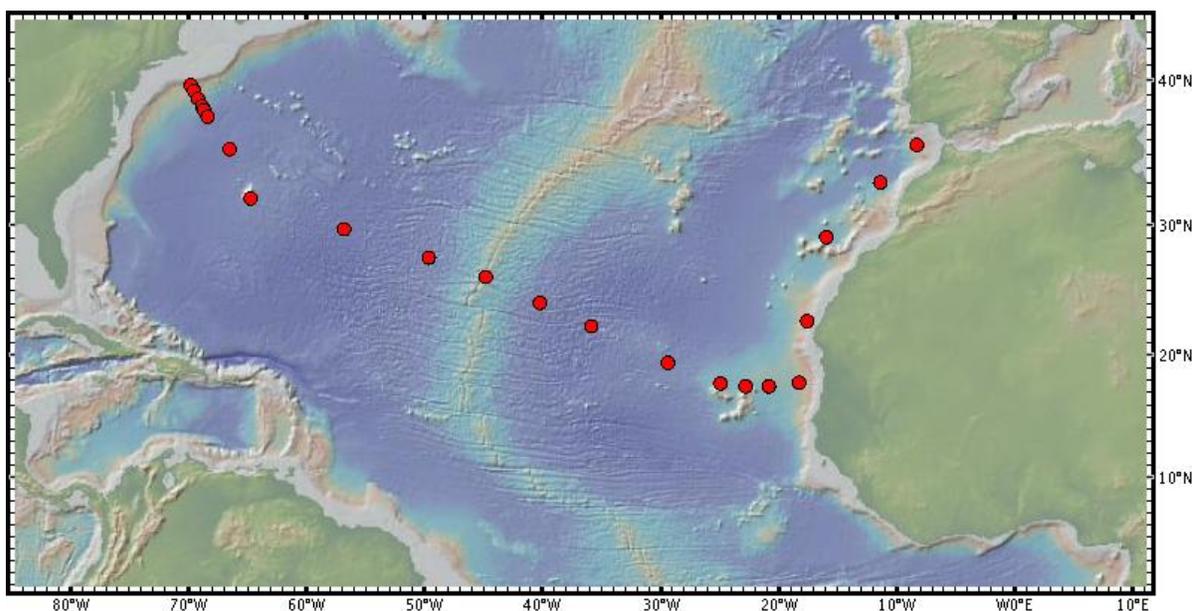


# U.S. GEOTRACES

## North Atlantic Zonal Section Implementation Plan



*Based on proceedings of a workshop  
Woods Hole Oceanographic Institution  
22-24 September, 2008*

Edited by Bob Anderson, Ed Boyle, and Bill Jenkins

23 December, 2008

## **U.S. GEOTRACES Atlantic Section Implementation Plan**

### **Historical Context and Process**

Following publication of the 2006 SCOR GEOTRACES Science Plan (hereafter referred to as GSP06), four international workshops (Pacific Basin, Honolulu, June 2007; Modeling and Data Management, Delmenhorst, Sept. 2007; Atlantic Basin, Oxford, Sept. 2007; and Indian Basin, Goa, Oct. 2007) were held to devise the global ocean sections and coordinate the activities of the individual participating nations. In May 2008, the US Science Steering Committee (US SSC) met at the Lamont-Doherty Earth Observatory to develop a strategy for implementing a US contribution to the Science Plan with approximately five US GEOTRACES sections to be occupied during the next 10-12 years. Taking into account existing data, readiness of techniques, and ship availability, the US SSC recommended two planning workshops to prepare implementation plans for a (1) North Atlantic Zonal Section in 2010 and (2) Pacific North-South and South Pacific East-West sections in later years. Based on the results of these workshops and the preliminary results of the June-July 2008 GEOTRACES Intercalibration cruise, the US SSC will consider recommending a section for submission of proposals to NSF beginning in Feb. 15, 2009 for the first GEOTRACES section cruise tentatively occurring in the latter half of 2010.

This implementation plan is a synthesis of the three breakout group reports produced at a meeting funded by NSF and hosted by E. Boyle and W. Jenkins in Woods Hole, September 22-24, 2008 (see <http://www.whoi.edu/conference/geotracesAtlantic>). The workshop was an open meeting to design the first U.S. GEOTRACES North Atlantic Section that was originally proposed in a preliminary form during the International Atlantic Basin Workshop held in Oxford, U.K. in September, 2007. The Woods Hole workshop was attended by approximately 25 scientists from throughout the U.S. (see Appendix 1 for a list of attendees, and Appendix 2 for the agenda). After a number of plenary presentations and discussion, three breakout groups were formed and tasked with writing (1) an overall rationale, (2) a detailed logistical implementation strategy, and (3) a data management protocol for the section. Please see Appendix 3 for the list of breakout groups, attendees, rapporteurs, and discussion leaders.

### **Rationale and Justification**

It is recognized that many trace elements and isotopes play important roles in biogeochemical processes and the carbon cycle - or in tracing changes in these processes in the past - yet very little data is available defining their large-scale distributions and the regional-scale processes that affect them. Recent advances in sampling and analytical techniques, along with advances in our understanding of their roles in enzymatic and catalytic processes in the open ocean lead us to a natural opportunity to make substantial contributions to understanding these important properties. Moreover, we are motivated by the prospect of ongoing global change and the need to understand the present and future workings of the ocean's biogeochemical cycles.

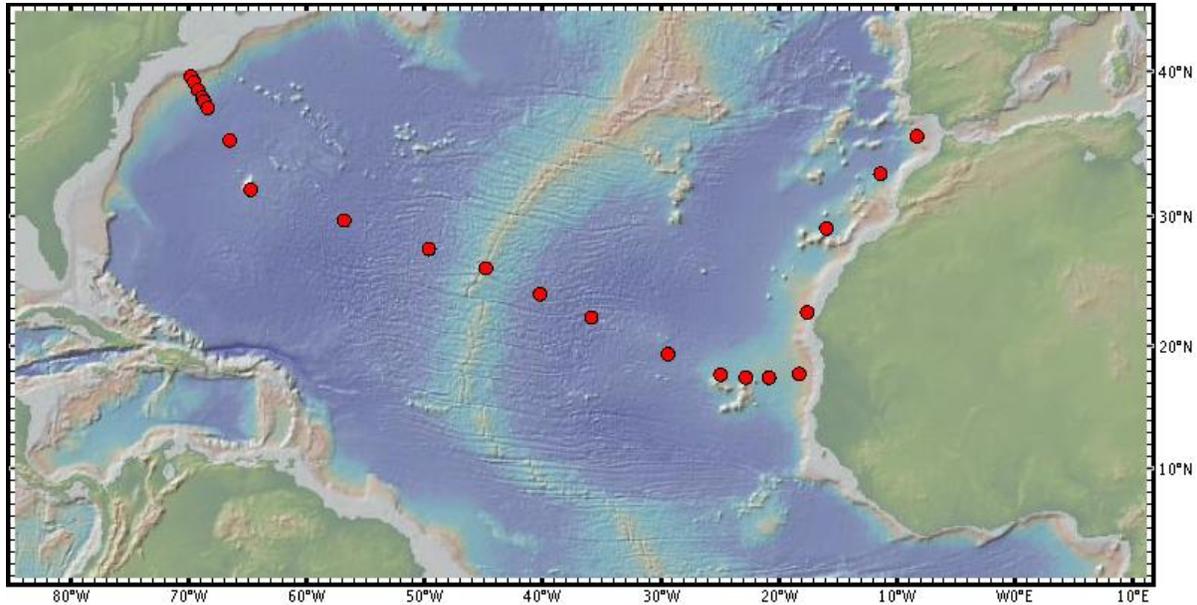
The mission of GEOTRACES is to improve knowledge of the distributions, sources, and sinks of Trace Elements and Isotopes (TEIs) in the global ocean (GSP06, p1). The strategy is to accomplish this by characterizing their distributions throughout the world oceans in a systematic fashion (the Global Survey), as identified in the Science Plan as Goal 1 (GSP06, p1), and addressed in detail by the three basin workshops. The North Atlantic section described here is intended to follow the combined efforts of inter-calibration and capability building that are currently in progress, and represents the first U.S. contribution to the Global Survey. The section was designed to complement and fit within the framework of other national cruises scheduled or planned to occur in the Atlantic within the 2009-2011 timeframe.

The North Atlantic section was chosen for a number of reasons. First, the North Atlantic represents the “starting point” for the planetary Meridional Overturning Circulation (MOC), and a complete characterization of “initial” TEI properties is an important step. Second, inasmuch as the North Atlantic appears as an important climate pivot point in past climate-related ocean circulation reorganizations, a better understanding of TEI distributions and behavior constitutes a significant benefit for paleo-proxy work (GEOTRACES Goal 3, GSP06 p1). Third, the Atlantic basin contains the full suite of physical and biogeochemical processes that affect TEIs, including strong meridional advection, boundary scavenging and sources, aeolian deposition, an input of intermediate waters from the Mediterranean and Labrador Seas, and evidence of anthropogenic impacts (GEOTRACES Goal 2, GSP06, p1). Fourth, the effort is timely: execution of the U.S. zonal Atlantic section in late 2010 fits well within the context of a number of Atlantic sections being carried out by other nations in the time frame of 2009-2011, effectively leveraging international resources and enhancing the value and utility of an approximately synchronous characterization TEIs within an important ocean basin.

### **Description and General Justification of the Cruise Track**

A zonal, mid-latitude North Atlantic section allows a characterization of both limbs of the MOC, and transects key areas of the ocean basin where important processes are known to affect TEIs (see next section). Several attributes of the North Atlantic Ocean can be exploited in fulfilling the GEOTRACES mission to assess the sources, sinks and internal cycling of TEIs. As a relatively small basin surrounded by land masses, the North Atlantic is expected to be influenced by sources of TEIs related to continental weathering to a greater extent than occurs in other major basins. Continental sources are further enhanced by atmospheric deposition, including both natural (*e.g.*, Saharan dust) and anthropogenic (*e.g.*, industrial emissions from Europe and North America) sources. The small size of the North Atlantic basin also affects the removal of TEIs that are sensitive to scavenging by particles. The enhanced scavenging that occurs in regions of high particle flux in the vicinity of ocean margins imposes an overall removal rate on scavenged TEIs that is expected to be greater than in other basins.

After detailed discussion of a number of possible refinements, the workshop unanimously recommended the cruise track shown in Figure 1 based on key science objectives and



**Figure 1:** Station locations along the US GEOTRACES North Atlantic cruise track. Red dots represent stations where full water column TEI sampling is anticipated. Additional sampling of surface waters, and shallow (e.g., to 1000 m) hydrocasts, will be employed to provide greater spatial resolution in selected areas of the cruise track. This map was produced using GeoMapApp: <http://www.geomapapp.org/>.

practical issues such as cruise duration and available ports. The station locations shown as red circles in Figure 1 represent “full GEOTRACES” sampling sites. Additional ship-time was included in the plans for underway and surface sampling, as well as additional shallow and/or limited sampling stations in between to provide necessary resolution of hydrographic and property gradients along the cruise track (see below). The cruise track transects the relatively well-ventilated western basin of the North Atlantic, intersects the Mid-Atlantic Ridge at a well-characterized hydrothermal site, transects the more slowly ventilated eastern basin, cuts into the northern part of the African upwelling and low-oxygen zone, and ends with a line into the Mediterranean outflow.

More than in any other basin, TEI distributions in the North Atlantic are influenced by advective processes. These include southward transport by mode waters and by North Atlantic Deep Water (NADW), together with the counterbalancing northward transport associated with surface waters, Antarctic Intermediate Water (AAIW) and Antarctic Bottom Water (AABW). Lateral injection from quasi-point sources influences TEI distributions as well, including water from Arctic basins delivered as surface transport along the coast of Greenland and water from the Mediterranean Sea, which is injected at mid-depth. Advective transport may serve as both a supply and removal mechanism for TEIs in Eulerian mass budgets, and as an agent for internal cycling by redistributing TEIs within the basin.

The cruise track transects significant regional gradients in biological productivity, starting in seasonally productive waters off the New England coast, moving into the largely oligotrophic subtropical gyre, and then into the highly productive African

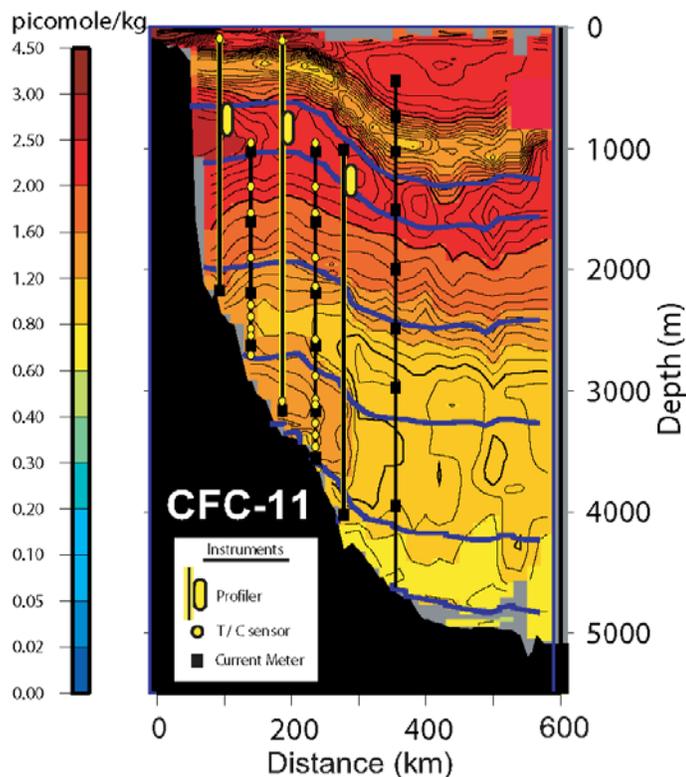
upwelling region. This track presents investigators with the opportunity to contrast the TEI distributions and inter-relationships among significantly different oceanic biomes. The section also provides an opportunity to contrast the more poorly ventilated deep waters of the eastern basin with those of the western basin. Finally, segments approximately perpendicular to morphologically different continental shelves and slopes permit a characterization of important shelf-slope-open ocean exchange and boundary scavenging processes.

### **The Cruise Track Relationship to Key TEI Processes**

The primary strategy employed by GEOTRACES is to carry out a global survey of TEIs (GSP06, p2), and the proposed section fits well within the broader international framework of planned and scheduled cruises in the Atlantic over the 2009-2011 period. For example, a zonal section will be carried by the French in the sub-polar North Atlantic, and there is a German study of the African upwelling region to the south. The British are performing a zonal section in the South Atlantic in 2010. More-or-less synchronous zonal sections will permit a crude estimate of meridional material transport divergence within the Atlantic, which is a useful first step toward quantifying global fluxes of TEIs. A reoccupation of the original GEOSECS western Atlantic section is planned by the Netherlands, documenting downstream evolution of the lower limb of the MOC. The intersection of our proposed cruise with this last section provides an extra opportunity for intercalibration as well.

As discussed in the Science plan (see Table 1 in GSP06, p7), the distributions of TEIs are affected by combination of physical and biogeochemical processes. Next, we discuss those aspects of the proposed section that can advance our knowledge of these processes.

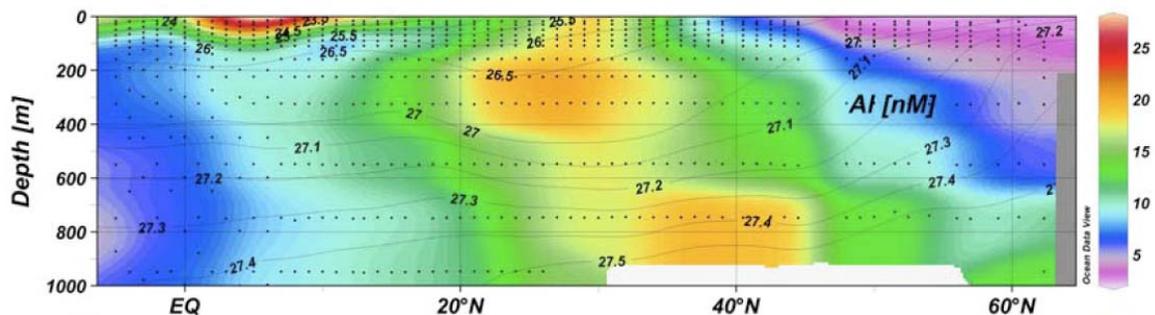
***Meridional Advection and the MOC:*** The proposed section cuts across the upper and lower limbs of the MOC (e.g., see Kuhlbrodt et al, 2007). It starts with a relatively dense section at “Line W”, a CLIVAR repeat hydrography and mooring section running southeast from Cape Cod to Bermuda. The cruise track cuts across both the dominant northward-bound returning limb of the MOC embodied in the Gulf Stream and also the westward-intensified, southward-flowing deep western boundary currents (DWBC) constituting the lower limb of the MOC. The newly ventilated DWBC is highlighted by elevated levels of anthropogenic tracers, like CFCs (see Figure 2), radiocarbon, and tritium. Such tracers are useful for characterizing ventilation of the deep oceans (e.g., Schiltzer, 2007). Simultaneously determining the abundances of TEIs in these currents is important for characterizing the fluxes, budgets, and transformation rates for these properties. The section also extends diagonally across the deep western basin of the North Atlantic, permitting the measurement of TEIs in the abyssal, zonally-oriented recirculation gyres that are known to “buffer” and influence the net southward transport of TEIs in the lower limb of the MOC.



**Figure 2:** Section plot along Line W of contoured concentrations of CFC-11, an anthropogenic contaminant introduced mainly during the latter half of the 20th century and incorporated into deepwater via gas exchange within regions of deepwater formation. The section plot also depicts the locations of moored instruments that are maintained by the repeat hydrography program. Station locations along the NW portion of the cruise track shown in Figure 1 coincide with the mooring locations shown here. Figure courtesy of John Toole.

Buoyancy loss at high latitudes generates new deep waters that inherit a chemical composition diagnostic of their surface source (i.e., generally low concentrations of nutrients and of TEIs removed from surface waters by biological uptake and/or chemical scavenging), albeit modified by entrainment and mixing before deep water masses develop their characteristic compositions. Low concentrations of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  carried by recently ventilated deep waters are reported to influence dissolved concentration profiles of these TEIs throughout the North Atlantic basin. Similarly, concentrations and the isotopic composition of dissolved Pb reflect the history of atmospheric deposition over North Atlantic regions of deep water formation and the penetration of the anthropogenic Pb signal into deep waters. Other TEIs are expected to have their distributions influenced similarly by deepwater ventilation. Sampling along the proposed section, particularly when done in conjunction with sampling for anthropogenic tracers (e.g., CFCs and  $^3\text{H}$ ), will enable investigators to evaluate the impact of overturning circulation on TEI distributions in the deep North Atlantic Ocean.

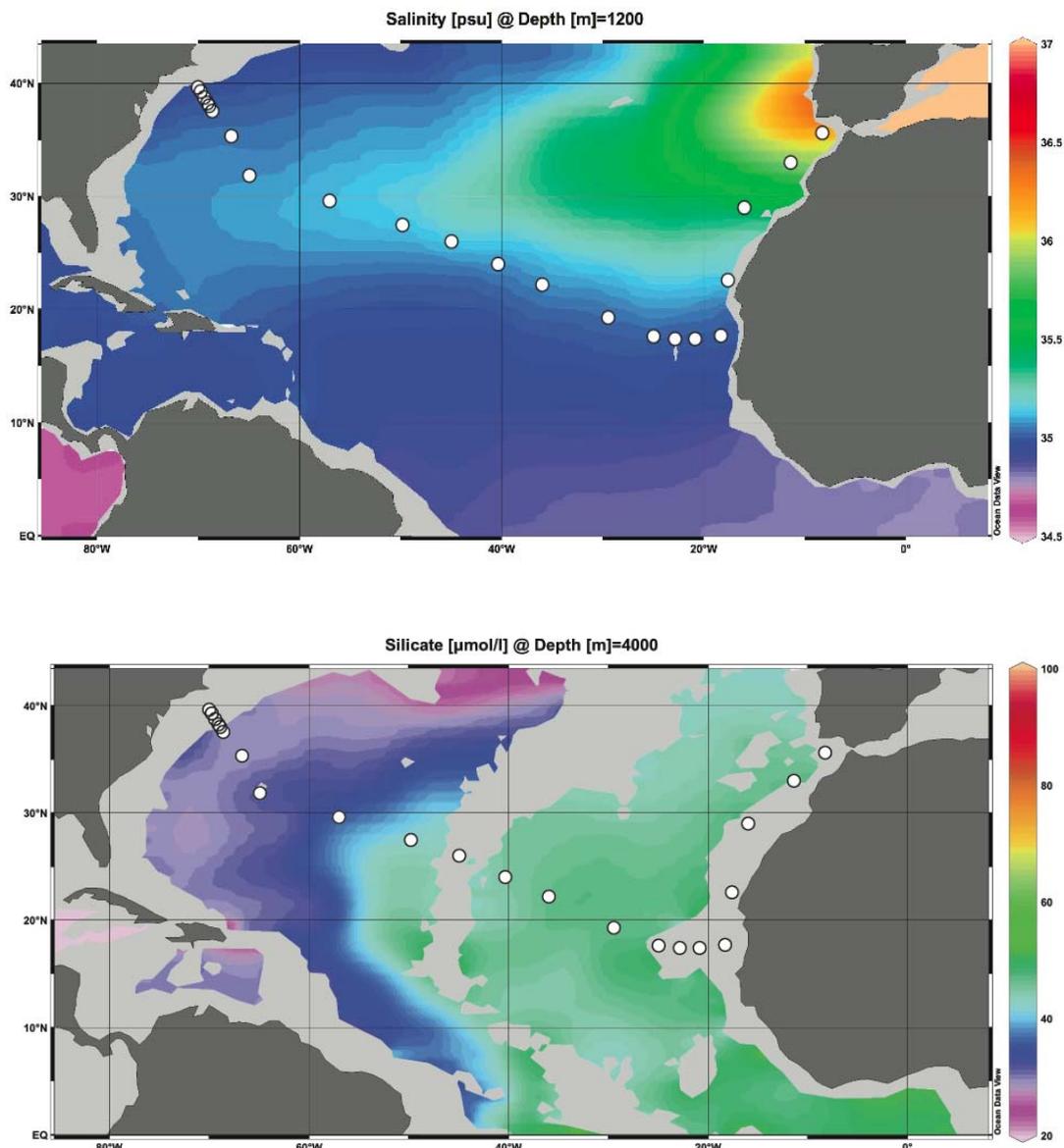
In shallow waters, the proposed cruise transects the relatively well-ventilated subtropical gyre recirculation region, including the south-westward advection of subtropical mode waters from their formation region north-east of the Gulf Stream extension. Mode water formed along the northern fringe of the subtropical gyre carries a distinct chemical signature into the ocean interior. For example, elevated concentrations of dissolved Al observed at depths of 200 to 400 m, between 20° and 35° N along a meridional section in the eastern N Atlantic (Figure 3), are attributed the dissolution of mineral dust in surface waters throughout the region of mode water formation, and spreading of the Al signal into the thermocline. Sampling along the proposed cruise track will allow investigators to assess the impact of these processes on other TEIs. Including transient tracers such as CFCs and  $^3\text{H}$  will add information about the time scales for transport of the TEI signal into the thermocline. The eastward extent of the section penetrates the so-called “shadow zone” which is excluded from direct ventilation by subducted waters (Luyten et al, 1983).



**Figure 3.** Dissolved Al concentrations (nM) along the CLIVAR A16 section in the eastern N Atlantic Ocean. High concentrations at the surface between the equator and 10°N reflect dissolution from recent dust deposition. The elevated concentrations between 200 and 400 m (20°N to 35°N) are associated with Mode Water advection, while the elevated concentrations between 800 and 1000 m (30° to 45°N) are associated with high salinity water from the Mediterranean Sea. From Measures et al., (2008).

The aluminum section also highlights the intrusion of Mediterranean Water in the section, and its contrast to surrounding water masses. Key questions can be asked about the relative contributions of the three dominant intermediate water masses (*i.e.*, Mediterranean Outflow, Labrador Sea Water, and Antarctic Intermediate Water) to the distributions of TEIs in the North Atlantic. For example, the northward transport of water masses originating in the Southern Ocean may influence TEI distributions as far north as the proposed section. Remnant Antarctic Intermediate Water (AAIW) can be seen as a local minimum in the CFC section shown in Figure 2, at a depth of about 1000 m along the seaward end of the transect and shoaling toward the coast. The confluence of the three intermediate water masses can be seen in relation to the proposed cruise track in the upper panel of Figure 4, plotted on the distribution of salinity at 1200 m depth.

Finally, the northward penetration of Antarctic Bottom Water plays a potentially important role in affecting the ultimate TEI characteristics of NADW, and hence the lower limb of the MOC. Although Antarctic Bottom Water has been modified extensively by mixing before it enters the North Atlantic Ocean, high dissolved Si concentrations provide a diagnostic chemical signature of southern sourced deep water



**Figure 4 Upper Panel:** Station locations along the US GEOTRACES North Atlantic cruise track plotted on a map of salinity at 1200 m. Dots represent stations where full water column sampling is anticipated. High salinity in the east is associated with outflow of Mediterranean water. Note the intrusion of relatively lower salinity from the south (Antarctic Intermediate Water) and the north (Labrador Sea Water).

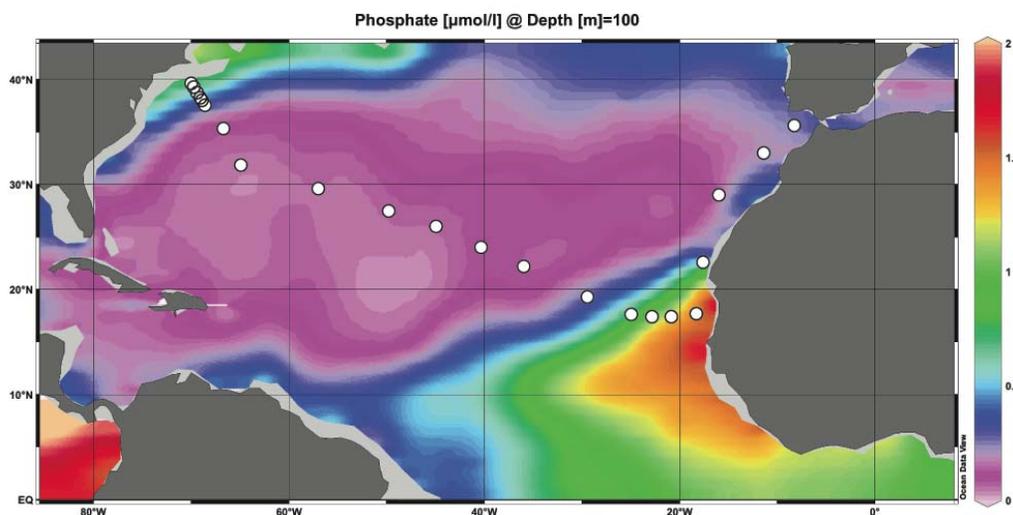
**Lower Panel:** Station locations plotted on a map of silicate at 4000 m. The southward penetration of low-silicate NADW is seen along the western boundary. Note the northward penetration of high silicate bottom water in the eastern basin and along the western flank of the Mid-Atlantic Ridge. These and subsequent maps in this document were created using Ocean Data View, courtesy of Reiner Schlitzer. Data plotted here are from the World Ocean Atlas (Garcia et al, 2006).

masses, as evident in the bottom panel of Figure 4, where Si-rich deep water can be seen penetrating northward at 4000 m against the Mid Atlantic Ridge along the eastern margin

of the western basin. At this depth, the entire eastern basin has deep water enriched in Si, indicating admixture of a component of southern sourced deep water. Comparing TEI-Si relationships across gradients in Si concentration will aid in identifying advective sources of TEIs associated with NADW and/or with AABW. These relationships will be expanded spatially by combining results from the U.S. section with those from sections undertaken by other nations to the north and south of the U.S. section.

**TEIs and the Carbon Cycle:** A number of trace metals serve as essential micronutrients (e.g., GSP06, p3). This can be inferred from the fact that the distributions of many trace elements in the ocean appear to mimic macronutrients. Classic textbook examples include the similar distributions of Cd and phosphate, or of Zn and silicic acid. While metal-nutrient relationships inform us about the processes of uptake, regeneration and internal cycling of TEIs; departures from constant relationships further inform us about processes that have a specific impact on a particular trace element, and about the regions where these processes are important. Benefits of studying these relationships range from developing more reliable interpretations of TEIs used as paleoceanographic proxies to new insights into the metabolic function of trace metals in marine biota. In particular, extending studies of metal-nutrient relationships to ultra-low nutrient concentrations, and to simultaneous studies of multiple TEIs, may reveal synergistic as well as antagonistic relationships among macro and micro nutrients, as well as taxa-dependent preferences for specific micronutrients (e.g., preferences for Co by cyanobacteria and for Zn by diatoms).

The cruise track offers excellent opportunities to examine these relationships. The section cuts through both regions of very high and very low productivity. The contrast is best seen in the distribution of phosphate at 100 m depth shown in Figure 5. Downwelling and subduction of nutrient depleted waters throughout the subtropical gyre lead to low nutrient availability for winter convection, resulting in oligotrophic conditions in the



**Figure 5:** Station locations plotted on a map of dissolved phosphate at 100 m. Downwelling of nutrient-depleted surface waters maintains low nutrient concentrations at 100 m throughout the gyre. Higher concentrations near the margins reflect upwelling and/or seasonal deepening of the mixed layer, both of which bring nutrients into the euphotic zone.

central gyre. Upwelling off the African coast, on the other hand, leads to high productivity.

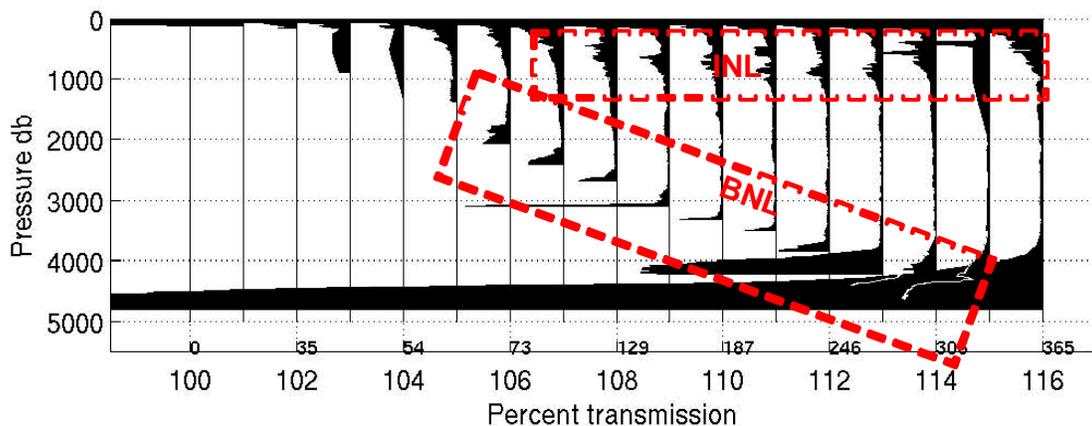
Another advantage of this section is that advection brings many water masses to the North Atlantic region. Stations are well positioned to sample metal-nutrient relationships in subpolar and subtropical mode waters, while also characterizing any departures from metal-nutrient relationships in North Atlantic water masses relative to Si-rich water from the Southern Ocean in the deepest part of the basin and salty Mediterranean outflow water injected into the eastern side of the basin. Phytoplankton taxa also vary markedly along the proposed section. For example, cyanobacteria dominate in low-nutrient waters of the central gyre while diatoms are abundant in the upwelling region off NW Africa. Incorporating measurements of nanomolar nutrient concentrations together with simple measures of phytoplankton taxa (e.g., HPLC pigments) along the section will enable investigators to interpret spatial variability in metal-nutrient relationships, as well as relationships among TEIs, in the context of the range of different phytoplankton taxa that may influence the uptake and regeneration of TEIs.

***Exchange with the Ocean Margins:*** Continental shelves act to filter the supply of TEIs introduced to the ocean by continental weathering. Some TEIs are removed on continental shelves whereas others are thought to be mobilized (e.g., Fe and, perhaps, other micronutrients). The east coast of North America is incised by estuaries while being surrounded by a broad continental shelf. The west coast of North Africa, in contrast, has no large estuaries and a narrow continental shelf. The proposed cruise track intersects these margins with higher than average spatial resolution (Figure 1) allowing investigators to quantify continental sources in these contrasting continental shelf regimes. Continental sources of dissolved TEIs, whether by direct river influx or submarine discharge or exchange, can be traced seaward by measuring dissolved Ra isotopes. Short-lived isotopes ( $^{223}\text{Ra}$ ,  $^{224}\text{Ra}$ ) trace coastal inputs to shallow waters over time scales of several days to weeks. Concentrations of  $^{228}\text{Ra}$  in the thermocline can be (and has been) used to estimate average subsurface groundwater inputs over decadal time scales. In each case, the Ra isotopes are used in conjunction with measured gradients of other TEIs to estimate fluxes from the continent as well as in situ processes.

Detached nepheloid layers represent another process introducing continental material into the interior of the ocean. Whereas evidence for these layers has accumulated for decades in transmissometer data, little work has been done to assess their contribution to dissolved TEI distributions in the ocean. Detached nepheloid layers are common along Line W, the western portion of the proposed cruise track (Figure 6), extending hundreds of kilometers into the ocean basin. This section will allow investigators to evaluate the role of shelf-basin exchange of both dissolved and suspended forms to TEI budgets by careful sampling within and across the features. Moreover, characterizing the TEI composition (and evolution) of suspended particles is diagnostic of their origins.

Margin sediments may also serve as a source of dissolved TEIs to deep waters. Whereas studies with benthic flux chambers have indicated significant fluxes for biogenic elements and for TEIs mobilized by redox chemistry, little work has been done to assess

benthic sources of TEIs traditionally considered to be refractory or lithogenic. High-resolution sampling of bottom waters for concentrations of dissolved Al,  $^{232}\text{Th}$ , and other



**Figure 6:** Transmissometry profiles along Line W, depicting both intermediate and benthic nepheloid layers extending a large distance away from the shelf. Small numbers just above the x-axis labels are distance in kilometers from a station just landward of the shelf break. Figure courtesy of John Toole

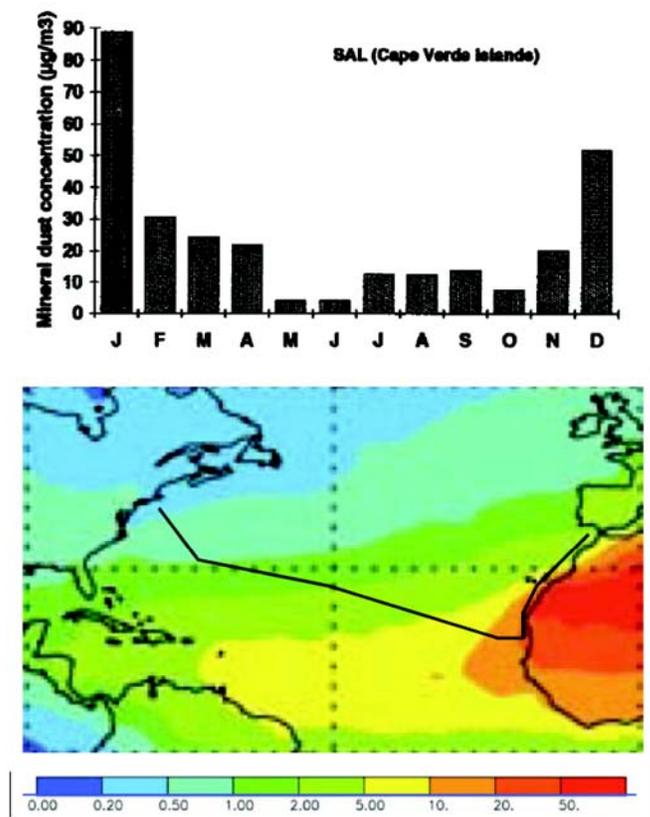
refractory TEIs will allow the significance of this potential source to be evaluated. Net fluxes of biogenic and redox-sensitive TEIs will be assessed by this strategy as well.

Complementing the studies of benthic sources of TEIs, Nd isotopes will be used to estimate the net effect of exchange reactions along the flow path of deep water in contact with the sediments. Regional variability of Nd isotopic composition in continental sources of lithogenic material offers a unique opportunity to evaluate solid-solution exchange processes at the sea floor in the absence of net fluxes. This strategy will be most effective when combining results from this section with those of other GEOTRACES sections collected at additional points along the flow path of NADW (see complete plans for the Atlantic Ocean in the GEOTRACES Atlantic Basin Report). Along the west coast of North Africa, Nd isotope results will provide additional constraints on sediment-water exchange fluxes in the absence of strong lateral transport.

**Atmospheric Deposition:** Atmospheric deposition is particularly important as a source of TEIs in the North Atlantic Ocean due to the combined effects of anthropogenic emissions from industrial and agricultural sources together with mineral dust mobilized in the North Africa. Mineral aerosols are thought to be a significant source of Fe and other micronutrients for much of the central North Atlantic Ocean, while atmospheric deposition may be a significant source of fixed nitrogen in some regions as well. Where that is true, the isotopic composition of aerosol nitrogen can be diagnostic of its source.

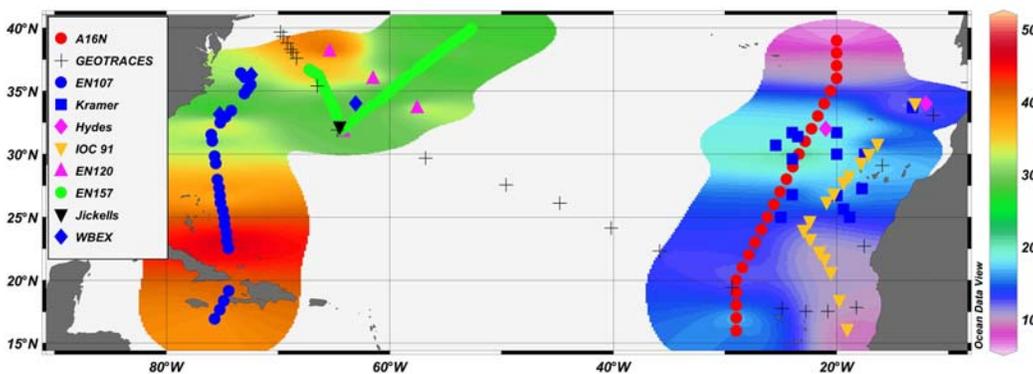
Radiogenic isotopes can be exploited to constrain the provenance of selected aerosol constituents. For example, Pb isotopes readily discriminate between European and American sources of Pb, while Nd isotopes are diagnostic of the age of source rocks from which mineral dust is generated, thereby constraining its source as well.

Aerosol deposition is seasonal (see upper panel of Figure 7), so that sampling during a cruise could give a biased view of the mean annual supply of TEIs by atmospheric deposition. Consequently, a clearer picture of the mean and variability of atmospheric deposition can be derived by studying aerosol-derived TEIs having a range of residence times in surface waters. For example, by analogy with  $^{234}\text{Th}$ , lithogenic  $^{232}\text{Th}$  that dissolves from mineral aerosols is expected to have a residence time of a few weeks, whereas Al mobilized by similar processes is thought to have a residence time in surface waters of a few years. Other lithogenic TEIs (e.g., Fe, Nd) are expected to have intermediate residence times. In addition, comparing  $^{210}\text{Pb}$  with lithogenic TEIs may help resolve the relative importance of wet and dry deposition. The strong seasonality of dust deposition should be considered in choosing the timing of the cruise. Furthermore, peak dust deposition occurs at different times of the year along different segments of the section. For example, near the Cape Verde Islands, in the vicinity of the eastern end of the section, dust deposition begins to rise in the boreal Fall and peaks in Winter (Figure 7). Thus, a cruise beginning in Woods Hole in mid autumn would reach the eastern portion of the section at about the time of the initial seasonal increase in dust deposition, allowing investigators to assess the immediate response of TEIs to increasing dust flux.



**Figure 7:** Seasonality (upper panel, from Chiapello et al, 1995; reproduced with permission from the American Geophysical Union) and distribution of dust deposition (lower panel, in  $\text{g m}^{-2} \text{y}^{-1}$ , from Jickells et al, 2005; Reproduced with permission from AAAS, <http://www.sciencemag.org>.) in the North Atlantic. Proposed section shown in lower panel as a black line.

Sampling along the proposed cruise track will enable investigators to examine potential causes for the enigmatic “reverse zonal gradient” in surface concentrations of dissolved aluminum, as well as the implications for sources of other aerosol-derived TEIs. To illustrate this point, compare the spatial pattern of mean annual dust deposition in the lower panel of Figure 7, showing higher values in the east than in the west, with the much greater values of dissolved Al concentration observed in the Western North Atlantic Ocean compared to the east (Figure 8, below). Higher concentrations of dissolved Al in the west may indicate one of two things: either the actual spatial pattern of dust deposition differs from that illustrated in Figure 7, or the residence time of dissolved Al in surface waters is much longer in the west than in the east. In either case, the implications for aerosol-derived TEIs are important. The proposed cruise track is well located to examine this problem.



**Figure 8:** Surface Al concentrations (nM). Modified from a figure in Measures et al. (2008) Proposed stations are shown by “+” symbols.

**Hydrothermal Sources and Sinks:** Hydrothermal fluids vented at the crest of mid-ocean ridges bear a chemical composition created by reaction of seawater with host rocks at high temperature. This interaction may result in biogeochemically significant fluxes of TEIs either into, or from the circulating seawater, and may play a role in the long term control of the chemical composition of the oceans. Products of rock-water interactions vary with the composition of the rock, which, in turn, differs between slow spreading ridges such as the Mid-Atlantic Ridge and fast spreading ridges such as the East Pacific Rise.

The proposed cruise track intersects the Mid-Atlantic Ridge at a well-studied hydrothermal vent site, the TAG hydrothermal Field. Hydrothermal fluids at the TAG site on the Mid Atlantic Ridge have low sulfur contents, thereby allowing relatively high concentrations of iron in the effluent fluids. Oxidation of iron (and manganese) and its subsequent precipitation as the effluents mix with surrounding seawater generates an abundance of oxyhydroxide phases (approximately tens of nanomolar Fe at a depth where plumes reach neutral buoyancy compared to surrounding seawater) capable of scavenging numerous TEIs from seawater. Samples collected at a station located within the

hydrothermal plume “downstream” from the TAG vents will enable investigators to evaluate TEI/Fe relationships for a wide range of TEIs, while also evaluating the depletion of dissolved TEIs within the plume. Examining dissolved and particulate TEIs together will offer a more complete view of TEI removal than would be obtained by investigating either phase alone.

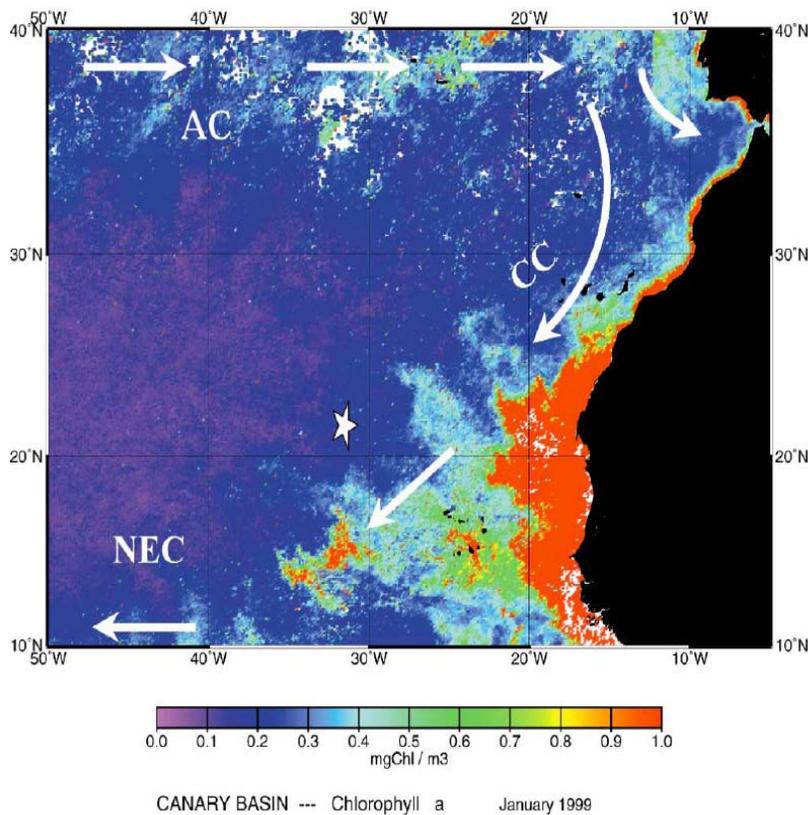
Hydrothermal systems may also serve as a source for certain TEIs. For example, both the concentration and speciation of Hg may be uniquely influenced by hydrothermal systems. Sampling at the TAG site will allow sources to be identified as well as sinks, and will provide investigators with the opportunity to examine chemical speciation of TEIs associated with hydrothermal systems.

### **Measurement Strategy**

The strategy underlying GEOTRACES is to measure a broad suite of TEIs to constrain the critical biogeochemical processes that influence their distributions. The reason for including a broad suite is that although many individual TEIs are influenced by the same processes, the relative importance of those processes differs between the TEIs and the individual boundary conditions are different. Some TEIs are dominated by a simpler balance of processes that can be used to inform investigators about the distribution of tracers affected by a more complex mix of processes. In addition to these TEIs, more traditional properties, including macronutrients (at micromolar and nanomolar levels), CTD hydrography, bio-optical parameters, and carbon system properties can be enlisted to illuminate the processes that regulate the global TEI distributions.

***Boundary Scavenging (Margin sinks):*** Several factors combine to enhance the scavenging and removal of TEIs near ocean margins. Concentrations and fluxes of lithogenic particles tend to be high due to the proximity of sources derived from continental erosion. Resuspension of margin sediments and their transport into the ocean interior, often as detached nepheloid layers (Figure 6), adds to the burden of lithogenic particles in ocean margin waters. Concentrations and fluxes of biogenic particles also tend to be greater near ocean margins than in the interior, reflecting coastal upwelling and the supply of macronutrients that fuels phytoplankton growth. Strong gradients in subsurface nutrient concentrations along the proposed section (Figure 5) reflect, in part, the physical processes that regulate nutrient supply to surface waters. Consequently, one expects biological productivity and related fluxes of biogenic particles to be much greater near the margins than in the central gyre. This is especially true in the vicinity of the eastern boundary current off NW Africa where coastal upwelling supports high productivity and where the combination of upwelling and offshore transport cause high biomass to be observed at a distance of up to 500 km off the coast (Figure 9).

Sampling along the US GEOTRACES section will allow investigators to evaluate, in many cases for the first time, spatial gradients in dissolved TEI concentrations that are associated with enhanced scavenging at ocean margins. However, for many TEIs, margin sources also exist (see above), thereby complicating the interpretation of spatial gradients in TEI concentration. A multi-step strategy is required to assess the relative importance of these competing processes. First, the relative scavenging intensity of U-series nuclides and of other TEIs can be evaluated by assessing their partitioning between



**Figure 9:** Phytoplankton biomass in January 1999 estimated using the SeaWiFS sensor illustrates the strong gradients in biological productivity and biogenic particle flux that are anticipated to occur along the eastern portion of the US GEOTRACES section. The white arrows indicate offshore transport by the Canary Current, which distributes the biogenic particles generated within the productive upwelling system over a larger area than would occur in a simple linear coastal upwelling regime. Reprinted from *Deep Sea Research Part II: Topical Studies in Oceanography*, Vol. 48/Iss. 10, I. Dadou, F. Lamy, C. Rabouille, D. Ruiz-Pino, V. Andersen, M. Bianchi, V. Garçon, An integrated biological pump model from the euphotic zone to the sediment: a 1-D application in the Northeast tropical Atlantic. *JGOFS Research in the North Atlantic Ocean: A Decade of Research, Synthesis and modelling*, Pages 2345-2381, Copyright (2001), with permission from Elsevier. <http://www.sciencedirect.com/science/journal/09670645>.

dissolved and particulate phases along the transect. Second, complementary information about the scavenging intensity of U-series nuclides in ocean margin waters can be derived by modeling the radioactive disequilibrium between particle-reactive U-series nuclides (e.g.,  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ ,  $^{234}\text{Th}$ ,  $^{228}\text{Th}$  and  $^{210}\text{Pb}$ ) and their soluble parents ( $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$ , respectively). Combining these two essential pieces of

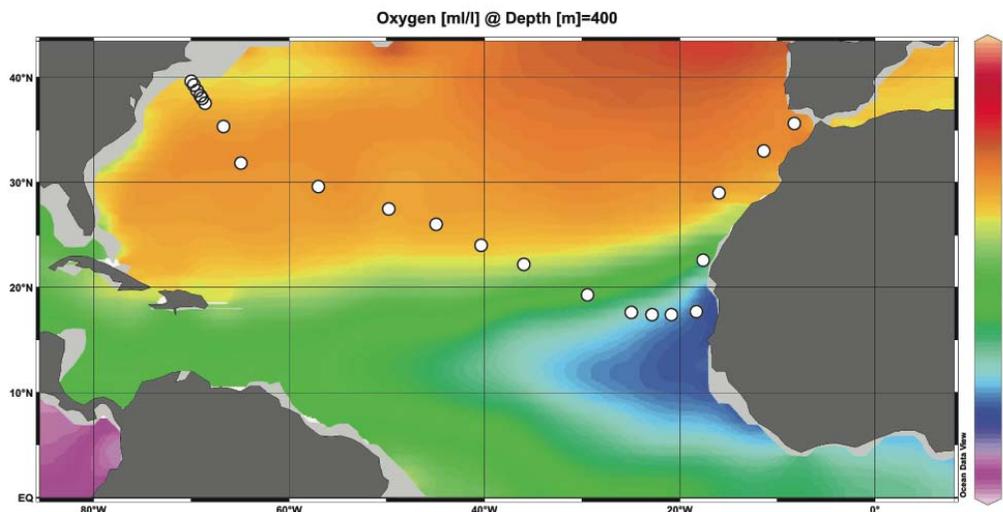
information, one can then estimate the scavenging rate of a broad suite of TEIs in ocean margin waters. Finally, by comparing measured distributions with those expected for a range of model boundary conditions one can constrain the sources of TEIs at ocean margins that cannot be measured directly. This situation illustrates the benefit of applying the GEOTRACES philosophy of examining multiple TEIs simultaneously.

***Regeneration and Scavenging at the Abyssal Sea Floor:*** Diagenetic processes in surface sediments are responsible for regenerating labile particulate phases, while often transforming the more refractory phases that are preserved in the sediment record as well. Fluxes into and out of sediments associated with early diagenesis have been assessed for many years using a variety of techniques; for example, by modeling concentration gradients in pore waters and by more direct measurements using benthic flux chambers.

With the exception of limited GEOSECS-era data suggesting uptake of dissolved  $^{210}\text{Pb}$  by scavenging at the sea bed, little has been done to evaluate uptake and regeneration of the more insoluble TEIs during early diagenesis. In part this reflects the large volumes of seawater required for their analysis, which precludes their measurement in pore waters or in samples from benthic flux chambers. Therefore, at several stations along the Atlantic section high-resolution sampling of near bottom waters (e.g., the bottom 500 m) will be undertaken to estimate fluxes into and out of the sediments. Although lateral transport may influence near-bottom concentration profiles and thereby preclude quantitative estimates of fluxes, near-bottom profiles will enable investigators to establish for the first time whether or not there are significant net sources or sinks of these TEIs associated with early diagenesis.

***Sources, Sinks and Internal Cycling Associated with Redox Processes in an OMZ:***

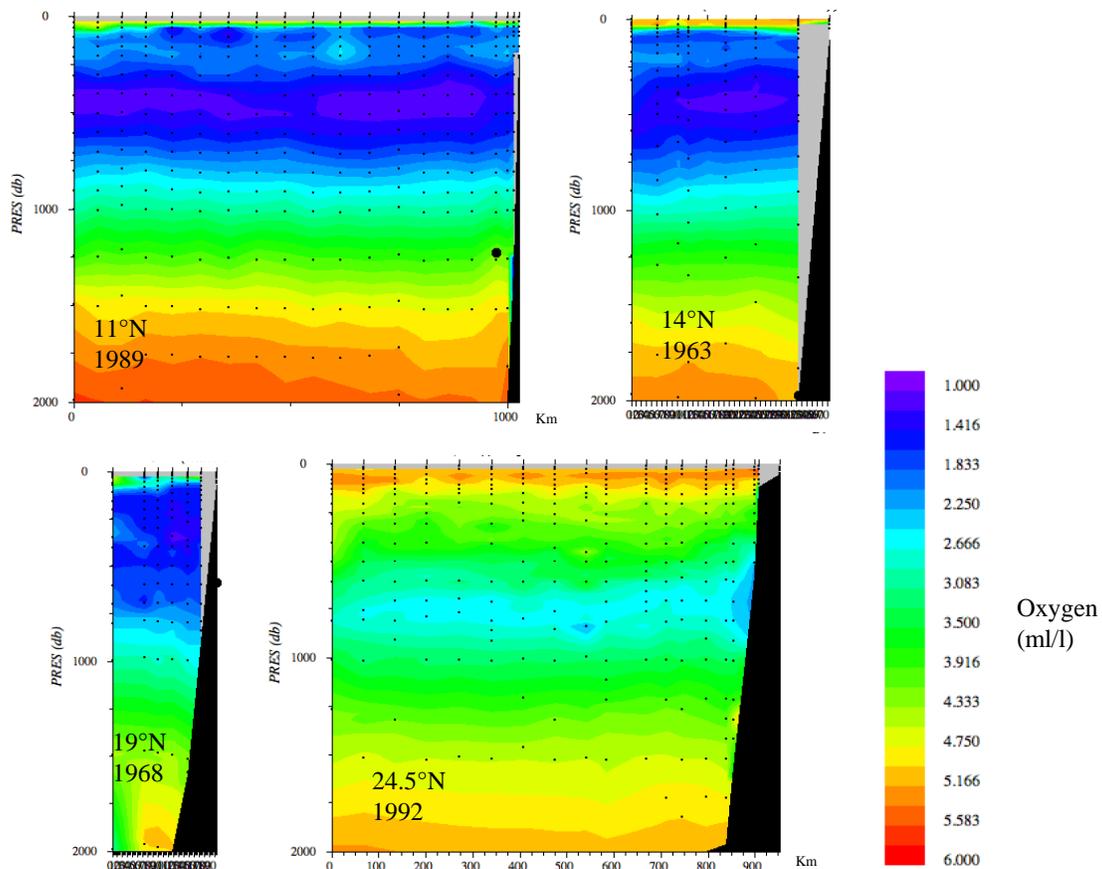
Chemically reducing conditions and associated redox processes in sediments, and in the water column under Oxygen Minimum Zone (OMZ) conditions, serve to mobilize some TEIs (e.g., Fe, Mn and TEIs adsorbed to Fe-Mn oxyhydroxides), sequester others (e.g., U, Mo, Cd, Re, Cr), influence TEI speciation (e.g., oxidation state and complexation by organic ligands) and alter stable isotopic compositions (e.g.,  $\delta^{15}\text{N}$  of nitrate via



**Figure 10:** Station locations along the US GEOTRACES North Atlantic cruise track plotted on a map of dissolved oxygen at 400 m, approximately the depth of lowest oxygen concentration (see also Figure 11).

denitrification). Detailed scientific objectives related to these processes are described in the GEOTRACES Science Plan.

Minimum oxygen concentrations found in the Atlantic water column are not as low as in the eastern tropical Pacific Ocean, or in the Arabian Sea, but they are low nevertheless. For example, oxygen concentrations in the OMZ of the eastern tropical Atlantic are  $\sim 1.0$  ml/l ( $\sim 45$   $\mu\text{mol/liter}$ ; Figure 10). Although this level of dissolved oxygen is not low enough to allow for water column denitrification, sediments along the NW African margin are anoxic, allowing redox processes there to serve as sources and sinks of TEIs. Furthermore, oxygen concentrations within the OMZ may be sufficiently low to retard the oxidation of TEIs mobilized in reducing sediments, thereby allowing them to be transported seaward over substantial distances prior to their oxidation, scavenging and removal from the water column. Therefore, the US GEOTRACES Atlantic section has been designed to intersect the northern portion of OMZ waters (Figure 10) to examine the



**Figure 11:** Zonal sections of oxygen concentration in the northeastern Atlantic crossing the oxygen minimum zone to the African continental shelf. Minimum oxygen concentrations occur between 400 and 500 m. Figure compiled by Bill Smethie. (see also Figure 10).

impact of redox processes on the sources, sinks and internal cycling of TEIs. Oxygen concentrations are influenced both by respiration (i.e., linked to high biological productivity), which consumes  $\text{O}_2$ , and by circulation, which regulates the supply of  $\text{O}_2$ . Within the eastern tropical North Atlantic Ocean, the OMZ is offset to the south of the

position of peak biomass/productivity. As can be seen by comparing Figures 9 and 10, peak biomass (productivity) occurs roughly between 17° and 23°N, whereas minimum oxygen concentrations occur at about 13°N. The US GEOTRACES cruise track was set to provide a compromise that captures both high-productivity and low-oxygen conditions along the NW African margin. Historical zonal sections of dissolved oxygen illustrate how the lowest oxygen concentrations lie between 400 and 500 m (Figure 11). Furthermore, the oxygen section at 19°N indicates that concentrations of oxygen along the proposed cruise track at ~18°N are expected to be nearly as low as under the minimum oxygen concentrations in the region further to the south, whereas locating the cruise track to the north of 20°N to sample a region of greater productivity could place the stations in a region with a much less intense OMZ (note the higher O<sub>2</sub> concentrations in the section at 24.5°N in Figure 11).

***Trace Element Affinity for Scavenging by Different Particulate Phases:*** Both laboratory experiments and field observations indicate substantial differences among trace elements in terms of their affinity for adsorption to major particulate phases. For example, protactinium has a high affinity for sorption to biogenic opal, whereas thorium has a low affinity for opal but a much higher affinity for sorption to lithogenic particles. Until now, field observations have been limited largely to compilations based on data collected for other purposes, and further limited to a small number of TEIs (mainly U-series radionuclides). The proposed GEOTRACES section offers the opportunity to test systematically the affinity of various trace elements for sorption to major particulate phases.

Natural variability in the concentration and composition of particles expected to occur along the cruise track can be exploited to test the sensitivity of different TEIs toward scavenging by major particulate phases. Among the ubiquitous major phases, high concentrations of lithogenic particles are expected in the western portion of the section, reflecting resuspension from the broad continental shelf together with the seaward transport of detached nepheloid layers (Figure 6). Maximum concentrations of biogenic opal are expected to occur within the high-productivity upwelling region at the eastern end of the section (Figure 9). Although total biological productivity is low throughout the central gyre, the abundance of CaCO<sub>3</sub> there relative to other phases is expected to be at its maximum. Concentrations of particulate organic carbon vary with biological productivity, and are expected to be highest near the margins. While each of the major phases (aluminosilicates, opal, calcium carbonate, organic matter) occurs throughout the ocean, the relative abundances of these phases vary independently of one another, allowing the affinity of each TEI for these phases to be estimated by multivariate statistical analysis of paired dissolved and particulate TEI concentrations measured across the entire section.

In addition to the ubiquitous major phases described above, high concentrations of particulate Fe and Mn oxyhydroxides will be sampled within the hydrothermal plume at the TAG site, and may also be encountered within the fringe of the OMZ where oxidation of dissolved Fe and Mn may be expected. Oxyhydroxide phases have a high affinity for

adsorption of many TEIs, and the proposed cruise track will allow the affinity for oxyhydroxides to be compared with other major phases.

Two independent strategies can be employed to constrain the relative affinity of individual TEIs for different particulate phases. As noted above, statistical techniques can be applied to paired measurements of dissolved and particulate TEI concentrations across the full range of variability of particle composition. While these methods are well established, this approach is limited by the need to discriminate between adsorbed and “detrital” (i.e., contained within aluminosilicate minerals) TEIs. Normative procedures have been applied in past studies to separate total particulate TEI concentrations into lithogenic and bioauthigenic components, however these approaches require that some element (e.g., Ti, Al) can be considered to be entirely lithogenic, which may not be true. The method also suffers from uncertainties in the appropriate lithogenic ratio (e.g., TEI/Al) to be used in correcting for the lithogenic TEI concentration. An alternative strategy is to employ leaching procedures that selectively remove one or more particulate phases. Chemical procedures to selectively dissolve a particulate phase are well established. However, uncertainty is introduced by the inability to constrain the readsorption to refractory particulate phases of TEIs dissolved in the leaching procedure. Given the important role of particles in the transport, removal and internal cycling of TEIs, it is recommended that both strategies be employed, and that careful comparison of results focus on artifacts that may be introduced by either method.

***Internal cycling:*** Biological uptake and chemical sorption incorporate dissolved TEIs into particulate phases. Regeneration of particulate phases through oxidation (e.g., POC) and dissolution (opal and calcium carbonate, but also Fe-Mn oxyhydroxides under chemically reducing conditions) releases TEIs back into solution. Uptake and regeneration by particulate phases regulates the internal cycling of TEIs within the ocean. Quantifying fluxes of TEIs and identifying the processes associated with this internal cycling is a major objective of the GEOTRACES program (see Science Plan).

In past studies, fluxes of TEIs associated with internal cycling have been estimated using sediment traps, benthic flux chambers, and other methods that involve direct, or near-direct measurement of fluxes. In GEOTRACES, a new strategy will be employed whereby inverse models will be applied to measured TEI distributions to estimate the uptake and regeneration associated with internal cycling. This approach was applied successfully to the distributions of dissolved inorganic carbon and nutrients measured by the WOCE and JGOFS programs, providing estimates both for the export flux of POC from surface waters and for the depth scale over which POC regeneration in the thermocline occurs. In order for this approach to be successful, it is critical that TEI measurements be of high quality on all GEOTRACES cruises. That is, investigators must be certain that differences in TEI concentrations reported among different sections reflect true spatial variability and not analytical bias. High quality data requires application of rigorous intercalibration protocols. A detailed description of the protocols will be provided in the final report of the GEOTRACES intercalibration initiative. Briefly, these will include:

- 1) Participating labs will have demonstrated consistency with other labs through analysis of samples distributed through the GEOTRACES intercalibration initiative;
- 2) Where new labs are involved that have not participated in the intercalibration, investigators will collect replicate samples to be analyzed by independent labs to demonstrate internal consistency of results,
- 3) Wherever a section crosses the track of a previous section, a station will be taken at the crossover point to allow results to be compared in deep water where concentrations are not expected to change significantly between cruises, and
- 4) Aliquots of homogenized seawater collected during GEOTRACES intercalibration cruises will be analyzed as internal working standards.

Complementing the inverse method approach, paired concentrations of dissolved and particulate TEI concentrations measured to establish TEI affinity for scavenging to different particulate phases (see preceding section) will provide insights into internal cycling as well. For many TEIs, especially those taken up actively by biota, the maximum enrichment in particles is expected to occur in surface waters, and the enrichment will decrease in deeper waters following regeneration of labile biogenic phases. In some cases, normalizing labile TEIs to refractory elements may be used to estimate the regeneration of labile TEIs. For example, in the central gyre, where lateral supply of lithogenic phases may be negligible, ratios of labile to refractory TEIs are expected to decrease with increasing depth in the water column, reflecting regeneration of the labile TEIs. Lateral injection of particles from margins (Figure 6) and resuspension of sediments near the bottom precludes the use of this strategy to estimate regeneration of labile TEIs in those regions. However, post-cruise analysis of spatial patterns of lithogenic phases (assessed by measuring concentrations of refractory TEIs such as Al, Ti or  $^{232}\text{Th}$ ) may reveal regions where lateral transport of lithogenic particles can be neglected, and where simple one-dimensional models can be applied to vertical profiles of particulate TEI concentrations. If these conditions are found to exist in the central gyre, then simple measurements of the ratios of labile to refractory particulate TEI concentrations will help constrain the depth scale for regeneration of labile particulate TEIs.

The rates of dissolved TEI uptake and particulate flux can also be obtained using naturally occurring U-Th series radionuclides. Given the range of half-lives, scavenging can be examined on different time-scales, which for many of the TEI's will be dominated by processes associated seasonal production and remineralization of labile particles. Rates of processes occurring over time scales of days to weeks can be constrained using  $^{234}\text{Th}:$  $^{238}\text{U}$  disequilibria, while processes occurring over longer time scales (mo-yrs) can be constrained using  $^{228}\text{Th}:$  $^{228}\text{Ra}$  disequilibria. For example, subsurface maxima in dissolved Fe that have been observed in earlier Atlantic sections (Measures et al., 2008) are likely impacted by near surface scavenging and mid water regeneration from sinking particles. Measurements of U:Th series radionuclides will provide rates of dissolved:particulate uptake, and by comparison to the flux of  $^{234}\text{Th}$  and  $^{228}\text{Th}$  at depth, relative to the particulate TEI ratio on sinking matter, provide a measure of the local sinking flux of many TEIs.

Similarly, in the deep water column, downward fluxes of particulate TEIs can be estimated by measuring the ratio of the concentration of any TEI to that of  $^{230}\text{Th}$  on particulate material. At any point in the ocean the downward flux of particulate  $^{230}\text{Th}$  is approximately equal to its integrated rate of production in the overlying water column by uranium decay. Knowing the downward flux of  $^{230}\text{Th}$  allows the corresponding flux for any TEI in the same sample of particulate material to be estimated by measuring the ratio of its concentration to that of  $^{230}\text{Th}$ . While this approach is elegant in its simplicity, it is limited by the implicit assumption that particulate material sampled by any method is representative of the particulate material carrying the downward flux of labile TEIs. As noted above, individual TEIs have varying affinities for sorption to different particulate phases, and there could be some fractionation among different particulate phases related to particle size or sinking rate. Incomplete sampling of a heterogeneous standing stock of particles could introduce errors in using this approach.

Each method to be employed in assessing internal cycling has limitations. Through collaboration among multiple investigators, GEOTRACES will simultaneously apply multiple strategies to multiple TEIs. Adding complementary modeling strategies to the suite of experimental approaches offers the greatest possible chance to quantify internal cycling of a broad range of TEIs.

***TEI/Nutrient Relationships:*** Observation of the relationships between trace metals and the major nutrients will be an important tool for studying their role in biogeochemical cycling. Because of its role in the planetary scale Meridional Overturning Circulation, the North Atlantic represents a nexus point for water masses from a wide variety of geographical sources. Stations in this section are well positioned to sample metal-nutrient relationships in mode waters, intermediate waters, and in NADW while also characterizing any departures from metal-nutrient relationships in North Atlantic water masses related to Si-rich water from the Southern Ocean in the deepest part of the basin (Figure 4 lower) or to salty Mediterranean outflow water injected into the eastern side of the basin (Figure 4 upper). The broad range in water mass origins produces significant variations among the nutrient properties whose inter-relationships with trace metals offers a powerful diagnostic tool for exploring the role of these elements in biogeochemical processes.

As noted in the Science Plan (*e.g.*, GSP06, p3), the scientific objectives of GEOTRACES extend beyond trace metals to include the processes that affect the stable isotopic composition of minor dissolved constituents in seawater. For example, the proposed cruise track is well positioned to examine the impact of nitrogen fixation, which is thought to be prevalent in the North Atlantic subtropical gyre, on the  $\delta^{15}\text{N}$  of nitrate in the region. Furthermore, the range of water masses, nutrient concentrations and dominant phytoplankton taxa to be sampled along the section will enable investigators to examine the simple relationships between  $\delta^{13}\text{C}$  of dissolved inorganic carbon and nutrient concentrations that are thought to result from the biogeochemical cycling of organic matter, and to identify regions and associated processes that may cause observed  $\delta^{13}\text{C}$  distributions to deviate from simple expected relationships. This is particularly important in the North Atlantic Ocean where paleoceanographers frequently use the stable carbon

isotopic composition of benthic foraminifera to reconstruct past changes in the structure of deep water masses.

### **Station Water Budgets and Sampling Plan**

By international agreement, participating scientists are expected to measure the full suite of “key” trace elements and isotopes defined in Table 2 of the Science Plan (GSP06) on every GEOTRACES section. Formulation of the sampling plan and budgets described below should be regarded as a “model” plan aimed at demonstrating the feasibility of acquiring the minimum set of core measurements. This is not meant to be an “exclusive laundry list” of a limited number of properties. We plan to accommodate sampling for other related properties that can be argued to contribute toward the GEOTRACES objectives, and this is reflected in the water budgets drawn up for the station plan below. The water budgets are based on experience with the intercalibration exercise and reasonable expectations balanced by pragmatic constraints of ship time and space. We would, however, urge prospective collaborative programs to communicate with the cruise organizers to ensure that their needs are met with this plan. In addition, it is expected that a number of ancillary parameters will be measured (see Science Plan).

Taking into account the volumes of water required to support the measurement of key TEIs, and the water needs of ancillary measurements likely to be proposed for the US GEOTRACES section, participants at a planning workshop (22-24 September, 2008, Woods Hole Oceanographic Institution) recommended that three types of stations will be occupied during the cruise:

- 1) Full water column stations that will include sampling for all key TEIs as well as for most ancillary parameters. These are the stations shown in Figure 1.
- 2) Shallow stations that will involve one or two casts to a nominal depth of 1000 m, to sample for selected parameters in locations where greater spatial resolution is desired. Shallow stations will be interspersed between full depth stations. Locations of shallow stations, and parameters to be measured, will be determined once funding decisions have been made and more is known about the studies that have been funded. When submitting proposals, PIs may indicate their desire to sample at shallow stations, providing appropriate justification of the need for greater spatial resolution, with the understanding that final decisions concerning the shallow stations will be made so as to best accommodate the needs of all funded PIs.
- 3) “Super” stations that represent full water column stations with additional sampling to provide water for TEIs that do not require sampling at every station. These may include TEIs that are at an exploratory stage of development, or those for which new insights concerning their sources, sinks and internal cycling can be derived from sampling at a limited number of stations. Potential TEIs in this category include hafnium isotopes, artificial nuclides from nuclear weapons testing and from nuclear fuel reprocessing, and oxygen isotopes in phosphate.

Additional casts for high-resolution near-bottom concentration profiles of selected TEIs may be taken at super stations, although these casts may be relocated to other stations if justified by the relevant scientific objectives. In any case, super station sampling and near-bottom casts will take place at the location of normal full water column stations. New stations will not be inserted into the cruise plan to accommodate these sampling needs.

In addition to sampling vertical profiles at the stations defined above, underway samples of surface water for selected TEIs, including micronutrients and tracers of aerosol input, will occur at a nominal spacing of every four hours when the ship is underway between stations.

Finally, in a manner analogous to underway sampling of surface water, aerosols will be collected along the full length of the cruise track.

Five general types of sampling devices will be used to fulfill the sampling plan described above: 1) A trace metal-clean carousel with 24 x 12-liter GO-Flo bottles and CTD with fluorometer, transmissometer and oxygen probe that was designed and constructed specifically to support the U.S. GEOTRACES program, 2) a standard ship's rosette with either 24 X10-liter or 12 X 30-liter Niskin bottles, 3) *in situ* pumps, 4) a towed fish designed for trace metal-clean sampling of surface waters, and 5) aerosol samplers.

The U.S. GEOTRACES carousel/CTD is maintained as part of a facility at Old Dominion University. In addition to the carousel, the facility includes a Dynacon winch with 7800m of conducting Kevlar cable and a clean lab set up in a van designed for sampling from GO-Flo bottles, as well as a 10m aluminum boom and stand for the towed trace metal-clean sampling fish. The facility is available for use by leaders of this or any U.S. GEOTRACES cruise on a cost-recovery basis. In addition, when not being used for a GEOTRACES cruise, the facility is available for use by the broader chemical oceanography community. It is anticipated that the standard Niskin rosette will be provided by the operators of the ship assigned to the cruise.

High volume aerosol samplers and automated rainfall samplers have been acquired with NSF funding for use on all US-led GEOTRACES cruises. The aerosol sampling system consists of three Tisch 5170VBL high-volume aerosol samplers configured for (1) total aerosol sampling using Whatman-41 (8"x10") cellulose filters for inorganic TEIs, (2) total aerosol sampling using Whatman quartz microfiber filters (8"x10") for N species and organic carbon species, and (3) size-fractionated aerosol sampling for inorganic TEIs using a 5-stage slotted impactor loaded with special Whatman-41 cellulose slotted filters. A wind sensor and datalogger/relay driver system is included for wind-sector and wind speed control of the sampling. The automated rainfall samplers are equipped with 182 cm<sup>2</sup> plastic funnels connected to receiving bottles using PTFE Teflon connectors. Thus, a 1 cm rain event will yield about 180mL of sample. One sampler is designed to collect unfiltered rainfall. The 2<sup>nd</sup> sampler is designed so that a 47mm filter holder can be inserted between the rain funnel and the receiving bottle so that rainfall can be filtered immediately as it is collected. It is anticipated that shipping and operating costs for the

aerosol and rainfall samplers would be provided by individual PIs in their proposals. In addition, PIs who propose to collect aerosol and rainfall samples will need to consider logistics and costs for distributing subsamples to other members of the GEOTRACES science team, including those who are not actually participating on the cruise.

In situ pumps will not be included in the infrastructure (management and logistics proposal) nor supported directly by the GEOTRACES facility. Reasonable accommodation (in ship space and station time) will be provided for these activities, and it is anticipated that these sampling systems will be provided by individual PIs with all operating costs covered by their proposal(s). Furthermore, it is anticipated that PIs funded to operate these sampling systems will provide sample aliquots in reasonable amounts to other investigators funded to participate in the cruise. The U.S. GEOTRACES project office will serve as an information center for shared samples. PIs who intend to submit proposals to collect samples using these systems are invited to make their intentions known by e-mailing the project office at <geotraces@ldeo.columbia.edu>. PIs who wish to obtain samples from these devices are invited to make their needs known in this way as well.

Once final funding decisions are made, all funded PIs will work together to finalize the cruise plan and allocation of samples from shared systems. Water depths to be sampled, as well as the distribution of sample aliquots, will be decided at that time. Individual proposals should acknowledge that final sample depths will reflect a compromise that best serves the needs of the entire program, and allow for some uncertainty in specific sample depths when the proposals are composed. PIs should plan to attend a pre-cruise planning meeting where these and other issues will be resolved. Travel expenses for this workshop will be covered by the management proposal or by the U.S. GEOTRACES project office.

A preliminary water budget for the rosette samplers and in situ pumps has been developed with the understanding that these water budgets are likely to be adjusted once the nature of the proposals to be funded is known. Certain parameters will be measured only in surface waters, while others will require telescoping water volumes that either increase or decrease with water depth. Based on reasonable expectations, it is anticipated that two GO-Flo bottles will be tripped at each depth to meet the sample requirements at standard full-depth stations (Table 1). The depth range to be covered by the shallow and deep casts will be decided by funded PIs.

Table 1. Anticipated water volumes from the U.S. GEOTRACES Clean Rosette required to meet the needs for key TEIs and for ancillary parameters. Separate estimates are given for standard full depth stations and for super stations (see text).

Parameter	Full-depth Vol (liters)	Super Vol (liters)		Full-depth Vol (liters)	Super Vol (liters)
<b>Shallow GO-Flo</b>			<b>Deep GO-Flo</b>		
Fe, Al, Zn, Mn, Cd, Cu	2	2	Fe, Al, Zn, Mn, Cd, Cu	2	2
Pb isotopes	2	2	Pb isotopes	2	2
Nutrients/sal/oxygen	0.5	0.5	Nutrients/sal/oxygen	0.5	0.5
Low level nuts (surface)	0.5	0.5			
Other properties (e.g. total Co, As, V, Ag, ancillary TEIs, Hg, Os, speciation of Cu, Zn, Fe, Co; trace metal isotopes)	19	43	Other properties (e.g. total Co, As, V, Ag, ancillary TEIs, Hg, Os, speciation of Cu, Zn, Fe, Co; trace metal isotopes)	19.5	43.5
(particulate TMs share volume)			(particulate TMs share volume)		
<b>TOTAL</b>	<b>24</b>	<b>48</b>	<b>TOTAL</b>	<b>24</b>	<b>48</b>

Similarly, if the rosette to sample for parameters not prone to contamination involves 24 X 10-liter bottles, then it is anticipated that two Niskin bottles must be tripped at each depth to meet the sample requirements for standard full-depth stations (Table 2). If a rosette with 12 X 30-liter bottles is used, then a single bottle will be tripped at each depth. The depth range to be covered by the shallow and deep casts will be decided by funded PIs.

Table 2. Anticipated water volumes from the ship's Niskin Rosette required to meet the needs for key TEIs and for ancillary parameters assuming a rosette with 24 10-liter bottles. Water budget created assuming a total of four shallow casts and three deep casts per super station.

	Full-depth Vol (liters)	Super Vol (liters)		Full-depth Vol (liters)	Super Vol (liters)
<b>Shallow Ship Rosette</b>			<b>Deep Ship Rosette</b>		
15NO3 18O-NO3	0.5	0.5	15NO3 18O-NO3	0.5	0.5
Th, Pa,	5	5	Th, Pa,	5	5
Nd, REE	5	5	Nd, REE	5	5
Nutrients	0.5	0.5	Nutrients	0.5	0.5
O2	0.5	0.5	O2	0.5	0.5
Salt	0.25	0.25	Salt	0.25	0.25
14C/13C	0.5	0.5	14C/13C	0.5	0.5
Other properties (e.g. d30Si, 18O-PO4, 234Th, 226Ra, artificial radionuclides, CFCs/SF6, 3H,3He, 210Pb, 210Po)	8	67.75	Other properties (e.g. d30Si, 18O-PO4, 234Th, 226Ra, artificial radionuclides, CFCs/SF6, 3H,3He, 210Pb, 210Po)	8	47.75
<b>TOTAL</b>	<b>20.25</b>	<b>80</b>	<b>TOTAL</b>	<b>20.25</b>	<b>60</b>

A shallow cast using the ship's rosette will be scheduled for each full depth station to sample for pigments, DOC, CDOM and related parameters within the euphotic zone. It is anticipated that these casts will each require only a few minutes of ship time, so they are not included in the budget for station time and cruise duration described below.

A number of TEIs have been identified for which it will be desirable to measure their concentrations in particulate material as well as in solution. A combination of sampling strategies involving bottles and *in situ* pumps will be used to fill these sample requirements. For contamination-prone TEIs that require only small volumes of water, particles will be filtered from GO-Flo bottles. Several liters of water will be allocated

from each depth sampled by GO-Flo bottles (Table 1). Tests conducted during the first U.S. GEOTRACES intercalibration cruise demonstrated that this strategy is feasible (R. Sherrell, personal communication).

*In situ* pumps will be used to collect particles for TEIs that require sampling from volumes larger than can be accommodated by GO-Flo bottles. Workshop participants developed a tentative water budget to assess the feasibility of filling the anticipated sample requirements using commercially available battery-powered pumping systems (e.g., McLane), which typically filter particles from ~600 liters for each sample. That assessment (Table 3) indicated that battery powered pumps should be capable of meeting the sampling needs for particulate TEIs in deep water, where concentrations are greatest for TEIs requiring the largest sample volumes (e.g.,  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ , Nd isotopes), and where pumping is least likely to be slowed by clogging of filters. In surface waters, where concentrations are lowest for those TEIs requiring the largest volumes, and where filter clogging may limit sample size to substantially less than 600 liters, other strategies may be needed to cover all sample requirements for particles. Options include redesigning battery powered pumps with multiple filter holders to permit filtration of larger volumes of seawater, or using pumping systems that have the capacity to filter volumes of water significantly greater than that provided by battery powered pumping systems that are currently available. A final plan for *in situ* filtration that meets the needs of funded PIs will be negotiated between the management team and NSF, with advice from the U.S. GEOTRACES SSC, as part of an iterative process to be used in reaching final funding decisions.

Additional samples of particulate material will be available for TEI analysis by filtration from surface water pumped from a towed fish.

It is anticipated that the GEOTRACES community will settle on a limited number of filter types (e.g., quartz fiber and Supor membranes) and pore diameters following review of results from the first intercalibration cruise. However, at the time of this writing a final decision on filter type has not been made. In developing their proposals, PIs should check the GEOTRACES web site for updated information about filter types to be used. In addition, in preparing their proposals, PIs should consider the volume of water available for filtration using each method (see above) as well as the need to share samples with other investigators.

Table 3. Anticipated water volumes from in situ pumps required to meet the needs for key TEIs and for ancillary parameters.

<b>Shallow pump</b>		Volume (liters)	<b>Deep Pump</b>		Volume (liters)
POC, PON		10	POC, PON		10
BSi		5	BSi		5
Ca		1	Ca		1
Al, Ti		10	Al, Ti		10
Ra isotopes	cartridge	*	Ra isotopes	cartridge	
228Th	0 non destructive		228Th	0 non destructive	
234Th		50	234Th		50
Transition metals		20	Transition metals		20
230Th, 231Pa		100	230Th, 231Pa		100
Nd, REE		300	Nd, REE		300
Ba		10	Ba		10
210Pb, 210Po		100	210Pb, 210Po		100
<b>TOTAL</b>		<b>606</b>	<b>TOTAL</b>		<b>606</b>

\*Deep casts are similar to shallow casts except that Ra and Th-228 would not be measured in the mid-gyre sites. Measurement of Ra isotopes and Th-228 are desirable in the margin regions at each end of the section

## Station Time and Cruise Duration

Filling the water requirements for each standard full depth water column station identified above in Tables 1 - 3 will require two casts of the clean rosette (one shallow and one deep), two casts of the Niskin rosette (one shallow and one deep) and two casts of in situ pumps at each station. Total station time required to complete these activities is estimated to be 28 hours (Table 4).

Table 4. Station time for a standard full-depth station.

<b>Activity</b>	Duration (hours)	Number per Station	Time per activity (hours)
Shallow GO-Flo rosette cast	1	1	1
Deep GO-Flo rosette cast	5	1	5
Shallow Niskin rosette cast	1	1	1
Deep Niskin rosette cast	5	1	5
Shallow in situ pump	6	1	6
Deep in situ pump	10	1	10
<b>TOTAL (hours)</b>			<b>28</b>

A cruise of 50 days duration is proposed, where 20 days would be required for steaming and 30 days (720 hours) is allocated to station time. A total of 22 standard full depth stations are planned (Figure 1) which, at 28 hours per station, totals 616 hours of station time. The remaining 104 hours of station time are to be divided between shallow stations (nominally one hour each) and super stations. For example, the time available could accommodate one cast to 1000 m at each of 14 shallow stations as well as three deep casts (5 hours each) at each of 6 super stations. Actual station plans and allocation of station time will be determined once full information about the individual efforts to be funded is known.

## Proposal Plan

The process of securing funding for cruise management and general logistics as well as ship time for this effort will proceed as follows: Upon the recommendation of the US GEOTRACES SSC, a management proposal securing ship time and ancillary services will be submitted by Feb. 15, 2009. The proposal will outline the cruise framework and general goals of this GEOTRACES cruise. The PIs will describe their plan for (1) handling project logistics, (2) securing the necessary ship-time and cruise support services, and (3) arranging for hydrography, basic nutrients, shipboard Zn analyses, and sample return to the US since the cruise terminates in a foreign port. This proposal will be aimed at providing the basic project management and will not include individual PI science activities. All of the GEOTRACES science activities described in this Implementation Plan will be solicited by independent proposals to the Chemical Oceanography Program at NSF. This proposal process is open to the entire Chemical Oceanography community for this proposal deadline (and subsequent deadlines as necessary). The GEOTRACES Science Plan, the Basin Workshop reports, and this Section Implementation Plan are all available on the GEOTRACES web site as a resource for those wishing to submit proposals. All of these proposals (including the management proposal) will be reviewed by the normal NSF process, and the fate of the proposals will be decided through the normal process of mail reviews, Chemical Oceanography panel review, and final program manager assessment.

Logistical support sought within the management proposal will include shipboard staffing for the maintenance and deployment of the standard and the trace-metal clean rosette systems, acquisition, processing, and calibration of the CTD, nephelometer, and oxygen sensor data, as well as sampling, analysis, and quality control of “routine hydrographic parameters”, including salinity, oxygen titrations, and macronutrients (nitrate, nitrite, silicate, and phosphate) on all bottle samples. Shipboard Zn measurements will be included in this proposal for the purpose of diagnosing and rectifying trace metal contamination issues during the cruise. Shipboard support will include coordination of other sampling activities, and assembly and quality control of the hydrographic, appropriate navigational, and associated metadata as stipulated by GEOTRACES practices. Individual investigators will be expected to provide support for shipboard sampling and processing of their individual measurement programs within GEOTRACES. Because ship’s berthing will be a limiting factor, these individuals are encouraged to coordinate their plans, proposals, and logistics with the P.I.’s of the Management Proposal and other investigators planning to work on the cruise.

Proposals that require specialized nutrient measurements, or measurements in addition to those provided for each hydrocast should budget for them in their proposal. Although ports will not be known until a short time before the cruise, budgets should include sufficient funds to cover shipping and travel assuming that the cruise will begin in Woods Hole and end in Cadiz, Spain. The management proposal will arrange for the shipment of samples from Cadiz back to the east coast of the US (likely Norfolk, VA) via containers. The individual PI proposals should include funds for transport of empty bottles to the ship at WHOI and transport of full sample bottles from the US east coast to the participating institution. The individual proposals should also include shipping of the PIs personal equipment to the ship and returning from Cadiz. The individual PI proposals

should include funds for sample analysis and specify how many samples of what type are included within that budget.

Voluntary coordination between PIs submitting proposals is highly recommended. The U.S. GEOTRACES Project Office will maintain a web site where those who are interested in submitting proposals can identify their interests. Interested PIs are encouraged to submit a brief description (< 1 page) of their interests to the project office at <geotraces@ldeo.columbia.edu> well in advance of the proposal deadline (tentatively, 15 February, 2009). Advance posting will enable groups with common interests to develop collaborative proposals if they choose to do so.

Readers of this document who have not been receiving announcements via the GEOTRACES e-mail distribution lists and who wish to have their names added to the lists can do so by sending a request to <geotraces@ldeo.columbia.edu> along with their name, institutional affiliation, and e-mail address.

Each proposal to participate in the North Atlantic section should have a title that begins with "US GEOTRACES North Atlantic Section: ..." and should contain a statement acknowledging that the PI(s) will comply with NSF data submission policy (see below).

### **Data Management Plan**

Investigators who participate in US GEOTRACES cruises will be expected to comply with the International GEOTRACES data policy. This policy requires the collection and submission of all data resulting from the cruise including underway systems, instrument deployments, and the analytical determinations on water samples and particulate material collected during the cruise. Also required will be reporting of all appropriate meta-data (data describing methods and protocols). Data must be submitted in a timely manner to the Biological and Chemical Oceanography Data Management Office (BCO-DMO) (<http://www.bco-dmo.org>) at Woods Hole. This office will in turn submit it to the International GEOTRACES data office which is currently hosted at the British Oceanographic Data Centre in Liverpool, UK. The International GEOTRACES data office will be ultimately responsible for the permanent archiving of the data sets and their international distribution.

To facilitate the process and to ensure complete reporting of required meta-data, BCO-DMO, in conjunction with International GEOTRACES Data Management committee will produce a series of templates that can be used by cruise planners and data originators to submit data. An outline of the major policy requirements is given below, to a large degree these policies have been based on those developed for previous large scale hydrographic programs, e.g. WOCE, CLIVAR. Full details of the GEOTRACES data policies can be found <http://www.geotraces.org/DataManagement.html>.

Metadata should be delivered as soon as created, from the planning stage onwards, and should be made publicly available immediately. Data (not finalized) should be submitted

within 1 month (of collection, or end of cruise), with possible approved extension as tabulated. Cruise or project reports should be submitted within 6 months of the end of the cruise. Final data, following NSF policy, should be submitted within 2 years of cruise completion, with exceptions possible from the GEOTRACES SSC.

Since the goal of GEOTRACES is to build a comprehensive understanding of geochemical processes, data sharing amongst participants is vital but is also designed to protect the intellectual property rights of the individual data generators. Data should be shared with other participants in the cruise or process study from an early stage. In the case of data generated on board ship it is anticipated that this will be made available rapidly via an interactive shipboard database system to all cruise participants. After the cruise these preliminary shipboard data sets will be made available via a password protected web-based server to all cruise participants and other individuals at the discretion of the data generator and the Chief Scientist. Data produced from shore based determinations are expected to be reported promptly to BCO-DMO who will make this available to cruise participants with the knowledge and permission of the relevant data generating PI. Investigators will be able to revise data sets and submit them to BCO-DMO for a reasonable amount of time following the cruise, as defined in the GEOTRACES data policy.

Public release of data will normally be two years from the end of the cruise or field activity, in line with NSF policy. These deadlines may be extended in particular cases by the International GEOTRACES steering committee when justified by analytical procedures that have inherent built-in delays.

The Chief Scientist, or their designee, will be expected to provide the BCO-DMO datacenter with a complete underway and shipboard data set from the cruise including all associated metadata. Specifically, this will include navigation and meteorological data, surface water data, raw and processed ctd data, all configuration files for sensors, all available ADCP data, and parameters that are determined on board ship from discrete samples. The Chief Scientist (or designee) is also expected to provide BCO-DMO with a cruise report in the time frame to be established in the final GEOTRACES data policy. BCO-DMO will provide a template to illustrate the type of information that is desired in a cruise report.

Meta data reporting requirements are currently being developed and will vary significantly amongst the various shipboard activities. In many cases previous programs have already developed these requirements for standardized procedures, e.g. ctd casts, underway data systems etc., and where appropriate these will be adopted by GEOTRACES. In the case of the meta data requirements for individual trace elements and isotopes (TEI) this is a new field and it is expected that individual reporting requirements will vary significantly depending on the particular protocols employed to make standardized measurements. It is expected that the development of meta data requirements for TEI will be accomplished on a case by case basis through collaboration between the expert data generators, BCO-DMO, the GEOTRACES standards and intercalibration committee, and the international GEOTRACES data management office.

The sampling log sheet that records the disposition of each subsample obtained from any particular sampling operation is fundamental to tracking samples and to ensuring that all parameters for which samples are obtained are subsequently reported to the data office. Standardized log sheets that will capture all necessary information pertaining to discrete sample acquisition and sub-sampling for each over the side sampling system will be designed in collaboration with participants and provided to the Chief Scientist. In addition electronic pdf versions of the completed forms will be archived and transmitted to BCO-DMO.

**Acknowledgements:** This implementation plan is based on the breakout group reports produced at the Atlantic Implementation Workshop held in Woods Hole September 22-24 (see Appendix 1 for a list of attendees). The workshop was funded by the National Science Foundation through the GEOTRACES U.S. Project Office. We are grateful for Moanna St. Clair and Mary Zawoysky for their considerable help with arranging the logistics of the meeting.

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The SCOR GEOTRACES Science Plan (GSP06) is available on the web at  
<http://www.geotraces.org/sciencePlan/documents/GEOTRACESFinalWebVersion.pdf>

### Appendix 1: List of Meeting Attendees

Anderson	Bob	Lamont-Doherty Earth Observatory
Boyle	Ed	MIT
Buesseler	Ken	WHOI
Casciotti	Karen	WHOI
Chandler	Cyndy	WHOI
Charette	Matt	WHOI
Cutter	Greg	Old Dominion University
Hearn	Malcolm	BODC Representative
Hooker	Stan	NASA
Jenkins	Bill	WHOI
Lam	Phoebe	WHOI
Maiti	Kanchan	WHOI
Mawji	Ed	GEOTRACES DMO/BODC
Measures	Chris	University of Hawaii
Moffett	Jim	University of Southern California
Pahnke	Katharina	Lamont-Doherty Earth Observatory
Rice	Don	NSF
Robinson	Laura	WHOI
Saito	Mak	WHOI
Sherrell	Rob	Rutgers University
Smethie	Bill	Lamont-Doherty Earth Observatory
Wu	Jingfeng	University of Alaska, Fairbanks

## Appendix 2: Meeting Agenda

### MONDAY:

8:00-9:00 Breakfast  
 9:00-9:15 Welcome & Logistics (EAB & WJJ)  
 9:15-10:00 Overview of circulation and climatology (Bill Jenkins)  
 10:00-10:30 Coffee Break  
 10:30-11:15 Trace Metal Overview (Chris Measures)  
 11:15-12:00 Particulates and U-Th series Overview (Bob Anderson)  
 12:00-13:00 Lunch  
 13:00-13:15 NSF Perspectives (Don Rice)  
 13:15-13:30 Hydrothermal Inputs (Chris German)  
 13:30-15:00 Advocacy talks (5 min each): We've reserved a series of 5 minute slots for individuals to make brief presentations on specific measurements or scientific themes they'd like to advocate.  
 15:00-15:30 Coffee Break  
 15:30-16:00 Advocacy talks continued  
 16:00-17:30 Plenary Discussion: Major Cruise Objectives & Relation to Program

### TUESDAY:

8:00-8.45 Breakfast  
 8:45-9:05 Data Management Issues (Cyndy Chandler)  
 9:05-9:30 Intercalibration Report (Greg Cutter)  
 9:30-10:00 Measurement Strategies: Defining and prioritizing key vs auxiliary measurements  
 10:00-10:30 Coffee Break  
 10:30-12:00 Measurement strategies continued  
 12:00-13:00 Lunch  
 13:00-15:00 Cruise Logistics and Station Plans  
 15:00-15:30 Coffee Break  
 15:30-17:30 Cruise logistics continued

### WEDNESDAY:

8:00-8.45 Breakfast  
 8:45-9:15 Plenary Discussion for Writing Breakout Groups  
 9:15-10:00 Writing Breakout Groups  
 10:00-10:30 Coffee Break  
 10:30-11:00 Writing Breakout Groups continued  
 11:00-11:20 Plenary Reports of Breakout Groups  
 11:20-11:40 Liz Caporelli (WHOI-UNOLS KNORR Scheduling)  
 11:40-12:00 Plenary continued  
 12:00-13:00 Lunch  
 13:00-15:00 Writing Breakout Groups continued  
 15:00-15:30 Coffee Break  
 15:30-17:30 Plenary Reports, and final discussion

### **Appendix 3: Breakout Groups**

#### **Section I. Program rational and description**

*Discussion Leader:* Ed Boyle  
*Rapporteur:* Mak Saito  
*Participants:* Bill Jenkins  
Jim Moffett  
Laura Robinson  
Abigail Noble

#### **Section II. Data Management Plan.**

*Discussion Leader:* Chris Measures  
*Rapporteur:* Chris Measures  
*Participants:* Cyndy Chandler  
Malcom Hearn  
Ed Mawji

#### **Section III. Cruise Logistics and *Station* Plan**

*Discussion Leader -* Bob Anderson  
*Rapporteur -* Katharina Pahnke  
*Participants -* Matt Charette  
Phoebe Lam  
Kanchan Mati  
Bill Smethie  
Jingfeng Wu