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## Intercalibration in chemical oceanography—Getting the right number

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### Abstract

Intercalibration has a strict metrological definition, but in brief, it's an open sharing of methods and results between laboratories to achieve the most accurate data with the fewest random and systematic errors. In the field of chemical oceanography where concentrations of many constituents can be in the nano- to picomolar range, the salt water matrix can be difficult to analyze, and knowing the exact concentrations, or even chemical forms, of biologically required elements is essential, intercalibration is a very relevant and needed tool. Implementing it is not simple because errors can occur at any step in the process of taking a water or particle sample, handling and processing it, and finally analyzing it and treating the resulting data. The international GEOTRACES program provides a good example of implementing intercalibration for studies of dissolved and particulate trace elements and isotopes, and is described here.

If you're a new biological oceanographer who is interested in the role of phosphorus in phytoplankton productivity and make up 10 L of a Redfield-like growth media with 3.2 mg nitrate-nitrogen and 0.3 mg phosphate-phosphorus, but the phytoplankton won't grow, you've made a systematic error. The Redfield ratio (Redfield et al. 1963) is atomic, not weight-based, and therefore your solution has an atomic N:P ratio of 16:0.7, not the 16:1.5 that you had planned for a phosphorus-enriched culture. Similarly, if you were analyzing a seawater sample for cadmium using ICP-MS and hadn't accounted for isobaric molybdenum interference, you'd overestimate the actual concentration of cadmium in your sample. In both cases, you're not getting the "right" number, either because of miscalculations or from an analytical error. Getting the "right" number in chemical oceanography may seem like an obvious goal, but what is right? Is it getting the same value every time

you analyze your sample, or the real value—something that you can trace to an absolute standard? The former is precision, the measurement of random errors, whereas the latter is accuracy, the measurement of random and systematic errors. A precise value is not necessarily accurate, but good accuracy requires good precision. The problem with determining the right or correct concentration of a chemical constituent in seawater is finding the best means to evaluate accuracy. Systematic errors can occur at each stage in the process of acquiring a sample, then storing it, and finally to analyzing it. Oceanic trace metals are in the nano- to picomolar concentration range, and thus working on metal ships assures that contamination is probable. In fact, sampling contamination was shown to be a factor that affected the accuracy of most trace metal data until the late 1970s (e.g., Bruland et al. 1979). From the analytical perspective, seawater is not a simple matrix, its high ionic strength makes analysis a difficult task, and combined with very low concentrations for constituents like trace metals, the quest for accuracy is made even harder.

Most chemical oceanographers have used certified reference materials to establish accuracy at the analytical stage of their studies. Nevertheless, many of these are not actual marine materials, but close substitutes. In this respect, the need for appropriate certified marine reference materials (water and particles) was thoroughly addressed by the US Committee on Reference Materials for Ocean Science (NRC 2002), although very few of these materials have been produced to date. Interestingly, numerous laboratories are now determining trace element isotopes in seawater (e.g., Lacan et al. 2006, John and Atkins 2012), and it is likely that these

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efforts may become limited by the unavailability of appropriate certified isotope reference materials. These isotope materials were not even addressed by the NRC Committee. There are notable exceptions to the lack of reference materials to assess accuracy, one being work by scientists examining the carbon dioxide system who spent considerable time and efforts producing appropriate seawater reference materials for total dissolved inorganic carbon and total alkalinity (e.g., Dickson 1998; Dickson et al. 2003). Another example is the marine dissolved organic carbon (DOC) reference materials that have been produced and distributed to establish the analytical accuracy of DOC determinations (Sharp et al. 2002). Both the CO<sub>2</sub> and DOC standards evaluate analytical accuracy, but sampling and sample handling can tremendously alter a sample's original composition and therefore accuracy. Toward this end, a group of chemical oceanographers studying marine colloids set up a program to evaluate how different cross-flow filtration methods affect the concentration of organic carbon (Buesseler et al. 1996) and other colloidal parameters (e.g., Fe and Al; Reitmeier et al. 1996).

The marine trace element community has long recognized problems with the sampling and analyses of metals at subnanomolar levels. In 1978, a large scale (>20 laboratories) evaluation of analytical variability for seven trace metals (Cd, Cu, Fe, Pb, Mn, Ni, and Zn) used North Atlantic seawater collected and pooled/homogenized for this purpose (Bewers et al. 1981). In retrospect, the seawater was likely contaminated via the collection and pooling methods, but the results showed that sample storage (frozen versus acidified) and analytical methods affected the reported concentrations and precision of the metals examined, particularly Fe and Zn. One other small experiment studied multi-trace element precision and accuracy in the early 1990s (Landing et al. 1995), but most recent attention has been focused on only the determination of iron in seawater. Bowie et al. (2006) presented intercomparison results from 24 laboratories using seven different analytical methods that determined the concentration of dissolved iron in a pooled, 700 L surface water sample from the equatorial Atlantic. Results from this large experiment showed a minor loss of dissolved iron during storage, and some of the analytical methods had systematic differences in the reported iron concentration compared with others.

The Bowie et al. (2006) study thoroughly covered the analytical aspects of seawater iron determinations with an international cadre of participants. Subsequently, the 2006 Sampling and Analysis of Iron (SAFe) program was undertaken to evaluate the accuracy and precision of dissolved iron measurements from start to finish—sampling to sample analyses (Johnson et al. 2007). Most of the SAFe goals were accomplished on a cruise in the North Pacific with four different sampling systems (GO-FLO sampling bottles [General Oceanics] hung on a nonmetallic cable typically made of Kevlar fibers and triggered with plastic messengers (Bruland et al. 1979; Vane samplers, Bell et al. 2002; CLIVAR (Climate Vari-

ability program) rosette system with GO-FLO bottles; Measures et al. 2008; and a surface pumping system; Bruland et al. 2005), 8 analytical methods (e.g., shipboard cathodic stripping voltammetry and flow injection analysis; preconcentration and inductively coupled plasma-mass spectrometry at shoreside laboratories), and 18 individual laboratories from 8 different countries. In addition to examining sampling methods and shipboard determinations, over 600 L of 0.2 μm filtered seawater were collected from surface waters, acidified, and mixed in two linked 500 L, fluorinated low density polyethylene tanks, and then placed in 0.5 L low density polyethylene bottles; this was repeated with water from 1000 m depth. These samples allowed more laboratories to participate in the SAFe program and the remaining bottles to become long-term reference materials. Perhaps the most significant aspect about this seminal cruise was that a true intercalibration was accomplished—all participants shared their data, found differences or problems, and then modified their procedures so that everyone got the same accurate results. Indeed, the metrological definition of intercalibration is “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).

The SAFe program found that most clean sampling systems obtained good, uncontaminated samples, but handling steps such as filtration and acidification could change results (e.g., iron-organic complexes may not break down and therefore affect analytical recoveries; Lohan et al. 2006). Analytical offsets due to contamination from handling, reagents, or artifacts from chemical speciation (not only organic complexation, but also redox state) were also observed. This intercalibration allowed a large group of investigators to develop and test their iron methods, but another benefit of SAFe was the creation of deep and surface seawater reference samples for which there is a consensus concentration of dissolved Fe (and now other trace elements: <http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials>) based on reports from intercalibrated laboratories. These consensus reference samples are available for other laboratories to validate their analytical methods. The SAFe intercalibration was limited to only one element and phase, dissolved iron, but chemical oceanography is clearly more encompassing than one element and phase. The GEOTRACES program is ongoing, provides a good example of how intercalibration can be applied to a large range of parameters in both the particulate and dissolved states, and is reviewed below.

### **Assessment: GEOTRACES Intercalibration Program**

GEOTRACES is an international program whose mission is “To identify processes and quantify fluxes that control the distributions of key trace elements and isotopes (TEIs) in the ocean, and to establish the sensitivity of these distributions to

**Table 1.** Participant summary for GEOTRACES Intercalibration Cruise Program, including those who participated directly in the cruises and those receiving and analyzing samples.

TEI (Diss and Part)	Nr of laboratories	Countries
Al*	8	Canada, China, Japan, Netherlands, UK, USA
Cd*	13	Australia, Canada, Germany, Japan, UK, USA
Cu*	16	Australia, Canada, Germany, Japan, UK, USA
Fe*	20	Australia, Belgium, Bermuda, Canada, China, Germany Japan, Netherlands, UK, USA
Mn*	12	Canada, Japan, Netherlands, UK, USA
Zn*	13	Australia, Canada, Germany, Japan, UK, USA
<sup>13</sup> C*	4	USA, China, Japan
<sup>15</sup> N*	8	Canada, France, Germany, Japan, USA
<sup>230</sup> Th*	11	Canada, France, Germany, Japan, Sweden, UK, USA
<sup>231</sup> Pa*	11	Canada, France, Germany, Japan, Sweden, UK, USA
Pb isotopes*	5	France, Germany, UK, USA
Nd isotopes*	9	France, Germany, India, Japan, Sweden, Taiwan, USA
Other TEI (e.g., Co, Ni, <sup>210</sup> Pb, Pu, Ra, REE, <sup>234</sup> Th)	59	Australia, Belgium, Canada, China, Denmark, France, Germany, India, Japan, Monaco, New Zealand, S. Korea, Spain, Taiwan, UK, USA

\*Listed in the GEOTRACES Science Plan as a “key parameter.”

changing environmental conditions” (GEOTRACES 2006). The key TEIs in GEOTRACES were selected on the basis of being micronutrients, paleoceanographic proxies, or tracers of sources, removal, transport, and contamination: Fe, Al, Zn, Mn, Cd, Cu,  $\delta^{15}\text{N}$ -nitrate,  $\delta^{13}\text{C}$ , <sup>230</sup>Th, <sup>231</sup>Pa, Pb isotopes, and Nd isotopes. There are many other TEIs critical to the success of GEOTRACES, but these listed are considered the minimum to achieve the GEOTRACES’ mission and are measured in both the dissolved and particulate phases. The GEOTRACES program began with a thorough intercalibration of all aspects of TEI sampling and analyses, and will continue throughout the 10+ year life of the program to ensure precision and accuracy, overseen by an international Standards and Intercalibration Committee.

The first effort in GEOTRACES intercalibration was undertaken by the USA on two cruises in 2008 (Atlantic) and 2009 (Pacific), but was international in scope and participation (Table 1). The overall goals for these cruises were to (1) test the precision and accuracy of the sampling systems, sample handling, and analytical methods for as many dissolved and particulate TEIs as possible; (2) evaluate aerosol and rainwater sampling and analyses; and (3) obtain and bottle >500 L of 0.2  $\mu\text{m}$  filtered deep (2000 m) and surface seawater to allow an international intercalibration for many TEIs and to supplement/replace the SAFe consensus reference samples. The Atlantic cruise in June-July 2008 (Figs. 1 and 2) occupied the Bermuda-Atlantic Time Series (BATS; 31°50' N, 64°10' W) station that was selected for its stratified, oligotrophic surface waters (low nutrient, low bioactive trace elements, low particle concentrations) and the wealth of existing TEI data (e.g., Weiss et al. 2003; Sedwick et al. 2005). An additional station at the shelf break off the eastern USA coast (37°02' N, 74°25' W)

was occupied to provide a contrasting environment with higher particle abundance and TEI concentrations, particularly short-lived radionuclides. Major efforts at the Atlantic stations were evaluating the US trace element sampling system for the acquisition of hydrographically representative and contamination-free samples for dissolved and particulate TEIs, and intercalibrating in-situ pumping systems for acquiring large volume, particulate TEI samples.

In May-June 2009 (Fig. 3), the SAFe station in the North Pacific Ocean (30° N, 140° W) was occupied due to its very low surface concentrations of many TEIs and the considerable TEI data base at this location (e.g., Johnson et al. 2007). In parallel to the Atlantic cruise, a coastal station in California’s Santa Barbara Basin (34°16.45' N, 120°02.55' W) was selected for its higher dissolved and particulate TEIs and its strong redox gradients, with suboxic waters in the deepest 100 m (Sholkovitz and Gieskes 1971; Reimers et al. 1990). This allowed not only the sampling system to be tested with high chemical depth gradients under such conditions, but also handling procedures for redox sensitive elements such as Fe to be evaluated.

Perhaps what sets GEOTRACES apart from previous large chemical oceanographic programs such as GEOSECS (e.g., Broecker and Peng 1982) is that particles are sampled in addition to dissolved constituents. Therefore, particular emphasis during the intercalibration was placed on evaluating the differences between particulate TEI sampling via filtration using GO-FLO bottle sampling (up to 11 L filtered) versus those from in-situ pumping such as the well-established MULVFS apparatus (Multiple Unit, Large Volume Filtration System; Bishop et al. 1985) in the upper 1000 m or independently powered units with a variety of filtration and handling procedures at greater depths. Given that many future GEOTRACES cruises may not



**Fig. 1.** Participants on the first leg of the 2008 GEOTRACES Intercalibration cruise in the North Atlantic Ocean aboard R/V Knorr.



**Fig. 2.** Participants on the second leg of the 2008 GEOTRACES Intercalibration cruise in the North Atlantic Ocean aboard R/V Knorr.



**Fig. 3.** Participants on the 2009 GEOTRACES Intercalibration cruise in the North Pacific Ocean aboard R/V Knorr.

have in situ pumps due to costs and station time, comparisons between low volume rosette bottle sampling and the large volume pumps were critical.

The scope of the GEOTRACES intercalibration cruises was large enough that none of the three lead investigators (G. Cutter at Old Dominion University, K. Bruland at UC Santa Cruz, and R. Sherrell at Rutgers University) had expertise to cover all TEIs, so a group of 18 “Elemental Coordinators” was put in place to oversee implementation and interpretation of final results from their respective, international TEI communities. More significantly, each TEI community established acceptance criteria as metrics to judge whether intercalibration was achieved for a given TEI (e.g., 5% accuracy and precision). In this respect, it is important to re-emphasize that GEOTRACES, and the intercalibration program, is international in scope (Table 1). After each cruise and subsequent analytical work, a workshop was held to present results for the entire suite of TEIs to all participants, and the GEOTRACES S&I Committee, to make an overall assessment of general sampling procedures and the success, or failure, for each TEI examined. One outcome from these workshops is the collection of papers found in the special issue of *Limnology and Oceanography: Methods*, Volume 10, Intercalibration in Chemical Oceanography. These articles include the following: evaluating the performance (hydrographic fidelity, degree of contamination) of the US Sampling system (Cutter and Bruland 2012; Fitzsimmons and Boyle 2012); comparing the composition and elemental concentrations of particles collected via in situ pumping systems and GO-FLO bottles (Bishop et al. 2012; Planquette and Sherrell 2012); optimizing the collection and handling, and then intercalibrating samples for neodymium isotopes and rare earth elements (van de Fliedert et al. 2012; Pahnke et al. 2012), anthropogenic radionuclides (Kenna et al. 2012),  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  (Church et al. 2012; Baskaran et al. 2013); radium isotopes (Charette et al. 2012); the suite of Th and Pa in the dissolved and particulate states (Anderson et al. 2012; Auro et al. 2012; Maiti et al. 2012); atmospheric aerosols (Buck and Paytan 2012; Morton et al. 2013); organic complexation of Fe and Cu (Buck et al. 2012); and a variety of other trace metals and their isotopes (Boyle et al. 2012; Lamborg et al. 2012; Sharma et al. 2012; Zurbrick et al. 2012).

## Discussion

GEOTRACES is but one example of a program that has intercalibration as an essential component of field-based efforts. The standing GEOTRACES Standards and Intercalibration Committee was initiated to ensure precision and accuracy throughout the program’s life. To facilitate consistent sampling and sample handling procedures between cruises and participating laboratories, the S&I Committee in collaboration with the Elemental Coordinators created a set of written protocols for each suite of TEIs (“Sampling and Sample Handling Protocols for GEOTRACES Cruises,” <http://www.geotraces.org/libraries/documents/Intercalibration/Cookbook.pdf>) to which

cruise participants can refer. The protocols are updated biennially. It is important to note that only a few specific analytical methods are listed in these protocols in order to not stifle the development of newer, better methods. Any new analytical procedure only needs to intercalibrate with existing, established methods. In a similar fashion, exact sampling systems are not specified as the only acceptable ways to acquire samples as long as they can be intercalibrated with existing methods.

To ensure full intercalibration throughout the program, each GEOTRACES transect across one of the world’s ocean basins occupies at least one “crossover station” that also has been sampled by another GEOTRACES cruise. The results for each TEI are then compared between the investigators from both cruises to determine if any significant differences in data are observed and then resolved based on the quality objectives set by the Elemental Coordinators; the net result is complete intercalibration between the two cruises. These intercalibrated data are submitted to the S&I Committee for final review and compiled in the GEOTRACES International Data Assembly Centre (<http://www.bodc.ac.uk/geotraces/>). The advantage of having crossover stations is that it includes all steps—from sampling to analysis to data reduction. However, if a cruise cannot occupy a crossover station, the protocols require more rigorous sampling at one station, including multiple hydrocasts and from these collecting multiple samples from 3 different depths, and the resulting samples then distributed to multiple laboratories for TEI determinations. Although these requirements cannot intercalibrate an individual sampling method, they at least help to evaluate sample handling to analyses. The international GEOTRACES program has tried from its beginning to incorporate procedures to acquire the most precise and accurate data possible, keeping in mind the wide variety of countries and their laboratories who are participating. The GEOTRACES intercalibration is an ongoing process and hopefully its lessons can provide a roadmap for other developing programs.

In the science of metrology, intercalibration is seen as an essential component to its successful practice. The discoveries of trace element-biological interactions in the ocean on a molecular level (e.g., Bruland et al. 1991; Saito et al. 2008) show that we really have to measure the elemental stoichiometry (e.g., Redfield ratio) correctly. Thus, getting the “right number” for the practice of modern chemical oceanography is essential. As a community, we must continue to develop and test new sampling and analytical methods through intercalibration to keep up with, and make, new discoveries.

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