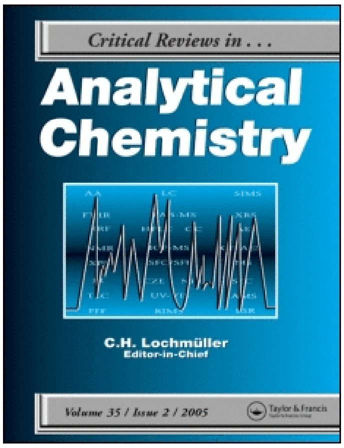

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SAMPLING OF SEAWATER FOR TRACE METALS

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I. INTRODUCTION

The analysis of seawater for trace metals has long been a challenge for marine chemists. It is only in the last decade that apparently reliable data have been available with the result that many past notions regarding the concentrations of trace metals in seawater have had to be discarded.

This is readily evident from most recent literature and is exemplified in Table 1 where values from Brewer's 1975 review of abundances of elements in seawater[1] are compared with the certified values of the open ocean seawater reference material NASS-1, collected southeast of Bermuda in the North Atlantic from 1300 m in 1981,[2] and with the consensus values of a coastal water collected for an International Council for the Exploration of the Sea (ICES) exercise in 1982, from 30 m in the Bay of Biscay, about 20 mi off the coast of France.[3]

The improved reliability of results arises from two main factors. The first is the recent general improvement in trace metal separation chemistry allied with major advancements in analytical instrumentation. The second is the general reduction and control of contamination during sampling, storage, and analysis.

While problems in sampling may not have been the major cause of poor analytical results in the past, it is obvious that unless the integrity of a material can be maintained during the sampling procedure, all other steps in the analytical scheme are a waste of time and effort.

Indeed, the two seawater samples, NASS-1 and ICES-5, listed in Table 1 have probably been contaminated with respect to lead during sampling.[2] However, there is growing evidence that a number of laboratories can now reliably sample seawater for a series of trace metals using a variety of sampling techniques.

II. SAMPLING METHODS

The first step in any chemical analysis of seawater is the initial collection of the water sample to be analyzed. Except for work in well-protected embayments and nearshore coastal waters, collection of seawater samples requires a seagoing vessel that is capable of deploying the sampling gear and accommodating the personnel who operate the equipment. It must be sufficiently large to provide reasonable stability in the sea conditions expected in the area of the study, have adequate endurance, and be capable of

Table 1
TRACE METAL CONCENTRATIONS IN SEAWATER (μg/*l*)

	Brewer (1975)[1]	NASS-1[2]	ICES-5[3]
As	3.7	1.65	1.4
Cd	0.1	0.029	0.020
Cr	0.3	0.184	0.08
Co	0.05	0.004	0.004
Cu	0.5	0.099	0.123
Fe	2	0.192	0.376
Pb	0.03	0.039	0.049
Mn	0.2	0.022	0.240
Mo	10	11.5	—
Ni	1.7	0.257	0.202
Zn	5	0.159	0.392

maintaining position and keeping an acceptable wire angle. With the exception of measurements of a very few chemical parameters, such as oxygen concentrations and salinity which can be measured directly *in situ* by a probe deployed through the water column, water must be retrieved from the ocean from an accurately known depth either by pumping water aboard ship or by trapping a parcel of water in a water sampling device.

Water samplers have been deployed in two ways. The traditional approach is to attach the open samplers to a weighted wire rope that is lowered over the side of the ship with a large winch. The bottles are closed by sending a weight (messenger) down the wire to trigger the mechanisms that close the samplers. A second and newer method has been to attach a group of samplers to a framework (rosette) equipped with electronic triggering devices that is deployed over the side attached to the end of an electromechanical cable. The samplers are then closed by signals from the surface when the rosette reaches the desired depth.

Once the samplers have been retrieved, samples for chemical analyses are drained off into appropriate storage bottles. Filtration of the samples will be required for many analyses. Filtration can be incorporated into the transfer of water from the samplers to the storage bottles or left to a later stage in the analytical procedure.

Another approach to sample collection, that has not been thoroughly developed to date, is to moor a collection device, such as an ion exchange or absorbant column, that will passively collect the analytes of interest at some depth in the water column and be retrieved at a later date.

The basic criterion for a water sampling device is that it will reliably collect water from an accurately known depth without contamination with water from other depths. Thus, the sampler must flush rapidly and freely as it is lowered through the water so that it does not drag water from shallower depths with it. It must also close reliably with positive sealing so that it does not exchange water with the surroundings as it is brought back to the surface. The tripping mechanism must be such that there is little risk of pretripping the bottle or failure to trip on command. These considerations are common to all sampling devices and have been described in many reviews.[4]

Another criterion of utmost importance in trace metal studies is that the sampler does not contaminate the sample by introducing metals, other chemicals, or particulates into the sample from its construction materials. In addition, the sampler should not remove chemicals from the water by adsorption or other processes.

Most early samplers were made of brass and, although coated with nickel or plastics, were subject to corrosion. As well as obvious consequences for metals in the sample, the reaction of seawater with brass can also lead to errors in oxygen, salinity, alkalinity, and pH measurements.[5]

Development of sampling techniques for trace metals has focused on avoiding contamination of the samples and many improvements have been achieved along these lines. Scientists investigating most other inorganic analytes do not appear to have been overly concerned about contamination from samplers. The type of samplers used often have not even been reported. The techniques used, and problems encountered, in collection of samples from surface waters and deep waters are rather different. It thus seems sensible to treat devices for these two regimes separately.

The collection of samples from surface waters is technically much simpler than deep water collection because of the proximity of the sampling vessel to the water to be sampled. However, this very proximity increases the risk of contamination from the sampling vessel. In addition, the air-sea interface and the surface film are unique regions of the ocean that complicate collection of surface water samples.

Collection of surface films requires specialized techniques. These techniques and the problems encountered in collection of surface films are unlike those of bulk water. It is also an area of sampling that is in a rapid state of development. The most commonly reported techniques for surface microlayer sampling depend on immersion of a plate or screen sampler through the microlayer into the underlying water and withdrawing it slowly through the microlayer. Glass plates,[6] stainless steel screens,[7] plastic screens,[8-10] and perforated Teflon® sheets[11] have all been used. These samplers will collect something like a 50- to 150-μm-thick surface layer, although the thickness of the layer is actually measured in nanometers. Use of a hydrophobic material such as Teflon® results in preferential collection of lipids and other surface-active components. Surface microlayer samplers which concentrate the microlayer on bubbles bursting at the surface have been reported by McIntyre,[12] Fasching et al.,[13] and Duce et al.[14] Good techniques for collection of bulk surface water should avoid collection of surface films along with the bulk water.

Sampling of surface waters, including surface films to a greater or lesser extent, has been accomplished in a number of ways. Samples have been collected using deep water sampling bottles on a hydrowire, with buckets thrown over the side of the ship, by pumping water onto the ship, and by hand from small launches. Undoubtedly, the best method of collecting "contamination-free" samples for metals is that adopted in Patterson and Schaule's studies of anthropogenic lead.[16] This method involves collection of surface water directly into precleaned polyethylene or Teflon® storage bottles from over the bow of a small launch as the launch is rowed slowly into the wind. The bottle is placed in the water upside down in order to avoid surface microlayer contamination by an operator wearing polyethylene gloves, inverted while it fills, then removed from the water, capped, and bagged in polyethylene before it is brought back on board. Similar, although perhaps less rigorous, procedures are used by others.[17-19] Any type of hand-held sampler or the inlet of a peristaltic pump can be deployed from a small boat in this way. Although Patterson and Schaule's technique will collect as contamination free a sample as seems possible at present, it is not always feasible. It requires calm seas, temperate climates, and relatively warm waters (or individuals prepared to endure severe physical hardships). It is also rather time consuming and potentially hazardous as a small boat must be launched from the ship and recovered.

It is seldom practical to wait for sea conditions that allow for operations from a small boat. Therefore surface samples must often be taken from an oceanographic vessel. Samples from ships have been collected both while the ship is underway and while on station. Sampling while underway can be accomplished by throwing a plastic bucket over the side or the bow, retrieving it, and pouring the water into a storage container, or by pumping water either through an inlet in or over the bow of the ship, or from a boom over the side of the ship. The bucket over the side has to be done at slow speeds, preferably as the ship stops on station. Pumped samples from a boom can be collected at fairly high speeds if a suitable towed body is used to keep the inlet under water. Sample collection with a bucket suffers from the added problem that the sample is open to the air on or near the ship until the sample can be transferred to a storage bottle. Pumping systems can be virtually sealed from the ship's atmosphere and easily allow for collection of large volumes of water. Surface samples for copper have been collected with a peristaltic pump and Teflon® tubing system in which the tubing was extended over the side of the ship with a 10-m-long boom while the ship was steaming slowly.[20] The intake was immersed at a 2- to 4-m depth with the aid of a Teflon® -covered weight. Kremling[21] collected trace metal samples by pumping water through polyethylene tubing attached to a towed stainless steel fish suspended under the ship. Boyle et al.[22] collected surface samples by extending plastic storage bottles attached to the end of a 15- to 20-ft pole over the side of the ship while steaming slowly at 2 kn. The bottles were immersed upside down and then inverted to collect the samples.

Sampling surface water from the ship while on station either with buckets, pumps, or hydrowire casts is plagued by potential contamination from the ship. Bender and Gagner[23] and Bender et al.[24] compared samples collected by hydrocast with those collected in the same samplers from a small boat and found almost twice as much copper from the hydrocasts but no differences for cadmium, manganese, and nickel. Spencer et al.[25] and Magnusson and Rasmussen[19] found no differences between surface samples collected with hydrocasts and those collected remotely from the ship for cadmium, copper, nickel, zinc, and lead. However, both of these studies were conducted in coastal waters at levels somewhat greater than those expected in pelagic surface waters. The magnitude of this problem will obviously depend on a number of factors such as the size of the ship, the length of time on station, and the sea conditions. The collection of surface samples against the side of a stationary ship will always lead to questions about sample contamination.

Although, theoretically, deep water samples can be collected by pumping water up to the ship, in practice, deep water sampling is almost exclusively done with bottle casts. There are two ways to collect deep bottle casts. In the first, the sample bottles are deployed on a hydrographic wire and closed mechanically with messengers. In the second, the samplers are clustered in a package at the end of an electromechanical cable and are closed electronically with signals from the surface.

The traditional hydrographic cast allows for the use of a large variety of types and sizes of samplers. Large volumes can be collected fairly easily. Its depth capability is limited only by the length of the hydrographic cable and sampling can successfully be undertaken in fairly severe weather conditions. It is also a reasonably inexpensive operation. However, hydrocasts present several potential sources of contamination.

A major source of contamination comes from the hydrowire and its weight. These have traditionally been made of steel and can easily become contaminated with oil and grease from the ship. Steel wires are an obvious source of iron contamination. Contamination of samples with particulate iron from the hydrowire was shown by Betzer and Pilson.[26] At present, stainless steel, kevlar, and plastic-coated steel wires are most commonly used. Stainless steel is an obvious improvement over regular steel, although it will still corrode on extended use in seawater. Kevlar and, as long as the coating lasts, plastic-coated wires avoid the problems of metallic hydrowires close to the samplers, but they are not as durable as stainless steel. Kevlar appears to be gaining fairly widespread acceptance judging from the number of experienced laboratories using this material.[17,27]

Another source of potential contamination is the messenger. These have traditionally been brass- or chrome-plated weights that slide down the hydrowire. The potential for contamination comes from the abrasion of particles from either the messenger or the cable as the messenger slides downwards. Since the samplers will close as soon as the messenger arrives, they are probably closed before any of the particles can enter the bottles. However, contamination from the messenger for the next sampler is always possible. Plastic-coated messengers have been used but normal use tends to wear off the plastic coating rather rapidly. Several types of solid plastic messengers have also been employed.[17,25,28] Ideally, plastic messengers and plastic, or plastic-coated, wire should be used, although good results have been obtained with stainless steel hydrowires.

One way to avoid the use of hydrowires, weights, and messengers is to deploy the samplers in a package attached to the end of an electrical cable and close the samplers with electronic signals from the surface. One such array is the General Oceanics rosette system used on the GEOSECS expedition and elsewhere. The electromechanical cable can be plastic covered as can much of the rosette framework, but many of the other parts are inevitably metallic and are situated quite close to the samplers. Samples can be collected, however, as the package is lowered and since the bottoms of the samplers are near the bottom of the package, it should be possible to collect clean samples in this way. Several studies using a combination of stainless steel hydrowire and rosette sampling could not detect any differences between the two methods for a number of metals.[24,29] Also, GEOSECS copper, nickel, and cadmium samples were collected with rosettes without apparent problems.[22-30,32]

III. SAMPLERS

The first reasonably uncontaminated trace metal samples were collected about 1970. Samplers in use at that time will be considered first. These would be Niskins (essentially Van Dorn samplers), Hydrobios TPN samplers (improved plastic Nansens), and NIO bottles with various modifications. As well as being the first plastic samplers and thus potentially useful for trace metal sampling and free from the corrosion problems mentioned earlier, these samplers also have improved flushing characteristics compared to those of Knudsens or traditional Nansen bottles.

The Niskin sampler consists of a polyvinyl chloride (PVC) cylinder attached to the hydrowire with two stainless steel clamps. Two PVC end plugs are joined together with a rubber spring that goes through the center of the bottle. TPN and NIO bottles both have external closing mechanisms. The NIO sampler is made of a polyethylene tube with two-point attachment to the hydrowire. Two rubber end plugs are activated by an external rubber spring. The TPN is made of a polycarbonate cylinder with plastic ball valves. It has an external stainless steel triggering mechanism and reverses on closing like a Nansen bottle.

The greatest contamination concern with the Niskin was with the internal black rubber springs. These have been replaced by surgical rubber springs,[23] Teflon®-coated shock cords,[33] and Teflon®-coated stainless-steel springs.[34] The NIO and Hydrobios TPN samplers have a potential advantage over the Niskin in that they have no internal spring. However, the NIO samplers have large neoprene rubber end caps that may cause contamination problems. These were covered with low density polyethylene sheeting by Topping.[35] The Hydrobios TPN samplers have generally been used without modification. The materials used in their construction (mostly polycarbonate and Teflon®) would suggest that they should be good samplers from the contamination point of view. However, they have the limitation of a rather small (1.7-ℓ) volume.

Although many of the early results of chemical analyses of samples collected with any of these bottles have been shown to be excessively high, it is unclear whether these errors were due to contamination or were incurred at some other stage in the analytical procedure. More recent results with some of the same samplers would suggest that analytical problems or problems resulting from inadequate cleaning of the sampling gear were responsible, not the samplers themselves.

In the early 1970s, the "top drop" Niskin, a General Oceanics PVC sampler with many similarities to the Niskin, became available. This bottle has no internal spring. The bottom plate drops through the bottle from the assembly at the top when tripped. These bottles were compared to standard Niskins and Niskins equipped with Teflon®-coated stainless steel springs by Segar and Berberian[36] who found that the "top drop" gave much lower zinc and iron results than the standard Niskin and perhaps slightly lower levels than the modified Niskin. They also noted concentration increases with time in both of the older types but not in the "top drop". There have been few subsequent reports of use of the "top drop" bottle for trace metal studies, perhaps because it was soon superceded by the Go-Flo sampler. The "top drop" is no longer produced.

The Go-Flo sampler is the latest in the General Oceanics series of PVC samplers. It is attached to the hydrowire and tripped in the same way as the Niskin. The main difference in its operation is that the sampler is sealed by large PVC ball valves at each end that are set so that the sampler enters the water sealed, opens automatically at about 10 m, and is finally closed at the desired depth by the traditional messenger. This sampler has two advantages. The ball valves are actuated by an external rubber spring and it goes through the ocean's surface layer in a closed configuration, avoiding the potential for serious contamination by the surface film. This is especially significant for lead and may be important for other metals as well.

A close-open-close sampler based on a modification of the TPN sampler has been developed by Hydrobois. This device has not yet been used extensively, but was tested in two sampler intercomparisons.[37,38]

The greatest effort at avoiding contamination during sampling has been devoted to studies of lead. These have led to the development of the specialized Teflon® CIT sampler.[16] The sampler, which operates on the principle of a syringe, is deployed on the end of the hydrowire. As the sampler is being lowered near the depth to be sampled it is tripped by a messenger. Water is drawn into a replaceable plastic bag by withdrawal of a central piston into the cylindrical body of the device. This mode of operation has several advantages. The sample is being collected in water unaffected by the presence of a hydrowire and its weight. The sample is only in contact with an easily cleaned polyethylene bag which can be replaced for each new sample. The sampler goes through the surface layer in a closed configuration. Disadvantages are the cost and the fact that only one sample can be collected per cast.

A second version of this sampler, reported by Mart et al.,[39] allows for the collection of three samples per cast and uses electronic triggering. Seakem Oceanography has also produced a Teflon® piston sampler whose operation is based on the same principle as the CIT device.[37]

Another approach to the avoidance of surface layer contamination is to lower a closed sampling device to the desired depth, open it with a messenger or pressure device, and bring it back to the surface open. If the opening for entry of the sample is sufficiently small, an insignificant amount of exchange should occur while recovering the sample. Obviously, this approach is only valid for shallow depths (less than 100 m) because hydrostatic pressure will crush the device at much greater depth. A sampler for trace metals based on this design has been described by Friemann et al.[38] Their study shows good agreement between this sampler and a close-open-close TPN sampler at coastal water metal concentrations.

Cleaning procedures for samplers have varied from rinsing with high quality water (distilled or distilled/deionized) and/or high purity dilute acids, to rinsing with detergent and water followed by leaching the bottles for several days with dilute high purity acid followed by more water rinses.[17] Wallace et al.[27] emphasized the importance of the initial extensive cleaning of newly purchased samplers to remove residues from the manufacturing process. Otherwise, their procedure is similar to that of Bruland et al.[17]

with the additional steps in which the whole bottle is soaked in dilute hydrochloric acid solution and deionized water. Even more rigorous procedures have been used for the polyethylene bags and Teflon® parts used in the CIT sampler.[40] Except for the lead work, the importance of the various steps in the cleaning procedures or the preference of one procedure over another has not been well documented. However, the high quality of Bruland's trace metal results[41] would recommend the more extensive cleaning procedures he describes.

Samplers are not, in general, cleaned between casts during cruises although some workers do report rinsing their devices with high purity acids between samples. Many marine scientists fail to report their cleaning procedures, or if indeed they clean their samplers at all.

IV. ON-BOARD SAMPLE PROCESSING

Once the samplers are brought back on deck, samples must be transferred to suitable storage bottles. Ideally, the transfer process plus any filtration, acidification, or other on-board processing of the samples should be done in a clean-room facility. Several workers have portable containers that are fitted out as clean laboratories that are used in this part of the operation. Water samplers can either be carried into these positive pressure, filtered air, trace metal labs[25] or clamped to a rack on the outside of the lab with the drain spigot connected to a clean tube that passes into the lab.[17] In the absence of a clean room, samples must be processed on deck or in the laboratory of the ship. In these cases there is a serious threat of contamination any time the samplers are opened to the air. Contamination from the atmosphere of the ship can be minimized by designing the procedures so that the samples are exposed to the air as little as possible and by using laminar flow benches wherever possible.

Water samples are often filtered as part of the sample collection and preservation procedures. Several investigators studying trace metals in offshore waters have avoided filtration because of the risk of introducing contamination at this stage. For subsurface, open ocean samples, the amount of particulate matter in the water is so low (less than 10 $\mu g/\ell$) that the contribution of particulate metals to the total metal concentration is sufficiently small that it can be ignored. However, in pelagic surface waters and in coastal waters, differentiation of dissolved and particulate metals is often important. This is normally done by filtering the water sample, either by placing an in-line filter in the tubing between the sampler and the storage bottle when the sample is first collected, or by a separate filtration step subsequent to the initial subsampling of the sample.

In-line filtration is generally accomplished by pressurizing the sampler with nitrogen and using plastic (often Teflon®) filter holders containing 0.4-μm pore size Nuclepore® or similar filters.[17,42] This technique can also be used to estimate the total concentration of suspended particulate matter by gravimetric analysis by preweighing the filters and filtering all the water in a large Niskin or Go-Flo.[49] Off-line filtration can be accomplished using any of a number of commercially available or homemade plastic filtration devices using either pressure or suction to force the water through the filter. Several of these systems have been described by Bewers and Yeats.[42] The results of various tests of these filtration systems[17,42] show that contamination-free filtration is possible with a variety of systems if suitable care is taken in their design and use.

V. ASSESSMENT OF SAMPLING METHODS

The ability of a particular sampling procedure to meet the basic requirements of sampling devices, i.e., to flush freely and close positively and reliably at the intended depth, can be shown most easily by collection and analysis of samples for chemical constituents with known oceanographic distributions and behaviors such as nutrients, oxygen, or salinity. All the samplers considered here meet these requirements.

Checking under realistic field conditions for freedom from contamination is not nearly as straightforward because sampler contamination problems may yield incorrect results for only one or a few types of measurements. If the contamination occurs for a type of constituent like the trace metals, whose distribution is not well established, identification and solution of contamination problems are not simple.

There are several ways of testing sampling gear for contamination problems. Several laboratories have reported individual tests of their samplers, such as Bender and Gagner,[23] who collected samples in various ways and compared the results. A number of intercalibration exercises designed to test sampling methodologies, involving one or two laboratories[17,19,36] and larger international exercises,[37,42,44] have been conducted. The final test is to look for the oceanographic consistency of reported results. Smooth profiles with depth and comparability of results reported by different workers for a particular water mass would be expected.

The most extensive and dedicated program to develop contamination-free procedures has been that of Patterson and colleagues in their studies of lead contamination of the environment. This program has continued for many years and has involved a tremendous amount of effort that has resulted in the adoption of very elaborate, expensive, and time-consuming methodologies. There seems little doubt that these procedures yield high quality results, but the extent to which such precautions are needed in all trace metal studies is open to question.

Less rigorous, but still apparently useful, testing regimes have been reported by others. Among the earliest of these were the studies concerning the potential contamination of manganese, copper, nickel, and cadmium from Niskin bottles with surgical rubber springs deployed on stainless steel hydrowire and tripped with brass messengers.[23,24] These experiments compared samples collected with Niskins on the hydrowire with samples collected from a small boat and samples collected by hand from the same small boat. The effect of the time the samples remained in the Niskin was also noted as well as the effect of the location on the ship where the subsamples were drawn from the Niskin. They observed that copper samples collected adjacent to the ship were contaminated by 0.13 to 0.33 μg/ℓ, but the Niskin did not appear to be responsible. No consistent effects were seen for nickel. Cadmium contamination of 0.006 μg/ℓ was found in the Niskin samples.

Spencer et al.[25] conducted a similar experiment comparing a standard Teflon®-coated Go-Flo (cleaned by rinsing with nitric acid solution and clean water) with hand-collected samples. They found no contamination from the Go-Flo for copper and cadmium, but significant contamination for lead and zinc of 0.2 to 0.3 and 1 to 2 nmol/kg, respectively. The lead and zinc values from the Go-Flo were equally high when the samples were collected by normal hydrocast (kevlar line and Teflon® messengers) and by hand away from the ship. A clean van was used for all sample processing and the hand-collected sampling was done by swimmers. Bruland et al.[17] compared samples collected in modified Go-Flos (Teflon® -coated, silicone o-rings, Teflon® spigots) with those collected by the CIT sampler and by hand from a small boat. Nickel, copper, zinc, and cadmium results showed no measurable differences. Magnusson and Rasmussen[19] compared results from Teflon® -coated Go-Flos with Teflon® taps with those from Hydrobios TPN and Danish RTN3 samplers. They found good agreement for cadmium and copper, slightly higher values from the TPN and RTN3 samplers for nickel, and much higher results from these two for lead and zinc. Go-Flo results compared well with those from the hand-collected samples.

A number of intercalibration experiments designed to test and improve capabilities for the measurement of trace metals in seawater have been conducted by the ICES and

Table 2
IOC INTERCALIBRATION RESULTS[44]

Concentration Differences for Various Combinations (νg/ℓ)

	Hydrobios	Standard Go-Flo	Niskin	Stainless steel	Kevlar
		vs.		vs.	
		modified Go-Flo		plastic-coated steel	
Cd	2	1	0	0	6
Cu	58•	29•	−3	6	15
Fe	39	37	−13	4	52•
Mn	4	−1	−2	0	4
Ni	93•	12	13	10	21
Zn	150	43	120•	22	30

• Differences of more than 20% from mean for modified Go-Flo.

other organizations. Most of these exercises have concerned themselves with analytical capabilities in the laboratory. However, three of the most recent experiments have dealt directly with field sampling problems. The first of these was the International Oceanographic Commission (IOC)-sponsored sampling device intercomparison,[44] the second was a NATO-sponsored device and analytical methods intercomparison,[37] and the third was the fifth round in the ICES seawater intercalibration exercises.[42] The ICES experiment was to test the various filtration procedures employed in coastal zone studies by ICES member laboratories as well as conduct a round-robin intercomparison for trace metals in coastal seawater.

The IOC experiment compared the results from a homogeneous water mass using four different types of samplers deployed on three different types of hydrowires. Analyses were conducted by a number of independent laboratories, all of whom analyzed samples from all the various combinations of samplers and hydrowires. Included in the experiment were Teflon®-coated Go-Flos, Teflon®-coated Go-Flos modified with silicone o-rings and Teflon® spigots, Niskin bottles with silicone rubber internal springs, and Hydrobios TPN samplers. The hydrowires were stainless steel, plastic-coated steel, and kevlar.

Sufficient results for significant comparisons between the various combinations were reported by as many as 15 laboratories for cadmium, copper, iron, manganese, nickel, and zinc. As might have been expected, many contradictory findings were shown. The situation had not been helped by the fact that the sampling had been done under very severe weather conditions making it difficult, if not impossible, to collect each sample under the same conditions.

A comparison of the results is shown in Table 2 which displays the average differences between the samplers and the hydrowires based on results from laboratories that reported concentrations within a factor of two of levels found in these waters.[2,45] In doing this it has been assumed that discrepancies of more than a factor of two from accepted levels result from contamination of individual subsamples or analytical problems at some stage after collection and not from the characteristics of the samplers or the hydrowires. The numbers presented for the different samplers are the concentration differences between the Hydrobios, standard Go-Flo, or the Niskin and the modified Go-Flo. The Hydrobios vs. modified Go-Flo comparison is based on samples collected on plastic-coated steel wire, the standard vs. modified Go-Flo comparison on stainless steel, and the Niskin vs. modified Go-Flo on kevlar. For the wire comparisons, stainless steel and kevlar are compared to the plastic-coated steel wire using only samples collected in modified Go-Flos. Differences of more than 20% are flagged. This treatment is slightly different than that of the same data by Bewers and Windom[44] who *did not have the benefit of more recently reported data on the distribution of metals in* the Bermuda area. However, the conclusions are much the same. The Hydrobios devices gave higher results for copper, nickel, iron, and zinc. The unmodified Go-Flo gave high results for copper, iron, and zinc, and the Niskin sampler gave high results for zinc. The hydrowires had less effect, with the plastic-coated wire generally giving the best results.

The relative performances of a Niskin sampler with a Teflon®-covered stainless-steel spring, a standard Go-Flo, a Hydrobios close-open-close sampler, a Seakem Teflon® piston sampler, and a peristaltic pump were compared in the NATO exercise reported by Wong et al.[37] All samples were collected from SEPEX enclosures and all were analyzed in the same clean-room facility. All cleaning procedures are documented and were very similar for all devices. They generally consisted of soaking the samplers with 0.05 to 0.1 *M* nitric acid solution followed by rinsing with distilled water. Samples were analyzed for mercury, lead, copper, nickel, cadmium, iron, zinc, cobalt, and manganese. The levels encountered were somewhat higher than those in the IOC intercomparison, but for most metals were reasonably representative of coastal seawater.

The enclosures appeared to have elevated the levels of mercury and lead and it is difficult to draw firm conclusions regarding the relative merits of the samplers, but some observations do seem justified. All samplers gave comparable results for lead, copper, nickel, zinc, and cadmium at the levels encountered. The piston device yielded higher results for mercury, the Hydrobios and the piston samplers gave high results for iron, while the Niskin and Go-Flo gave high results for manganese. Cobalt analyses yielded a rather extraordinary range of results. Only the peristaltic pump gave low values for all the elements.

The main experiment in the ICES fifth-round intercalibration was a test of filtration systems used in coastal waters.[42] Eight filtration systems used by five ICES laboratories were tested by filtering a large homogeneous sample of coastal seawater through the various devices. All laboratories analyzed samples processed by each device resulting in a large degree of redundancy and also in some disagreement regarding the relative merits of the various filtering systems. There was general agreement, however, that, with the exception of contamination with respect to two metals by two of the systems, contamination-free filtration of cobalt, manganese, iron, nickel, copper, and cadmium was accomplished near the lower end of the range of levels to be expected in coastal water by all systems. Contamination-free filtration for zinc and lead was accomplished at slightly higher levels.

VI. SUMMARY

The final test of sampling and analytical procedures is the observation of oceanographically consistent distributions and comparability between the results of independent workers. This is the ultimate test because it comprises all the steps in the procedures under true field sampling conditions, not artificial conditions designed wholly for experimentation. It is, of course, usually impossible to separate sampling competence from analytical competence.

Oceanographically sensible results are now being reported by a number of laboratories for an array of metals which include manganese, nickel, copper, zinc, cadmium, and lead. In several cases, results by different groups from the same water masses can be compared. In addition, similar relationships between metals and nutrients are being reported by a number of laboratories. Although metal nutrient relationships should not necessarily be invariant throughout the oceans, some consistency in the relationships could be expected.

Based on these studies and the earlier discussion of intercalibration and other equipment assessing experiments, the following reliable techniques may be identified for various trace metals.

A. Cadmium

Cadmium seems to present the fewest contamination problems. Reliable samples have been collected with a broad range of plastic samplers and different deployment systems. Detailed Pacific Ocean profiles that are internally consistent and show agreement between two laboratories were collected using Niskins with Teflon®-coated stainless steel springs on a rosette (GEOSECS)[31] and with Teflon®-coated Go-Flos, as well as the CIT sampler on a kevlar hydrowire.[17,41]

Equally consistent North Atlantic profiles, which show very similar relationships with phosphate, have been produced from samples collected with modified Go-Flos on a rosette and on stainless steel hydrowire,[29] NIO bottles and standard Niskins (wire not specified),[46] TPN samplers with silicone o-rings,[47] and modified Go-Flos on polyester line and a rosette.[48]

Sampler intercomparison exercises[19,25,37,44] also fail to detect any differences between samplers for cadmium, although the IOC experiment[44] did find higher concentrations with the kevlar hydrowire. No problems with kevlar are evident from the work of Bruland et al.[17] On the basis of the sampler intercomparisons, Niskins with silicone rubber springs, RTN3 samplers, Hydrobios close-open-close samplers, and the Seakem piston sampler would all have to be included in the reliable category for cadmium. Contamination from the ship has not been seen as a problem,[19,25] but shipboard filtration may lead to difficulties.[42]

B. Copper

Reliable copper samples can also be collected with an array of plastic samplers. Niskins with Teflon®-coated stainless steel springs,[32] modified Teflon®-coated Go-Flos,[2,17,29,41] the CIT sampler,[17,45] and standard Niskins and NIO samplers[49] all appear suitable. Kevlar and stainless steel hydrowires and rosettes were all used in these collections.

The IOC intercalibration indicated that silicone-springed Niskins are equally acceptable for copper, but Hydrobios TPN samplers and unmodified Go-Flos gave problems.[44] This study also found large, but inconsistent, differences between stainless steel, kevlar, and plastic-coated steel hydrowires. The alternate analysis of this work shown in Table 2 would indicate that the differences between wires are much smaller than previously concluded with perhaps higher results coming from kevlar. The NATO intercomparison[37] failed to find any differences between the pumped samples and those collected with Go-Flos, Niskins, Hydrobios close-open-close, or Seakem samplers. Problems associated with copper contamination of surface samples by the research ship were identified by Bender and Gagner,[23] but not confirmed by Magnusson and Rasmussen[19] or Spencer et al.[25] Both collection from launches and with pumping systems while underway have been used successfully for copper. This approach for surface samples may be advisable.

C. Manganese

Reliable samples for manganese have been collected using the Teflon® CIT sampler,[45] Go-Flos,[2,50,51] various Niskins,[24,46,52] and NIO samplers.[46] The IOC study,[44] found no differences between Go-Flos, Hydrobios, and silicone-springed Niskins, nor any differences between stainless steel, kevlar, or plastic-coated steel hydrowires. In addition, Bender et al.[24] detected no differences between stainless steel wire and the use of a rosette. The NATO experiment,[37] however, did see some differences between samplers, with Niskins (Teflon®-coated, stainless steel spring) and standard Go-Flos giving higher results than the peristaltic pump and the Hydrobio close-open-close or the Seakem piston sampler. The apparent manganese contamination reported for the stainless-steel-springed Niskin of 6 $\mu g/\ell$ is approximately equal to the discrepancy found by Landing and Bruland[50] between Pacific Ocean profiles collected with stainless-steel-springed Niskins and modified Go-Flos. Contamination from the vessel does not appear to be a problem with manganese,[24] nor are filtration procedures a source of contamination.[42,50,51]

D. Nickel

Good profiles for nickel have been generated with samples from Niskin bottles (stainless steel and surgical rubber springs),[23,30] the CIT sampler,[17,45] and Go-Flos.[17] The IOC intercomparison[44] indicates that Niskins with silicone rubber springs should also be acceptable, but that Hydrobios TPN samplers introduce significant nickel contamination. This experiment also indicated that plastic-coated wire gave lower nickel results than stainless steel or kevlar, but the differences were very small and may be insignificant. Problems with the TPN and RTN3 samplers have been indicated by Magnusson and Rasmussen.[19] Wong et al.[37] reported only slight differences between samplers for nickel in the NATO work. The Go-Flo and pumped results were slightly lower than those from the other samplers.

E. Zinc

The only reported reliable zinc profiles have been collected with modified Go-Flos and the CIT sampler.[17,45] The results of sampler intercomparisons[19,44] show that Niskins, TPNs, RTN3s, and unmodified Go-Flos are not acceptable for zinc.

The IOC work[44] suggested that plastic-coated wire may be superior to kevlar and stainless steel, but this conclusion is based on but few results. Bruland et al.[17] report results in their Pacific studies which would favor the reliability of kevlar. The National Research Council of Canada seawater reference material for trace metals (NASS-1)[2] was collected in the same water mass as Bruland and Frank's sampling in the Sargasso Sea[45] and has very similar zinc values for 1200 m. NASS-1 was collected with modified Go-Flos on a stainless steel wire, while the latter workers used the CIT sampler.

F. Iron

The very few reported profiles for iron would suggest that Go-Flos on kevlar hydrowire is a suitable combination.[27,53,54] Little can be said about other systems. The small number of iron analyses in the IOC study[44] and the inconsistencies between the conclusions based on the results of different laboratories invalidate any conclusions at all for iron from this experiment. The NATO intercomparison[37] also gave inconclusive results. The problem may be more in the analytical procedures than in the sampling.[3]

G. Lead

Even fewer results are available for lead. The most reliable samples have been collected with the CIT sampler.[16,39] There is some indication that suitably modified Go-Flos can be used to collect good samples for lead if the Go-Flo is attached to the end of the hydrowire with the weight above the bottom of the sampler and the sample collected while the device is being lowered.[39] The NATO study[37] showed that, at rather high levels of lead, all their samplers gave essentially the same results. Magnusson and Rasmussen[19] have apparently collected clean coastal water lead samples using modified Go-Flos.

H. Cobalt

Cobalt profiles for the Northwest Pacific Ocean that mimic profiles for manganese from similar areas have been reported.[55] The modified Go-Flo, kevlar wire combination of Bruland et al.[17] was employed. Very similar cobalt values are found in the reference material NASS-1 collected in the Sargasso Sea using similarly modified Go-Flos on a stainless steel wire.[2] The NATO work of Wong et al.,[37] on the other hand, found very large differences between samplers for this metal. They report the lowest concentrations of cobalt from the Hydrobios close-open-close sampler and the highest from the standard Go-Flo.

I. Other Metals

There have been very few reliable measurements for any other trace metals and no systematic studies of suitability of sampler systems reported for these metals. The reported profiles based on GEOSECS sampling, however, would suggest that Niskins (stainless steel springs) are suitable for barium,[56] strontium,[57] germanium,[58] and selenium.[59] Niskins (surgical rubber springs)[60] and Go-Flos[61] on stainless steel hydrowire or a rosette system seem acceptable for chromium.

Several silver profiles that correlate strongly with those of copper, collected using the CIT sampler and the modified Go-Flo, kevlar wire combination, have been reported recently.[62,63] A palladium profile based on Go-Flo, kevlar sampling has also been reported.[64]

Mercury samples have been collected in the last few years in Hydrobios TPN samplers, Go-Flos, and Niskins. These samplers have never been adequately intercompared for mercury. The IOC exercise[44] did not generate enough mercury results to be conclusive and the mercury values in the NATO study[37] were unreasonably high. In addition, the level of mercury in seawater is still very much in doubt. On the basis of reported profiles with concentrations of 1 *vg/ℓ* or less, Hydrobios TPN[47] or Go-Flo samplers[65,66] would seem to be acceptable.

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