GEOTRACES Intercalibration Planning Document
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OVERVIEW

The ultimate goal for the intercalibration component of GEOTRACES is to achieve the best accuracy possible (lowest random and systematic errors) for the suite of GEOTRACES' Trace Elements and Isotopes (TEI) as a prelude to the sampling program, and continuing effort throughout the sampling and analysis program. To achieve this goal, there will be two primary efforts:

(1) Evaluate and develop GEOTRACES sample acquisition, handling, and storage protocols during initial Intercalibration Cruises; and

(2) Identify existing GEOTRACES primary standards and certified reference materials (CRMs) for the TEI suite (and where needed, producing reference materials or primary standards), including the establishment of GEOTRACES Baseline Stations

that can be used to evaluate accuracy from sampling to analysis (to facilitate intercalibration for TEIs that do not have CRMs).

BACKGROUND

In order for the goals of GEOTRACES to be met, TEI data must be as accurate as possible (see Table 1 for definitions of relevant terms used here). The works of Bruland et al. (1979) and Schaule and Patterson (1981) showed that for certain trace elements, accuracy could be compromised at each step in determining elemental concentrations in seawater - sample acquisition, handling/processing, storage, and finally analysis. In the recent past, most efforts have been directed at the last step - analysis - and for many TEIs the effects of sample handling and storage have hardly been addressed.

Other chemical oceanographic communities have recently faced a similar problem and could be consulted for guidance in our efforts to optimize collection, handling, storage and analyses of TEIs. The DOC/DON community prepared a common aqueous reference material and blank, and preformed an exhaustive intercalibration for DOC (Sharp et al., 2002a), and a less rigorous intercomparison for DON (Sharp et al., 2002b). Similarly, the determinations of total carbon and nitrogen, and organic carbon, in oceanic (sediment trap) particles and sediments, have been intercompared (King et al., 1998). Both of these efforts were undertaken due to a lack of appropriate standards (i.e., with the same matrix as that of actual samples) or certified reference materials that are ideal for quantifying an analytical method’s accuracy. Indeed, the need for such certified marine materials (water and particles) that include many inorganic and organic parameters was thoroughly addressed by the US Committee on Reference Materials for Ocean Science (NRC, 2002).

While valuable, reference materials do not validate sampling and handling methods used at sea. Moreover, no reference materials are available for chemical speciation of dissolved constituents (trace elements, nutrients). One study has examined sample handling and analytical accuracy: the intercomparison program for marine colloids (Buesseler et al., 1996). This effort used a common water source, but varying cross-flow filtration systems to isolate colloids, followed by several analytical methods (in this case for the determination of organic carbon). Perhaps one of the most complete evaluations from sample acquisition to analysis for trace elements occurred as part of the Intergovernmental Oceanographic Commission’s 1990 Contaminant Baseline Survey (Landing et al., 1995). Samples were taken with a variety of General Oceanic’s Go Flo bottles, filtered or unfiltered, placed in a variety of bottles (supplied by the participating labs), stored for varying times, and analyzed using a suite of methods. Not unexpectedly, the results varied with the element. However, this was an ad hoc study, not specifically designed to rigorously evaluate the sources of error or with a sufficiently robust statistical design. It was also a bit ahead of its time in that TEI sampling and analytical knowledge has improved greatly over the past decade. None of these past efforts has paid much attention to sample storage, perhaps because earlier works (e.g., Subramanian et al., 1978) appeared to show that polyethylene bottles and acidification to <1.5 with nitric acid were sufficient; we now know that this is not correct for many trace elements.

Table 1. Terminology relevant to GEOTRACES Standards and Intercalibration Activities (not in alphabetical order, but by category)

Accuracy – *The degree of agreement of a measured value with the true or expected value of the quantity of concern* (Taylor, 1987). Accuracy therefore includes random and systematic errors.

Precision – *The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the closeness of results* (Taylor, 1987). Precision therefore is a measure of random errors in a method or procedure.

Standard (also, **measurement standard** or **étalon**) – *Material measure, measuring instrument, reference material or measuring system intended to define, realize, conserve or reproduce a unit or one or more values of a quantity to serve as a reference* (ISO, 1993). See **Primary Standard** for a definition more relevant to GEOTRACES.

Primary Standard – *Standard that is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to others standards of the same quantity* (ISO, 1993).

Reference Material – *Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials* (ISO, 1993).

Certified Reference Material – *Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence* (ISO, 1993).

Intercalibration – *The process, procedures, and activities used to ensure that the several laboratories engaged in a monitoring program can produce compatible data. When compatible data outputs are achieved and this situation is maintained, the laboratories can be said to be intercalibrated* (Taylor, 1987). Intercalibration therefore is an active process between laboratories that includes all steps from sampling to analyses, with the goal of achieving the same accurate results regardless of the method or lab.

Intercomparison – This is not well defined in the literature, but by implication is the comparison of results between laboratories, but is not the active process of ensuring that the same results are achieved as in an **Intercalibration**. It also may not include all steps, for example, sampling, sample handling, and analyses.

In context of the SCOR Working Group 109 on 'Biogeochemistry of Iron in Seawater' major progress was made on improving the accuracy of oceanic Fe data. Iron is, together with trace metals like lead and zinc, known to be very susceptible to inadvertent contamination. A strong focus on getting good Fe data was deemed to have positive spin-off effects on determining other trace metals in seawater. The book produced by WG 109

(Turner and Hunter, 2001) contains one chapter detailing all the steps (sampling, filtration, pre-treatments, and final analyses) and their pitfalls for determination of Fe in seawater (Bruland and Rue, 2001). At the Third International Symposium on Iron in the Sea held in Amsterdam (1998) under aegis of the SCOR WG 109, planning for an international Fe certification exercise was begun. The concept was a feasibility study towards eventual 'routine' production and availability of a certified reference material for Fe in seawater, akin to the major success and ensuing scientific breakthroughs of the CRMs for oceanic DIC (Dickson and co-workers; DOE, 1994) and DOC (Sharp et al., 2002a). A second dedicated, SCOR-sponsored, planning workshop (San Antonio, January 2000) was held, followed by field preparations including bottle cleaning. During the IRONAGES-1 cruise (Polarstern, Sept/Oct 2000) a large volume sample was taken and divided into several hundred 1 liter bottles. These were sent out to laboratories all over the world and eventually 24 laboratories confidentially reported their measured concentrations to the independent coordinator, Jim Moffett. A long term storage assessment also was done by Bowie, Worsfold, and co-workers as part of this effort. The results were presented and discussed at a third SCOR-sponsored workshop (San Francisco, December 2002). The workshop discussions led to improved insights amongst the participants, and these were summarized in one article reporting the overall procedure, findings and recommendations (Bowie et al, 2006). A preceding article reported on the shipboard comparison of 4 analytical methods for Fe during the actual sampling cruise (Bowie et al., 2003).

Next, the Sampling and Analysis of Iron (SAFe) program (coordinated by K. Johnson at the Monterey Bay Aquarium Research Institute) undertook the task of evaluating and improving the accuracy of oceanic iron measurements from sampling to analysis via an intercalibration cruise. For sample acquisition, many different systems were used, including: Go Flos suspended on Kevlar hydrowire and triggered with plastic messengers (the method of choice for historical reasons), the automated MITESS sampler, a trace metal clean rosette, and non-metallic pumping of surface waters. Most of the samples were filtered but the effects of different filtration methods were not examined closely (different methods were tested and these data may be available eventually). Samples were stored in various bottles at sea; some groups preferred fluorocarbon or polymethypentene bottles, but polyethylene was the most common material. Many iron determinations were done at sea, quantifying the t=0 time point. The effect of storage time is being examined by analyses done from hours up to (so far) a year. The stability of iron speciation samples may be evaluated as well since several groups made t=0 determinations at sea. Finally, large 500 L filtered and acidified composite samples were taken (surface and deep water) and placed in cleaned polyethylene bottles as an archive/reference material. This program is still underway and the results are just becoming available.

The SCOR-IRONAGES Certification exercise and the SAFe program provide models for the design of an equivalent GEOTRACES standards and intercalibration program for other TEI. The major differences are that GEOTRACES includes a large suite of elements and isotopes (including nutrients and tracers), chemical speciation studies, and both the dissolved and particulate phases. In this respect, some concepts on sampling and intercalibration were tested during the recent GEOTRACES Pilot Study on the RV Polarstern (Bremerhaven to Cape Town, 13 October – 17 November 2005) and some references to their experiences and recommendations will be made in the sections to follow. Another unique feature of GEOTRACES is that studies will focus on large-scale oceanic sections, requiring the most time-efficient sampling and analytical methods. For some of the TEI suite, particularly the radioisotopes and the measurements of chemical speciation, reference materials won't be available. This latter point necessitates the creation of "Baseline Stations" where investigators can compare their methods and data with the GEOTRACES data (particularly in deep waters where temporal variability should be minimized).

Overall, the GEOTRACES Standards and Intercalibration (S&I) Program needs to establish suitable (accurate and non-contaminating) sampling and sample handling protocols for TEI under the constraints of its sampling program (transects), identify existing or develop new primary standards and certified reference materials, and establish GEOTRACES Baseline Stations where the concentrations and speciation of dissolved and particulate TEI have been intercalibrated and can be used as future references ("in situ reference materials"). In addition, the S&I Program must ensure that the methods for the sampling and determinations of essential ancillary parameters, including salinity, oxygen, pigments, DOC, and DON, and nutrients (ammonium, nitrite, nitrate, phosphate, and silicate) at nanomolar concentrations are similarly accurate throughout the program. The initial phase of these activities must include several Intercalibration Cruises where actual procedures and equipment are evaluated and perfected prior to actual GEOTRACES transects. In addition to developing the field methods for GEOTRACES, these Intercalibration Cruises will have the added potential of establishing several of the planned Baseline Stations.

PROGRAM DESCRIPTION

1. Sampling, sample handling, and sample storage protocols, and methods for ancillary parameters.

Sampling

Water/dissolved.

Water samples have to be taken with the largest volume possible given the demand for efficient use of ship time. The sampling system must be contamination-free for as many TEI as possible and the sampling process must not alter the phase (size) or chemical speciation. Preliminary discussions suggest that 20-30 liters may be the largest samples at all stations, but larger samples could be obtained less frequently. As an example, during the Polarstern Pilot Study samples of up to 100 L were collected in deep waters by combining up to 8 12 L bottles from the same depth; this could be employed in shallower waters as well. Although many systems have been shown to be capable of collecting uncontaminated samples, for a program such as GEOTRACES it appears reasonable to suppose that a Go-Flo/rosette (powder-coated aluminum) system on a Kevlar conducting capable (such as a larger version of the CLIVAR system used by C. Measures and W. Landing; Figure 1) could satisfy the demands for most TEI work. Alternative systems such as that shown in Figure 2 are acceptable if they are shown to produce equivalent results (either on test cruises or station re-occupations). Go-Flo sample bottles are not appropriate for some elements (e.g. Sn, a major component of PVC stabilizer). It is possible that some TEI samples will have to be collected by different means. The rosette frame of the CLIVAR system currently uses zinc anodes to minimize corrosion; although the motion of the sampler upwards should minimize this source of contamination, it would be preferable to use magnesium anodes if this material lasts sufficiently long. In addition, large (>30 L) samples for some radionuclides may be collected using in situ pumps and adsorption cartridges (see particle discussion to follow), but the logistics and extraction efficiencies of these systems will have to be evaluated on the Intercalibration Cruises.

In the upper ~50m, it may be preferable to use pumping/tubing systems that can be deployed while steaming so as to avoid contamination from the ship (and potentially obtain larger volumes for some purposes). Systems using a towed “fish” and pumps (e.g., De Jong et al., 1998; Vink et al., 2000) have been used with great success in the IOC Contaminant Baseline Surveys, and most recently during the Polarstern Pilot Study where it was also used to fill a 200 L plastic tank in less than 45 minutes for intercomparison studies. However, before any pump system is designated to be the routine method for sampling the upper waters, test cruises should establish that the bottle and pumping systems obtain comparable samples.

Figure 1. Sampling system currently in use for iron and aluminum on the CLIVAR Repeat Hydrography Program (C. Measures and W. Landing).

Figure 2. Rectangular, ultraclean titanium frame with 24 Go-Flo samplers (12 L) and CTD, etc. sensors in front of its own ultraclean laboratory van. Deployment with 20 mm Kevlar cable (9000 m on winch drum) with internal signal cables for sensors data transfer and for tripping bottles from deck at any desired depth. Pneumatics for closing samplers allows any shape frame (i.e., departing from circular shape prescribed by traditional stepping motor/trip wires). Upon recovery, the complete frame enters its clean container and samplers are emptied via filter cartridges into sample bottles. The system was successfully tested November 2005 in the Canary Basin, and will be used in IPY GEOTRACES 2007-2008 sections during Polarstern expeditions.

Particles.

The above system for dissolved samples would allow the collection of filtered matter from 10-30 L volumes (through 142 mm filters held in Teflon or other non-contaminating materials), sufficient for certain TEIs and the determination of suspended particulate matter concentration (using pre-weighed filters), but these relatively small samples are entirely inadequate for many TEIs and probably do not represent the true spectrum of marine particles (e.g., Bishop et al., 1977). Therefore, in situ pumping systems would have to be utilized at stations where accurate particulate matter chemical composition must be determined (e.g., McLane, Challenger, Kiel in-situ pump or KISP). These systems are capable of sampling 500 L in 2 hours, and adsorption/coprecipitation cartridges (e.g., MnO_2) could be placed in line for sampling dissolved radionuclides such as radium or thorium. Thus, a crucial test for the GEOTRACES Intercalibration Cruises will be the evaluation of these pumps for logistical details (ease of deployment and recovery, wire time, etc), and comparison to bottle samples with particular reference to contamination and particle collection efficiency. A related task for the Intercalibration Cruises would be evaluating whether large volume particle samples can be taken with ship-board pumps for the upper 100 m (as noted above for dissolved samples). A further extension of this idea was tested on the Polarstern Pilot Study using a pump system and continuous centrifuge. The system is described in Schüssler and Kremling (1993) and used later by Kuss et al. (2001). The particles were collected on a Teflon sheet, mounted inside a stainless steel cylinder and used a titanium inlet and bottom.

Sample handling

Trace element workers agree that samples should be drawn from the sampling bottles in a filtered air environment, not on the deck of the ship. Although it may be ideal to move an entire rosette system into the clean area, it may not be practical to do this with a transportable system that will be used on many different ships. In that case, individual bottles will have to be removed from the rosette and moved into the clean lab area. It is practical to move ~12 liter samples manually, but ~30 liter sample bottles would require the development of a safe, seaworthy system that minimizes the required physical effort.

Dissolved.

In general, dissolved TEI determinations require sample filtration (although there may be some cases where filtration is not necessary because of small particulate loads and undesirable because of potential contamination). The standard routine for GEOTRACES should be filtration of (nearly) a complete sampling bottle through non-contaminating filters that are preserved for particulate matter analyses (see below). Appropriate filter types and pore sizes must be determined early in the preliminary stages of GEOTRACES. Divergent requirements for dissolved and particulate matter analysis may require a compromise of ideals to accommodate both, but it must be demonstrated that this compromise does not degrade the data quality of either. For example, many workers feel that 0.2 µm filters should be used to eliminate small bacteria from the dissolved fraction. However, it is difficult to filter large volumes of water through 0.2 µm filters appropriate for particulate matter analysis, so this pore size standard probably is not appropriate for the routine filtration of GEOTRACES samples for particulate matter samples. During the development of GEOTRACES protocols, significant effort should be directed at establishing methods for simultaneously obtaining high-quality particulate and dissolved TEI samples. There is anecdotal information that there is no significant difference in dissolved samples obtained from 0.2 µm and 0.4 µm pore size filters, but it is not obvious that this result would be true for all TEIs and in all environments (e.g. hydrothermal vent plumes). It may be worthwhile to investigate a dual in-line filtration system that first passes water through a larger pore size filter (for particulate analysis) and then through a 0.2 µm cartridge-style filter for the dissolved fraction. As a part of the Intercalibration Cruises, GEOTRACES should establish protocols for the appropriate filter materials (including polymer type as well as various trademark brands which may differ in cleanliness), appropriate cleaning protocols, and filtration procedures (e.g., dual in-line, etc).

Although some measurements may be made at sea soon after sample collection, many TEI measurements will be done in shore-based laboratories. Both types of analyses require some thought and testing to establish appropriate protocols for sample treatment. The recent SAFe project established that accurate shipboard Fe analysis required sample acidification to pH<2 for at least 24 h (room temperature) before all of the dissolved Fe could be detected.

Most TEI workers preserve samples using acidification, but differ on the type of acid and final pH of the solution. We suggest that in the absence of evidence to the contrary for an individual TEI (and leaving the thornier issue of speciation preservation to a later section), acidification with high-purity HCl is most appropriate because seawater is already high in chloride (so that this procedure achieves preservation with minimum alteration of the sample matrix). GEOTRACES-archived samples (not identified for specific TEIs) will also be collected and a separate protocol will be needed for these. Specifically, both filtered and unfiltered samples (1 L each) will be collected to avoid potential problems with contamination during filtration, likely in low-density polyethylene bottles. These will be acidified to $pH<2$ with HCl and a sample of the acid also will be archived (to assess blanks).

GEOTRACES should develop standard protocols for the addition of sample preservatives. While this work should be done under class 100 filtered air conditions, this step is particularly hazardous for the introduction of contamination: the acids will readily mobilize contaminants and multiple uses of pipettes etc. into reservoirs makes cumulative contamination possible. It might be worthwhile to spend some time exploring whether trace-element appropriate semi-automatic injectors exist or could be developed (e.g., like a Repipet, but made of more appropriate materials).

Because a large number of different sample bottles will be filled, we recommend that GEOTRACES settle upon a limited variety of sample bottles that can be organized into racks that minimize chaos when filling the bottles. Obviously this is not an absolute requirement, but a well-organized sample collection routine can help minimize problems.

The above discussion largely deals with sample handling for small-volume TEI samples, but for the TEIs requiring larger volumes (> 5 L; primarily the radioactive elements, but some stable isotopes as well), many factors will have to be evaluated on the Intercalibration Cruises. If large-volume samples are to be returned to shore, this would create logistical difficulties, given the number of stations and depths to be sampled. Thus, shipboard sample preconcentration methods such as iron hydroxide coprecipitation or manganese oxide cartridges could be used. The recovery and efficiency of these methods must be evaluated and optimized for the diverse suite of radionuclides in GEOTRACES as a part of the intercalibration program. During the Polarstern Pilot Study, parallel on-board $Fe(OH)_3$ precipitations were made for Nd, Be, and Hf in 2 L and 60-140 L samples. Results from these exercises will tell us whether large-volume precipitations can be carried out efficiently on-board ship. However, an additional consideration is that these sample preparation methods must not contaminate the ship or working spaces for other TEI samples (e.g., Fe and Mn).

Particles.

As noted above, there are many potential problems with the type of filter material and pore size used during the GEOTRACES program. For example, organic carbon (POC) samples must be taken on glass or quartz fiber filters (certain metal filters are available, but are expensive and difficult to handle routinely), but cannot be used for most

TEIs. Logistical problems further complicate the issue: a sufficient water volume must be available for different filters, in which sequence should filter samples be taken (e.g., POC first, then TEI, etc?), and later, how will these filter be digested and analyzed for as many TEIs as possible? All of these aspects will have to be evaluated on the Intercalibration Cruises to optimize this phase of sample handling. There should also be some effort directed towards appropriate digestion and/or subsampling methods that are suitable to establish the TEIs and major carrier phases (including at the least the organic, siliceous, carbonate, and inorganic mineral phases).

For some elements (e.g., Fe, Pu, Th) there is evidence that a significant fraction exists as <0.2 µm colloids. However, there is a pointed lack of agreement on how to isolate colloidal TEI. Various small pore-size filters, some with transverse flow filtration, have been used in these studies, but there is no agreement on which of these methods is optimal. For this reason, we believe that routine colloidal separations may not be appropriate for GEOTRACES in its early years, but that is not to say that the distinction is not important in terms of process. Dissolved and colloidal TEIs are both transported by advection, but the microscale laws governing exchanges of TEIs between colloids and dissolved and particulate forms are quite different. For this reason, we recommend that GEOTRACES encourage various methods of colloidal separations at GEOTRACES test stations in diverse environments to the largest extent practicable.

Sample storage

Dissolved TEI – total.

Sample storage requires appropriate sample bottle types and preservatives to prevent biological growth and adsorption on container walls. The preservatives and bottle types must be appropriate for the individual TEIs; different TEIs will have different requirements. Various types of containers are used with different cleaning treatments. Most TEI experts believe that some type of polyolefin (polyethylene in low and high-density, linear or branched, or polypropylene) bottle is appropriate for most purposes after a suitable cleaning treatment. However, polyolefins are not appropriate for aluminum analysis (because $AlCl_3$ is used as the polymerization catalyst) or mercury analysis (due to contamination of unknown origin). For these elements, other polymer types such as fluorocarbons (for either Al or Hg) or polymethylpentene (for Al) are appropriate. For ancillary parameters (salinity and nutrients) and selected tracers such as ^{13}C, well-established handling procedures and containers will be utilized (e.g., glass ampoules for ^{13}C). Overall, GEOTRACES should verify that appropriate container materials and cleaning treatments are used for GEOTRACES samples for each property.

GEOTRACES should do time-series studies of stored samples in order to establish that preservation methods are appropriate for the typical time between sample collection and ultimate analysis. For this exercise, on the Intercalibration Cruises (see below) large volume (> 200 L) composite/homogenized samples (surface and deep water; one of each left untreated and the others acidified to different pH levels (with HCl or HNO_3) will be placed in sample bottle of the types and volumes used currently (e.g., 1L low density polyethylene; FEP Teflon). The unacidified aliquots will then be immediately frozen and stored; the acidified aliquots will be stored in the dark at room temperature. Wherever possible, sample preservation should be tested by shipboard analyses shortly after sample collection (t=0), or immediately after the cruise. Since the typical practice is sample storage ranging from one month (i.e., time to return samples from a cruise) to one year or more, storage time points should be every few months for one year, with 3-4 bottles analyzed per time point. The preservatives used should be verified for low blanks before use and archived for later analysis to establish whether blank levels increase with time. The preservative must be stored in a container that is least subject to degradation or increasing blanks – fluorocarbon has obvious advantages in this regard but may not be the best for all elements. It is preferable that the laboratories that will do the ultimate TEI analysis should prepare the preservative and verify its low blank levels.

Such a seemingly straightforward evaluation of storage protocols is made much more difficult for TEIs requiring large volumes, particularly Nd isotopes and ^{230}Th, ^{226}Ra and ^{231}Pa. First, whether these TEIs can even be determined in stored acidified seawater needs to be evaluated before any Intercalibration Cruise, and then the container type and acid need to be evaluated (as with the other TEIs). However, the sheer volume required for these elements suggests that the number of time points and other variables (e.g., container or acid type) will have to be severely limited. Nevertheless, during the Polarstern Pilot Study entire rosettes of 24 bottles were filled at one depth (1500 m), filtered, and acidified with ultra-clean hydrochloric acid in 2 to 10 L aliquots for Nd, Pa, and Th intercalibrations.

Dissolved TEI – Speciation.

Dissolved TEI can exist in different chemical forms, including various oxidation states (e.g., Cr III/VI, As III/V), metal-ligand complexes, and covalent organo-metallic compounds (e.g., methyl mercury). The sample storage methods used in GEOTRACES should enable, when possible, the determinations of TEI speciation. For testing speciation stability on the Intercalibration Cruises using the large-volume composite samples, frozen storage (typical storage for metal-ligand samples) can be compared to acidified samples (as above), with the t=0 reference point being the speciation determined on board ship (e.g., competitive ligand CSV; selective hydride generation; etc.). The time points would be the same as the total TEI sample storage experiment. It is assumed that the speciation of most TEIs will not be stable with storage, and for these, shipboard determinations will be recommended.

Particulate TEI.

The presumed storage for filtered particulate matter will be immediate freezing, with thawing just prior to preparation and analyses. However, GEOTRACES should evaluate the efficacy of this storage as part of the Intercalibration Cruises.

Ancillary parameters

Data for more “standard” oceanographic parameters such as nutrients and oxygen will be crucial for GEOTRACES and WOCE-type protocols would seem to be sufficient. However, these parameters must be determined with sufficiently low detection limits to match those of the TEIs so that biogeochemical processes can be examined, particularly for the nutrients (i.e., at nanomolar concentrations). Moreover, given the sheer number of samples, the methods should be automated or require minimal technician time. Table 2 is a compilation of existing techniques that presently can be used for GEOTRACES, but these still must be intercalibrated with existing methods already in broad use (e.g., “MAGIC” method for phosphate; Karl and Tien, 1992) if more suitable ones are developed, GEOTRACES should be flexible enough to use them (i.e., just as with the TEIs – as long as accuracy and precision can be assured). It is important to note that this effort cannot be underestimated since no existing or past program has done nanomolar nutrients on a routine basis, and the Intercalibration Cruises will be an important test for their utility on the regular GEOTRACES transects.

Table 2. Ancillary Parameters and Example Methods for GEOTRACES

Parameter	Method	Detection Limit	Example Reference
Salinity	Conductivity	NA (not applicable)	Standard methods
Oxygen	Automated Winkler, amperometric end point	1 µmol l^{-1}	Culbertson and Huang, 1987
Ammonium	Automated colorimetric w/ liquid waveguide flow cell	5.0 nmol l^{-1}	Li et al., 2005
Nitrite	Automated colorimetric w/ liquid waveguide flow cell	0.1 nmol l^{-1}	Zhang, 2000
Nitrate	Automated colorimetric w/ liquid waveguide flow cell	2.0 nmol l^{-1}	Zhang, 2000
Phosphate	Automated colorimetric w/ liquid waveguide flow cell	0.5 nmol l^{-1}	Zhang and Chi, 2002
Silicate	Automated colorimetric	0.4 µmol l^{-1}	Parsons et al., 1984
Pigments	HPLC	NA	Bidigare, 1991
DOC/DON	Oxidative Combustion	NA	Sharp et al., 2002a, b
POC/PON	Oxidative Combustion	NA	Cutter and Radford-Knoery, 1990

Documentation of the GEOTRACES Methods

Given the international scope of GEOTRACES and multitude of laboratories that will be conducting transects and processes studies, it will be absolutely necessary that all aspects of sampling, from the operation of the equipment to sample processing/handling procedures, and the determinations of ancillary parameters, be completely described in GEOTRACES Users' Manuals. Therefore, a goal of the S&I Program will be creation of "cookbooks" that any qualified chemical oceanographic laboratory could use in the conduct of a GEOTRACES cruise. These also would be placed on the GEOTRACES web site, as well descriptions of, or plans for, all S&I Program activities. Of course, many of the intercalibration results will be documented in the peer-reviewed literature as well. An additional benefit of creating GEOTRACES Users' Manuals is one of outreach to scientists in developing countries who cannot devote the time and expenses to perfect their own methods. While it is clear that some GEOTRACES sampling gear such as non-contaminating rosettes may not be available, criteria for assessing their own equipments' efficacy will be documented, easily adoptable handling procedures will be described in detail, and the availability of reference materials will allow their own procedures to be validated.

2A. Identifying existing primary standards and CRMs and developing new ones.

TEI Primary Standards – Radioactive.

Most radioisotope primary standards can be obtained in the academic community or are commercially available with one notable exception, ^{233}Pa. This isotope can be "milked" every few months from ^{237}Np, and calibrated. Calibration could be done against a recognized ^{231}Pa certified reference material or by measuring in growth of its daughter ^{233}U using recognized uranium standards. It is hoped that the IAEA Marine Laboratory in Monaco could coordinate production of ^{233}Pa from ^{237}Np, as well as provide a ^{231}Pa primary standard.

TEI Primary Standards – Trace elements.

These standards are also commercially available and will not be an issue for GEOTRACES. However, a "proficiency standard" that can be obtained from government agencies such as the National Institute of Standards and Testing (NIST) in the United States, or a commercial standard from another source, should be used to regularly check the quality of any primary standard used in GEOTRACES' analyses.

TEI Reference Materials – Dissolved.

There are two CRMs presently available for seawater trace elements, NASS-5 and CASS-4 (NRC-Canada), which could be used for GEOTRACES. The problem with these two reference materials is that their TEI concentrations are at the high end (e.g., Fe, Cd, Zn are about 100 times greater than expected in surface open ocean waters). We need to develop Reference Materials that are at the lower concentration range (we are not a certifying agency, so these cannot be CRMs). The committee recommends the development of two RMs, one at the lower end while the other at the higher end, or open ocean surface water vs. deep water. In this respect, we should take advantage of the availability of the SAFe seawater samples and perform a multiple laboratory intercomparison (evaluating the errors in all but sampling and storage). This would then create a useful TEI reference material at relatively low cost. The limitation is that the total SAFe sample volume is limited (<300 L for three homogenized samples) and the individual bottle volume is only 500 ml, eliminating their utility for many TEIs (ca. 900 L of SAFe water from the California Current is currently unbottled – stored in large polyethylene tanks).

One accuracy check that GEOTRACES may want to employ is a double-blind sample intercomparison where ca. 30-60 L of a sample from one depth at a GEOTRACES station is bottled (in an appropriate container) and then sent to all labs doing a particular element or element suite. Such a procedure done on a regular basis would assure that the concentrations (and even speciation) being measured by GEOTRACES are as accurate as possible.

TEI Reference Materials – Particles.

A variety of solid phase certified reference materials are available for marine particles, but most of these are either pure biological materials (e.g., NIST Lobster Tissue) or sediments. The US NRC report on marine reference materials (NRC, 2002) recommended the use of algal cultures, and while these are more like suspended particles, they are devoid of detrital matter (e.g., alumino silicates). Therefore, the GEOTRACES program would encourage the development of a suspended matter reference material isolated by techniques such as continuous centrifugation (but, trace metal clean; see Schüssler and Kremling, 1993) from a coastal or upwelling regime. As noted above, GEOTRACES might also want to do double-blind sample intercomparisons for particulate TEIs.

2B. Establishing GEOTRACES Baseline Stations.

By establishing so-called “GEOTRACES Baseline Stations,” the program can use these as potential “anchors” on some of the transects (i.e., including sites where TEIs have been extensively examined and therefore accomplishing a de facto intercalibration) and as sites where new methodologies (sampling and analytical) can be tested (“in situ reference material”). At least 2 of these stations should be where the GEOTRACES sampling, handling, and storage methods are developed on the Intercalibration Cruises. Another way of establishing these Baseline Stations is for GEOTRACES transects to overlap at 1-2 sites such that the data from each cruise can be compared. Ideally, there would be one Baseline Station for every ocean basin to facilitate access. Another approach would be to locate them at existing time series stations such as: Pacific: US JGOFS Aloha, 22.75° N, 58° W; Canadian Ocean Station Papa, 50° N, 145° W; New Zealand, 46.5° S, 178.5° E. Indian: Arabian Sea, 15° N, 65° E; Indian Ocean DEOS, 25°

S, 97° E. Atlantic: US JGOFS BATS Station, 32° N, 65° W; PAP, 53° N, 50° W; South Atlantic DEOS, 35° S, 15° W. In any case, the occupation of 1-2 Baseline Stations should be included in every GEOTRACES transect as a part of making intercalibration a routine component of the program.

Specific Committee Recommendations and Timing

1. Establish a GEOTRACES S&I Program implementation committee to draft the actual working plan based on this report, the overall GEOTRACES plan, and community inputs/feedback. With respect to the latter, it is likely that some ad hoc meetings held in conjunction with an EU, AGU, etc meeting, be held. Obviously, this is the first step.

2. Perform intercalibrations of the core GEOTRACES TEI (and as many other TEIs as possible) using existing SAFe water samples (bottled, but also bottling the slightly Fe-contaminated water that remains in the SAFe homogenization tanks) with the goals of evaluating how applicable the SAFe sampling and handling procedures are to GEOTRACES and assessing which elements may pose the greatest analytical problems for the program. This phase of the S&I Program should be started immediately.

3. After a thorough review of the SAFe water intercalibration results (as above) and the SAFe, IRONAGES, Clivar, etc. equipment and procedures, conduct at least 2 Intercalibration Cruises. The complete sampling system (sampling bottles, rosettes, winches, etc.) to be tested would have to be agreed upon and acquired prior to any of these cruises (and would then be available for future GEOTRACES transects). The goals of these cruises, using intercalibration as the tool, will be to evaluate and select the best sampling devices and handling procedures for the greatest range of TEIs under the constraints (e.g., station time) of GEOTRACES transect and process studies. This first step probably will require at least one cruise, and while additional evaluations could occur on a second cruise, the specific rationale for the second cruise would be perfecting the overall procedures (including determinations of ancillary parameters) for full and complete documentation (i.e., writing the users' manuals) and collecting water and particles for GEOTRACES reference materials. Because any GEOTRACES transect cannot occur without established protocols and intercalibrations, these cruises have to be the first phase of the GEOTRACES field program. However, if any GEOTRACES-related cruises were to occur prior to completion of the primary S&I activities, they should at least acquire replicate samples (>3) at each station/depth that could be used for an analytical intercalibration (i.e., as in the collection of GEOTRACES archive samples discussed above).

4. Due to the lack of appropriate reference materials, the S&I Program will have to develop these during GEOTRACES or other program cruises, or in controlled lab conditions. This will be a continuing and long term effort, and while there is a clear lack of suitable reference materials, GEOTRACES' transects can begin without them after the completion of the Intercalibration Cruises. We also should encourage government labs involved in the production of standards and reference materials (e.g., US NIST, NRC-Canada, IAEA) to take on some of these tasks.

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