO air pressurization system, sampling with capsule filters, and sampling with membrane filters.

directly to the final Millipore Milli-Q Element system), and 4 ft clean air bench (CleanAir Systems Model 4000). The counter has cabinets and drawers below it for storage of supplies. Two vents in the center of clean area ceiling are fitted with HEPA filters through which air from the HVAC unit flows (average total flow of 28 CMS); this keeps the clean room section positive pressure. At each GO-FLO position, a stainless steel toggle valve (Swagelok # SS-1GS4-A) is connected to the common air compressor line (Fig. 2). A hydrophobic, 0.2 µm Teflon membrane filter (Gelman Acro 50ST) is placed in the line to the GO-FLO to ensure no particulate matter enters the sample bottle and to prevent water from back flushing into the toggle valve. The air pressure in the system is kept at 41.4 kPa via the regulator on the compressor. If suboxic or anoxic waters are being sampled, compressed nitrogen (41.4 kPa) can be used instead of air, with the cylinder and regulator kept outside the lab van (the van has 4 pass-through openings for such uses).

### Deployment procedures

Unless they are on the carousel during use, the GO-FLOs are always kept in the clean van. Prior to mounting on the carousel, the GO-FLO ball valves are fully rotated (to keep them closed and ready for attaching lanyards to the electronic triggers or monofilament loops) in the clean van and clear plastic shower caps (i.e., polyethylene with elastic bands) placed over both ends of the GO-FLO, and the Bev-a-Line plugs installed. Each GO-FLO is mounted on the carousel and its lanyard attached directly to the electronic triggers (for single bottle tripping) or to the monofilament loops (for tripping 2-3 bottles); the shower caps remain in place. The length of the lanyards is adjusted so that the GO-FLO bottle ball valves are completely open; the bottles are sent down open. A nylon webbing strap with plastic buckle is routed around all of the GO-FLOs (under lanyards and through handles) and securely tightened to prevent accidental loss if the bottle falls off its mounting pin. Immediately before deployment, the shower caps are removed, and the carousel is quickly lowered into the water at ca. 5-10 m depth. After the conductivity-temperature-depth (CTD) pumps turn on, and sensors are activated the carousel is lowered at 40-60 m/min (slower at shallower depths and if large seas are running). Bottles are tripped on the upcast: the carousel is raised at 60 m/min and 10 m before the selected depth, the winch is slowed to 3 m/min; when the depth is reached the bottle(s) is fired and the 60 – 3 m/min routine repeated for the rest of the hydrocast. These procedures are followed in order to minimize contamination from the carousel frame and sensors (e.g., Measures et al. 2008).

When the carousel is recovered and placed on deck, shower caps are immediately placed on the top and bottom of the GO-FLOs, the webbing removed, and the bottles transferred into the clean van (1-2 people in the clean room section receive the bottles from the anteroom section). Sampling procedures vary slightly for the trace element, whether the sample is filtered or not, and the type of filter/filter capsule used (see articles in this volume). However, to minimize contamination, the Bev-a-Line plug is removed from the Teflon sampling valve, the Teflon cap on the air pressurization fitting removed (water should squirt out if the bottle didn't leak), flow started at the sampling valve, and the air line connected (start air flow before connecting). The sample flow can then be stopped to fit sample tubing, filters, etc. onto the sample valve before actual sampling. Subsequent sampling details are given in individual articles in this volume and in the GEOTRACES Cruise Protocols (http://www.obs-vlfr.fr/GEOTRACES/libraries/documents/Intercalibration/Cookbook.pdf).

Note that prior to first sampling on a cruise, the GO-FLO bottles are all triggered at a depth in the permanent thermocline (typically 200-300 m) at the first offshore station of opportunity, and then left in the clean van for 12-24 h to soak/condition. This procedure is ideally repeated twice more before the first actual station to rinse and condition the bottles and minimize contamination. Shipboard determinations of a contamination-prone element like dissolved zinc should be used to evaluate contamination amongst all the bottles fired at one depth. After the last station of a cruise, the bottles are thoroughly rinsed with DI water in the clean room and left cocked open to dry. This eliminates the growth of fungus and mildew in the bottles, but necessitates the fill/empty conditioning recommended above. After drying, the bottles are closed, sealed in large plastic bags, and stored in the clean room racks.

### Sampling stations

Initial tests of the US GEOTRACES carousel system, including the winch and clean van, took place from 8 Jun–12 Jul 2008 at the Bermuda Atlantic Time Series (BATS) station (31° 45.92′N, 64° 04.95′W) using RV *Knorr*. This cruise focused on the trace metal cleanliness of the GO-FLO bottles (a total of 50), operating procedures, and comparisons of dissolved trace element depth profiles obtained with the carousel and two different vane-type samplers (i.e., MITESS ATE, Boyle et al. 2005; Bell et al. 2002; UAF Vane samplers, Wu 2007), as well as particulate trace element profiles from direct filtration from the GO-FLOs in comparison with those done with in situ pumps (i.e., MULVFS; Bishop et al. 1985) The second cruise evaluated the US GEOTRACES sampling system from 6-29 May 2009, used RV *Knorr* again, and occupied two stations: SAFe (30°N, 140°W; Johnson et al. 2007) and one in the Santa Barbara Basin (34° 16.45′N, 120°02.55′W). On this cruise, the primary goals were to finalize testing and development of the sampling and filtration protocols, conduct more contamination tests, and quantitatively evaluate the hydrographic fidelity of the moving carousel.

### Analytical methods

On the Atlantic Intercalibration cruise in 2008, the profile obtained with the US GEOTRACES sampling system was filtered with Osmonic capsule filters (PTFE Memtrex-FE filter capsule, #CMFE9208RR) with a rated pore size of 0.4 µm. During the Pacific Intercalibration cruise in 2009 profiles obtained with the US GEOTRACES sampling system used Pall Acropak 200 capsule filters (#12941) with a Supor membrane whose pore size is rated at 0.2 µm (for the Zn profile shown here), but also Osmonics (0.4 µm; MSI #DCF0400006) and Sartobran (P 0.2 µm 300 filter capsule #5231307H5—00—B) capsule filters. Since different labs analyzed these samples, a variety of analytical methods were used, with the exact methods referenced in the assessments to follow. Silicate was determined using the colorimetric methods of Parsons et al. (1984), modified for use by an Astoria-Pacific rapid flow analyzer. Salinity was determined using a Portasal salinometer with IAPSO standard seawater as the reference.

## *Assessment*

### Hydrographic fidelity

The inherent problem with a trace element sampling system described here is that triggering bottles while they are moving into clean water may get clean samples, but their hydrographic fidelity—whether they represent the depth at which they were triggered—is in question. In their evaluation of this same problem with the CLIVAR rosette, Measures et al. (2008) used comparisons between the salinities in the bottles versus the sensors and versus a conventional (stopped) hydrographic rosette sampling within several hours of the moving one. We used the same procedure of sensor versus bottle comparisons, but added two more—bottle salinities in the US GEOTRACES carousel stopped versus moving, and silicate in the stopped versus moving carousel. Presumably, a stopped carousel cannot be used for trace element sampling because of potential trace element contamination (e.g., Measures et al. 2008), but in the case of salinity and silicate where contamination is not an issue, the use of the same carousel stopped or moving allows a direct hydrographic comparison of "ideal" sampling (i.e., not moving) and with almost no time difference (see below). Furthermore, the use of two well-constrained parameters (high precision measurements of salinity and silicate) with differing gradients (where a large concentration gradient with depth allows the best resolution of sampling errors) sampled from the bottles themselves (i.e., no built-in sensor-bottle depth offset) yields a more robust evaluation.

For this set of experiments, the carousel was lowered to set depths (maximum of 600 m at the SAFe station and 430 m in the Santa Barbara Basin), allowed to equilibrate for 2 min before firing one bottle, then lowered 50 m below the preset depth and the moving procedure given above followed (i.e., raised at 60 m/min until 10 m below the set depth, whereupon the rate was slowed to 3 m/min, and the bottle fired when the carousel reached the preset depth). This was then repeated for the remaining 8 depths at SAFe and 5 at the Santa Barbara Basin. The depth profiles for salinity and silicate from the two stations taken with the stationary carousel are shown in Fig. 3. The most usable chemical/hydrographic gradients

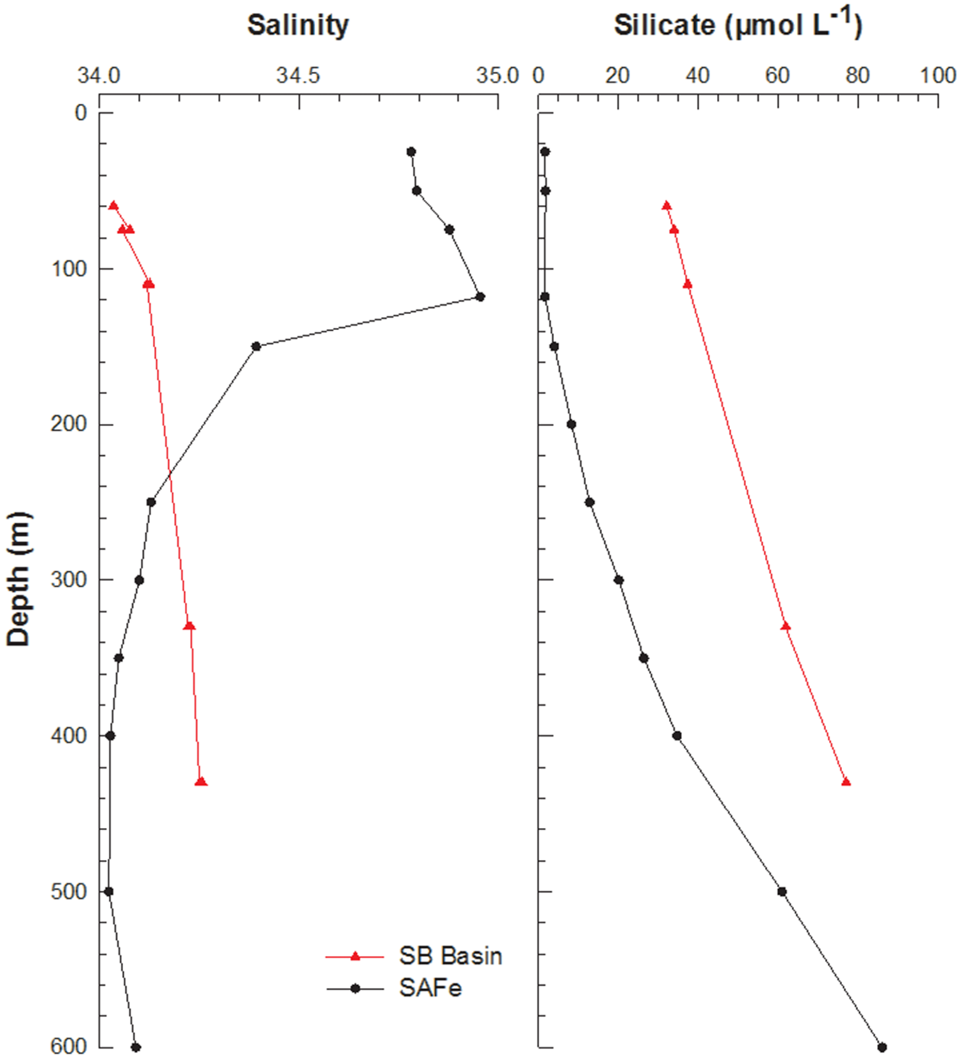

**Fig. 3.** Depth profiles for salinity and silicate from the SAFe and Santa Barbara Basin Stations in the North Pacific Ocean. Samples were from GO-FLO bottles triggered while the carousel was stationary.

are salinity in the upper 200 m at SAFe, and silicate below 125 m at SAFe and at all depths in the Santa Barbara Basin (Fig. 3).

Following the same evaluation of sample "smearing" used by Measures et al. (2008), the differences between the salinities in the GO-FLO bottles and the CTD sensor were first examined, but with the additional benefit of comparing them against the same system being held at a fixed depth. The plot of bottle salinity versus sensor salinity for the moving carousel (Fig. 4) shows a highly linear ($r^2$ = 0.9995; slope = 0.9978) relationship, but with the bottles consistently having a slightly higher salinity (0.0108 ± 0.0082; $n$ = 28) than the sensor (Fig. 4); there is at least one point that is definitely higher than expected and may actually be due to a leaking bottle (Note: Unless the GO-FLO bottle was obviously leaking [visual detection], all data are included.). These results are completely in accord with the behavior found by Measures et al. (2008) for the smaller CLIVAR system. Surprisingly, when the US GEOTRACES carousel and its CTD are held stationary for triggering the bottles, equivalent behavior is shown (Fig. 5; $r^2$ = 0.9996; slope = 0.9917; intercept = 0.292); the bottle salinities are always higher than those of the sensor (0.0079 ± 0.0076; $n$ = 28). It is important to note that these stationary data can be used to apply a correction/offset to the CTD sensor data for conventional hydrography (e.g., http://www.go-ship.org/HydroMan.html) so that the bottle and sensor data would be nearly identical, but given the possibilities of GO-FLO leaks, we have not applied any corrections. Combining the two data sets so that moving versus stationary bottles are directly compared (Fig. 6) yields a slope of 1.003 ($r^2$ = 0.9972; $r^2$ = 0.9992 and slope = 1.005 if the one errant point is ignored). A more rigorous statistical evaluation of these moving versus stationary data, and the trace metal data to be discussed below, uses the Pearson Product Moment Correlation (PPMC) if the data are normally distributed, or the Spearman Rank Order Correlation (SROC) if they are not normally distributed (Fowler et al. 1998). In this application the salinity data are not normally distributed, so the SROC results show that the moving and stationary salinities are indistinguishable ($r^2$ = 0.990, $P = 2 \times 10^{-7}$, $n$ = 28); sample smearing cannot be detected.

The corresponding silicate data for the moving and stationary bottles at the SAFe and SB Basin stations (Fig. 7) also show a highly linear behavior (ignoring the one errant point that is the same as that for salinity in Fig. 6: $r^2$ = 0.9998, slope = 1.01; $n$ = 28). Using the same statistical method, SROC, as that for salinity yields $r^2$ = 0.997 and $P = 2 \times 10^{-7}$, the moving and stationary silicates are identical and therefore any smearing is not detectable. Considering that these evaluations occurred in offshore and coastal waters, and the moving sampling system is much larger than that used in the CLIVAR Program, which could affect bottle flushing, this hydrographic fidelity is much better than one might imagine. In terms of routine evaluation of GO-FLO sample integrity, the sensor-bottle salinity method of evaluating smearing described by Measures et al. (2008) can

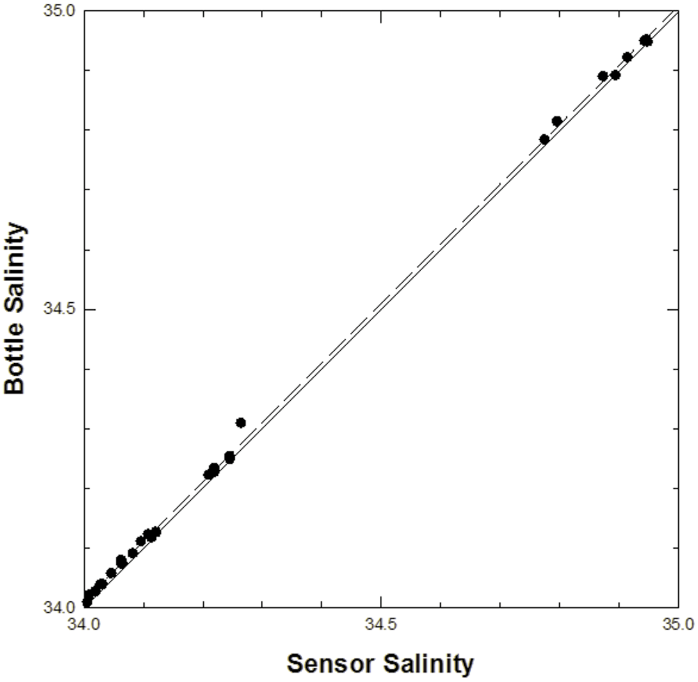

**Fig. 4.** Comparison of GO-FLO bottle versus CTD sensor salinities taken while the US GEOTRACES carousel was moving upward at 3 m/min. The plotted solid line is the perfect 1:1 agreement, whereas the dashed line is the actual fit to the data.

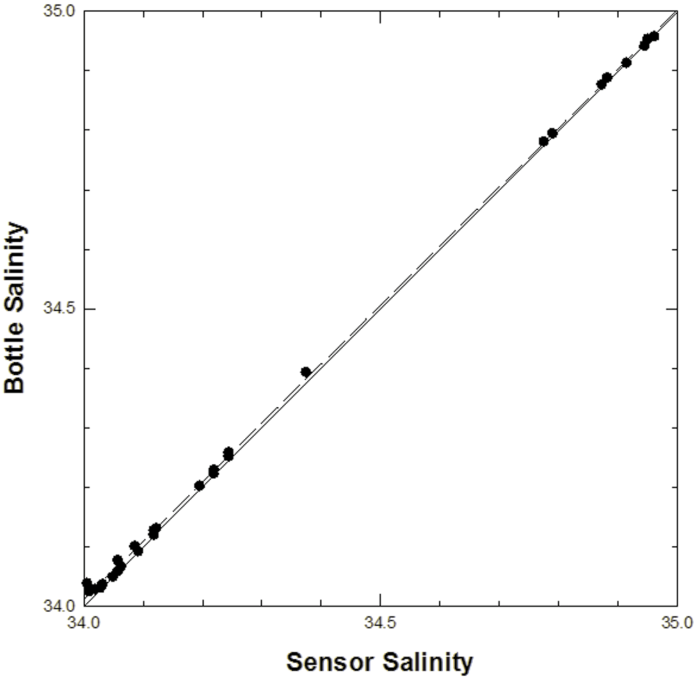

**Fig. 5.** Comparison of GO-FLO bottle versus CTD sensor salinities taken while the US GEOTRACES carousel was held stationary for 2 min. The plotted solid line is the perfect 1:1 agreement, whereas the dashed line is the actual fit to the data.

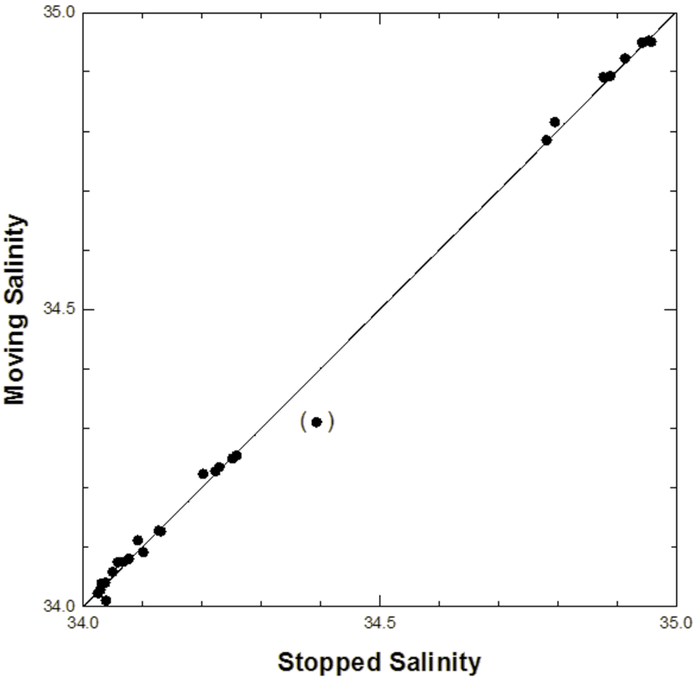

**Fig. 6.** Comparison of GO-FLO bottle salinities taken while the US GEOTRACES carousel was moving upward at 3 m/min or held stationary for 2 min. The plotted solid line is the perfect 1:1 agreement, whereas the dashed line is the actual fit to the data. However, the data point with parentheses around it was excluded from linear regression (see text).

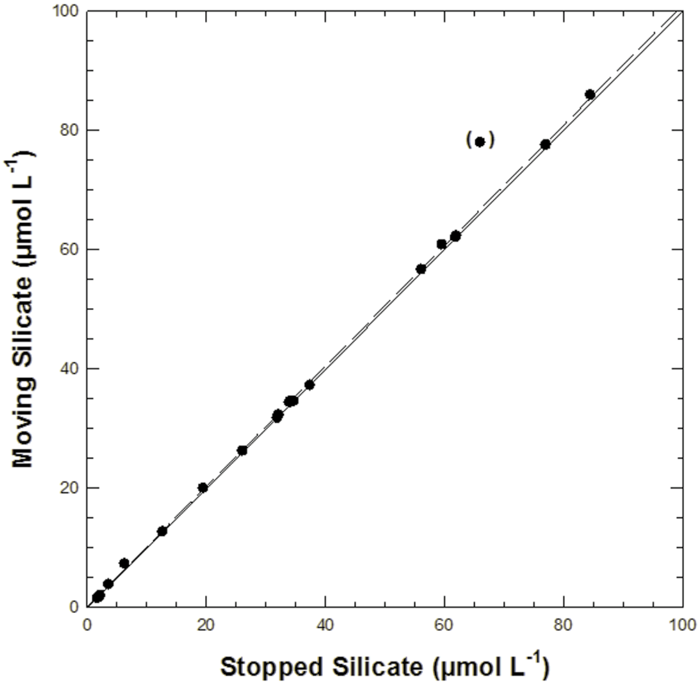

**Fig. 7.** Comparison of GO-FLO bottle silicate concentrations taken while the US GEOTRACES carousel was moving upward at 3 m/min or held stationary for 2 min. The plotted solid line is the perfect 1:1 agreement, while the dashed line is the actual fit to the data. However, the data point with parentheses around it was excluded from linear regression (see text).

still be employed to monitor problem sampling (i.e., either too much smearing or leaking bottles).

**Sample contamination**

The US GEOTRACES sampling system takes hydrographically representative samples, but to address how it performs for the collection of uncontaminated samples for trace metals, depth profiles of three dissolved trace metals, Cd, Zn and Fe, were used on the Atlantic and Pacific Intercalibration Cruises. For these comparisons the profiles are based on samples from the US GEOTRACES sampling system and those obtained with either MITESS ATE or UAF Vane samplers, systems that are well-established for taking uncontaminated trace metal samples.

The dissolved cadmium profiles at the BATS station sampled during the Atlantic Intercalibration cruise are presented in Fig. 8. These plots use density (Sigma theta) rather than depth because a mesoscale eddy passed through the station over the three days between the hydrocasts and strongly offset the depth features (e.g., subtropical mode water); plotting Cd versus density rather than depth normalizes the eddy-induced offsets. Although cadmium is not considered one of the most contamination-prone elements, it is one of the key trace elements to be determined in the GEOTRACES program. The data presented in Fig. 8 show the comparison between the Baseline profile obtained with the US GEOTRACES sampling system (filtered with an Osmonics capsule) and determined at UCSC using offline extraction with Nobias PA1 chelating resin and high resolution ICP-MS (Biller and Bruland 2012; B&B Carousel in Fig. 8), and samples collected with the MITESS ATE vane samplers, filtered with a 0.4 µm pore size Nuclepore membrane filter, and determined at MIT with a small volume NTA-resin batch method and isotope dilution ICP-MS (Lee et al. 2011; MITESS in Fig. 8). Fig. 8 also presents data from a second cast with the US GEOTRACES sampling system to obtain samples for contamination prone trace metal isotope measurements (Isotope Carousel in Fig. 8; filtered with an Osmonics capsule) and determined at MIT (Lee et al. 2011). Visual comparisons of the data show excellent agreement over the entire 4000 m of the water column sampled (but plotted versus density). Applying the Spearman Rank Order Correlation routine (as used for salinity and silicate since the data are not normally distributed) statistically confirms that any observed differences are only due to random errors (B&B carousel versus MITESS, $r^2 = 0.978$, $P < 0.001$, $n = 14$; B&B carousel versus Isotope carousel, $r^2 = 0.929$, $P < 0.001$, $n = 8$; and Isotope carousel versus MITESS, $r^2 = 0.976$, $P < 0.001$, $n = 8$). The Cd results are not affected by the sampling and sample handling systems, or analytical methods or laboratories, used to obtain them.

Zinc is arguably one of the most contamination-prone trace metals. Fig. 9 presents Zn profiles from the Pacific Intercalibration cruise plotted versus depth. There were three US labs that determined dissolved Zn on the profile of samples from the carousel that were filtered with the Acropak capsule: UCSC (method of Biller and Bruland 2012), FSU (offline chelating resin extraction with isotope dilution, high resolution ICP-

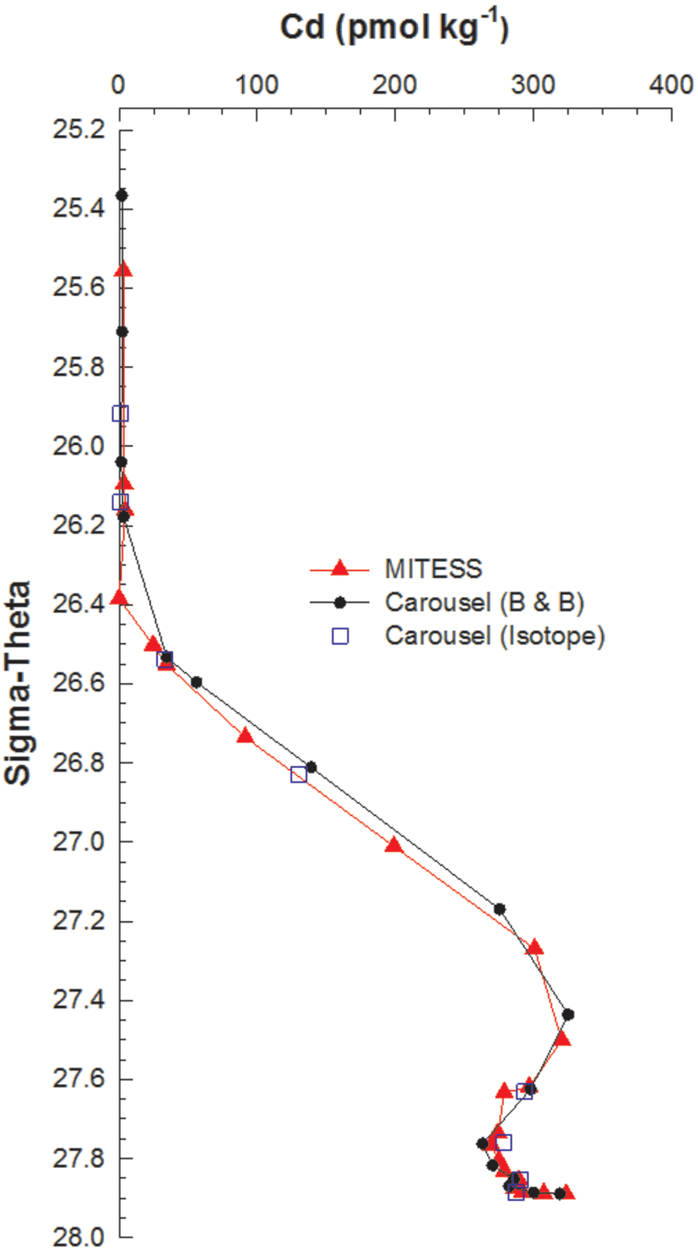

**Fig. 8.** Cadmium depth profiles at the BATS Station during the 2008 Intercalibration Cruise. The data are plotted as a function of density (roughly 0-4000 m) due to a mesoscale eddy that passed through the station between samplings. Two sampling systems were used, the US GEOTRACES carousel with which there were two hydrocasts and analytical methods ("B & B" is Biller and Bruland 2012, and "Isotope" is the cast for trace element isotopes and used the method of Lee et al. 2011), and the MIT MITESS vane samplers using the methods of Lee et al. (2011).

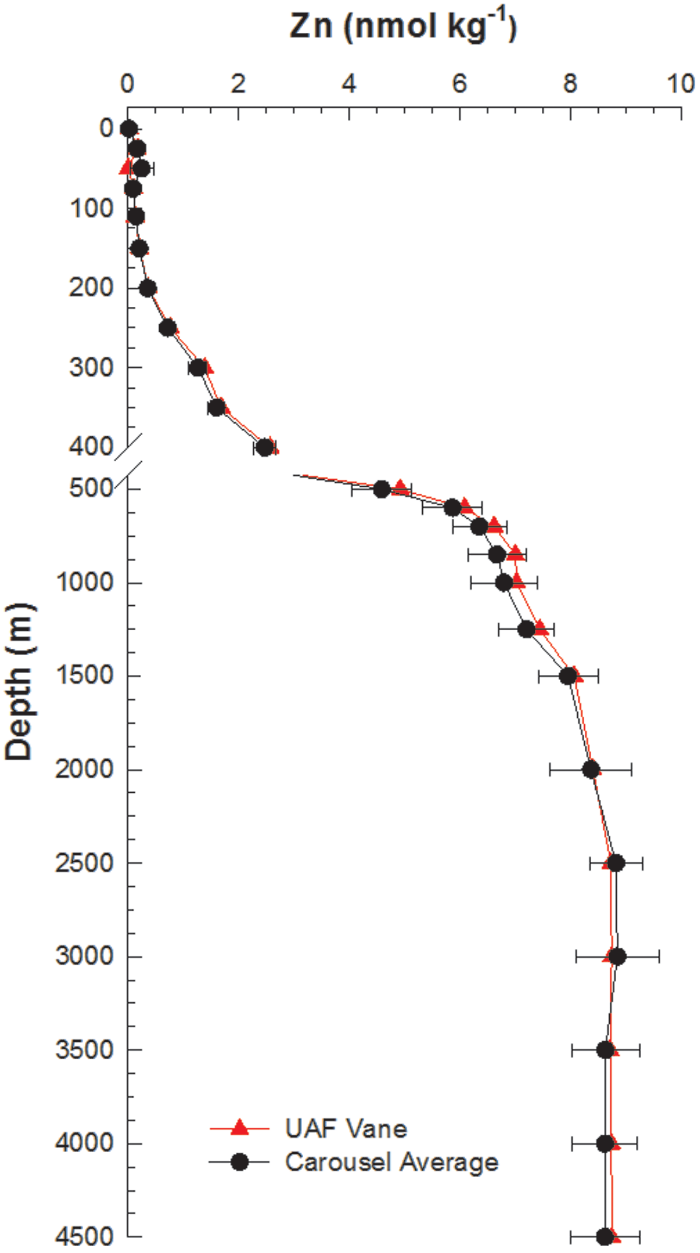

**Fig. 9.** Depth profiles for zinc at the SAFe Station during the 2009 Intercalibration Cruise. The US GEOTRACES carousel was used on this cruise, and three labs with 3 different analytical methods participated in the analyses: Biller and Bruland (2012), Milne et al. (2010), and Wu (2007). The UAF vane data are from the occupation of the SAFe station in 2004 (Wu unpub. data).

MS; Milne et al. 2010), and U. Miami (magnesium hydroxide coprecipitation with isotope dilution, high resolution ICP-MS; Wu 2007). The average and standard deviation values of these three labs for the US GEOTRACES profile are presented in Fig. 9 and compared with data obtained at the same station during the SAFe cruise with the UAF vane samplers 5 years earlier (method of Wu 2007; J. Wu unpubl. data). Excellent agreement between the two sampling systems is observed, and the SROC method statistically confirms this ($r^2 = 0.979$, $P < 0.001$, $n = 24$).

Iron is another of the contamination-prone trace elements and a key trace metal to determine in the GEOTRACES pro-

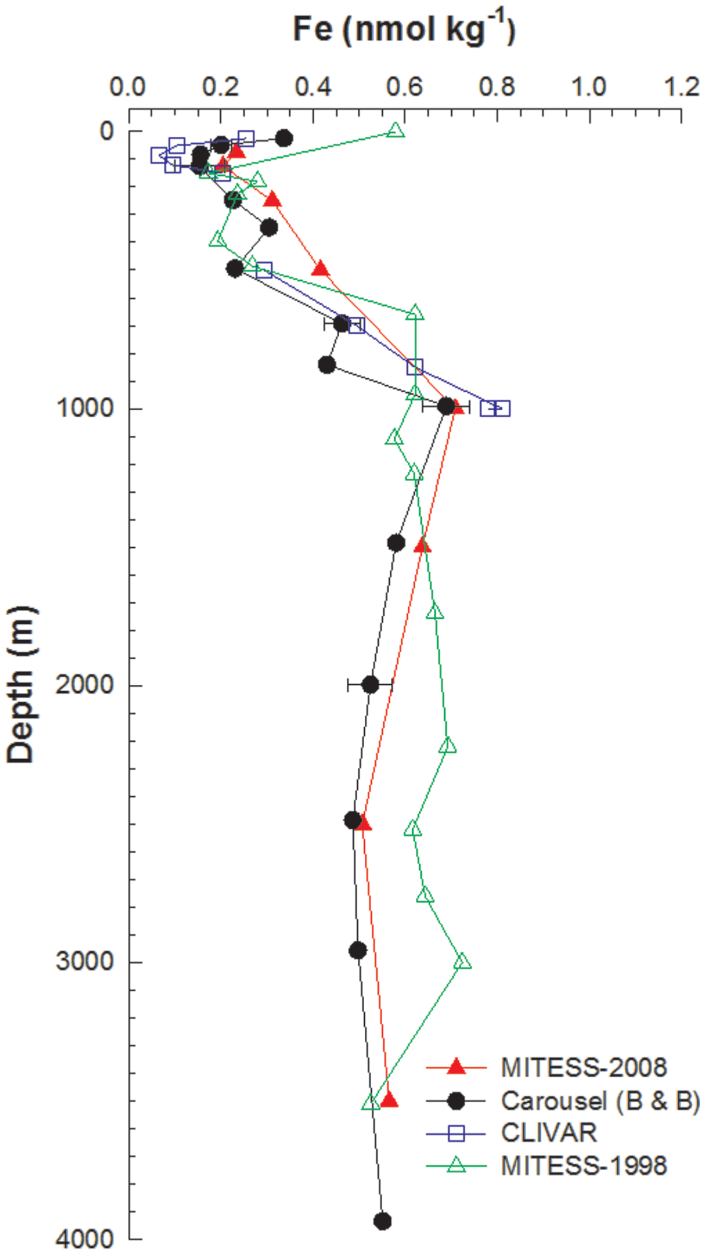

**Fig. 10.** Depth profiles for dissolved iron at the BATS Station during the 2008 Intercalibration Cruise. Three sampling systems were used, the US GEOTRACES carousel ("B & B" is Biller and Bruland 2012), the MIT MITESS vane sampler (Lee et al. 2011), and the CLIVAR rosette sampler (Milne et al. 2010). Also shown are data from a 1998 occupation of BATS using MIT MITESS vane samplers (Wu et al. 2001).

gram. Presented in Fig. 10 is the dissolved Fe profile and plotted versus depth obtained with the US GEOTRACES sampling system at the BATS station in 2008 and filtered with Osmonics capsules (Biller and Bruland 2012). The profile (Carousel-B&B, Fig. 10) agrees well with a separate profile obtained with the CLIVAR sampling system during the same cruise (Milne et al. 2010), with the PPMC method (iron data are normally distributed) giving $r^2 = 0.912$, $P = 0.00022$, $n = 8$. PPMC results ($r^2 = 0.941$, $P = 0.0003$, $n = 7$) also show that Fe data from the US GEOTRACES carousel are statistically indistinguishable from those of the MITESS ATE samplers used on the same cruise (MITESS-2008 in Fig. 10; Lee et al. 2011). MITESS data from 1998 at BATS (Wu et al. 2001) are plotted in Fig. 10 (MITESS-1998) and display similar behavior, but are not as well correlated with the 2008 carousel data (PPMC, $r^2 = 0.635$, $P = 0.057$, $n = 6$) or even 2008 MITESS results (PPMC, $r^2 = 0.561$, $P = 0.251$, $n = 4$). Overall, contemporaneous measurements of dissolved Fe, Zn, and Cd in samples from the US GEOTRACES carousel and proven sampling systems in both the Pacific and Atlantic Oceans, and using different analytical methods, show excellent agreement—statistically, systematic errors cannot be found.

## Discussion

Whereas there has been considerable interest in developing effective systems for taking trace element samples since the late 1970s (e.g., Bruland et al. 1979; Boyle et al. 2005), the international GEOTRACES program has really spurred developmental efforts. Indeed, the Dutch TITAN sampling system (De Baar et al. 2008) was designed for GEOTRACES and has been used successfully on numerous cruises (e.g., Klunder et al. 2011). The US GEOTRACES system was assembled with the same goals as those for TITAN, to take water samples without TEI contamination in the shortest possible time, but with an approach that used commercially available components to minimize costs and allow for parts exchange if needed (e.g., between the ship's CTD/rosette and the US GEOTRACES carousel).

The data presented here demonstrate that the sampling system takes hydrographically representative samples even though the bottles are trigged while slowly moving into trace metal-clean waters – statistically identical salinity and silicate samples are taken whether the carousel is moving or not. Moreover, the results for zinc and iron, in particular, show that the samples are uncontaminated below 20 m (sampling at shallower depths appears to result in contamination, perhaps from the ship's bottom paint and sacrificial zinc anodes). But for the system to be useful for long ocean basin transects with closely spaced stations, it must also be fast. Based on timing during the two GEOTRACES Intercalibration cruises, and the 2010 US North Atlantic Zonal transect, the system can be deployed, samples acquired (2 GO-FLOs per depth), and the carousel recovered in 1 h per 1000 m. High seas slow this rate down (ca. 1.5 h per 1000 m), but it is still fast compared with proven GO-FLO deployment on a nonmetallic cable (e.g., Bruland et al. 1979) or vane sampling (e.g., Boyle et al. 2005). Based on our experience with the recent North Atlantic cruise, processing samples from 12 depths in the clean lab, with one GO-FLO used for dissolved samples only (i.e., capsule filter like the Acropak; Fig. 2) and one for particulate and dissolved samples (i.e., using a membrane filter, Fig. 2; see Planquette and

Sherrell, in press), takes ca. 4-5 hours (faster for deep, low particle, samples; slower for upper water column ones). Thus, the US GEOTRACES sampling system described here meets the three main requirements for large ocean basin transects for TEI studies— rapid, representative, and noncontaminating. Of course, constant monitoring of these factors, particularly contamination, is an essential part of the GEOTRACES Intercalibration program. During a cruise, shipboard determinations of contamination-prone elements, such as dissolved zinc, can quickly assess contamination from individual GO-FLO bottles.

On a larger scale and for all the TEIs, the occupation of crossover (where different cruise transects occupy the same station) or baseline stations (long-standing stations where numerous investigators have carried out TEI intercalibrations and obtained the most accurate TEI profiles possible—largely in mid- and deep waters) allow careful intercalibration of the entire process: from sampling to storage to analyses. As an example, dissolved aluminum profiles determined on board ship by Matt Brown using a flow injection method with fluorescence detection of the Al-lumogallion complex (Brown and Bruland 2008) during the Atlantic Intercalibration cruise (BATS station) using the US GEOTRACES sampling system and filtered through both Osmonics capsule filters and 0.4 µm pore size Nuclepore membrane filters are presented in Fig. 11. These are compared with a shipboard dissolved aluminum profile determined by Rob Middag also using the flow injection method of Brown and Bruland (2008) in the spring of 2010 on the Netherlands occupation of the BATS station during their meridional transect through the western North Atlantic. This reoccupation of BATS, the Atlantic Intercalibration baseline station, used the newest generation of the NIOZ TITAN sampler (De Baar et al. 2008) equipped with "PRISTINE" polyvinylidene fluoride (PVDF) sampling bottles (in place of GO-FLOs), and filtered with a 0.2 µm pore size Sartobran capsule filter. Thus, it also provides an additional comparison with the US GEOTRACES sampling system. The upper 500 m values differ due to seasonal changes in the dust input and productivity of the surface waters (Fig. 11), but in the intermediate and deep waters, the agreement is excellent (PPMC method; Carousel-Osmonics versus -Nuclepore, $r^2$ = 0.943, $P$ = 1.001, $n$ = 7; Carousel-Osmonics versus TITAN-2010, $r^2$ = 0.954, $P$ = 0.0001, $n$ = 9). Such intercalibrations to verify accuracy and precision via reoccupation of the same station are essential for a program such as GEOTRACES where different sampling systems are being used and many different labs are analyzing the samples.

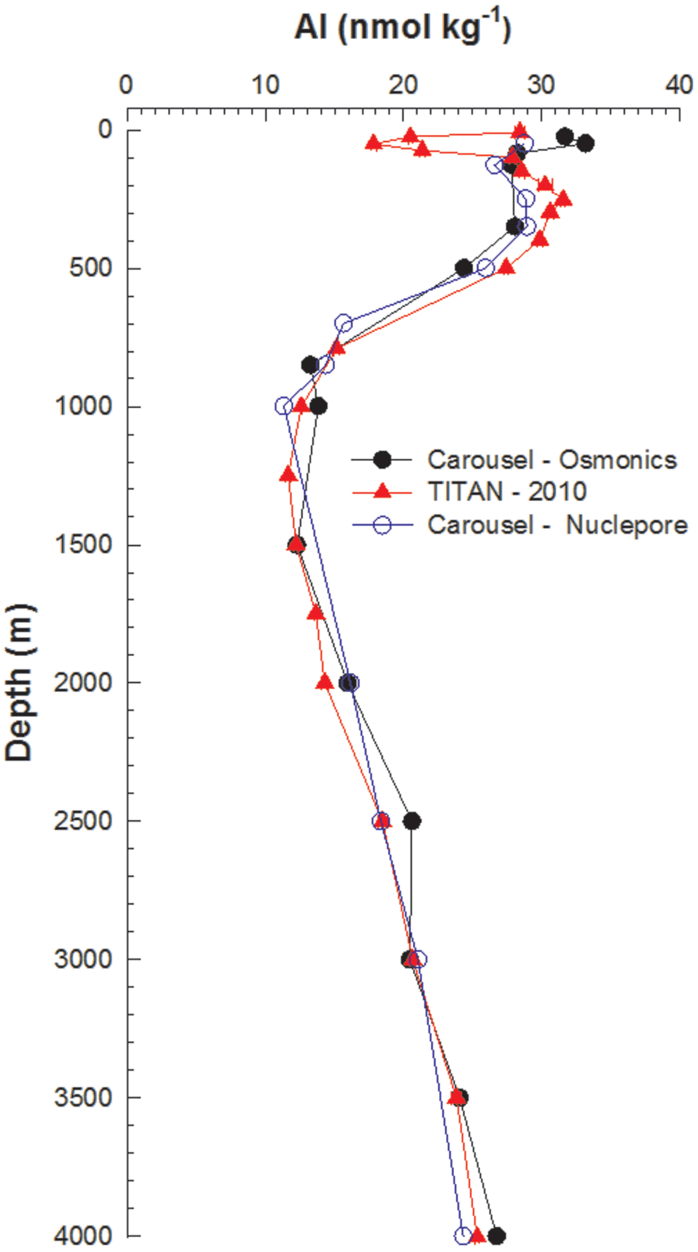

**Fig. 11.** Aluminum depth profiles at the BATS Station during the 2008 Intercalibration Cruise using the US GEOTRACES carousel and filtration with either Osmonics filter capsules or 0.4 µm Nuclepore membrane filters. Also shown is the Al profile from the 2010 Netherlands occupation of BATS and using the NIOZ TITAN sampler (De Baar et al. 2008) with PRISTINE PVDF sampling bottles.

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