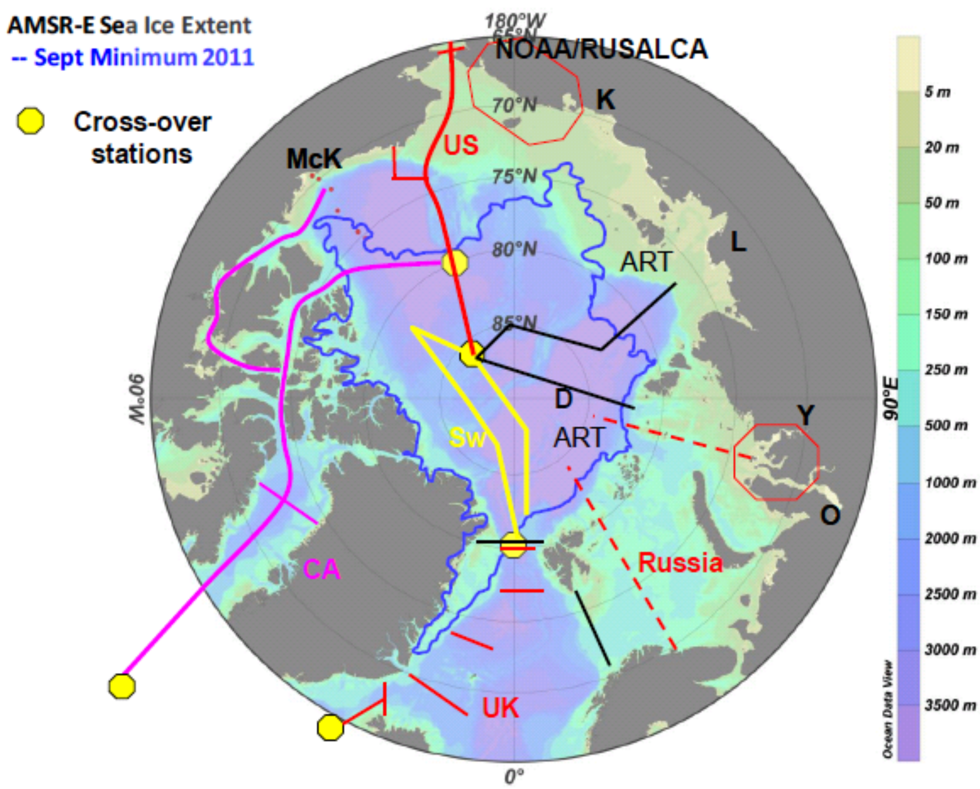
Arctic Implementation Plan



Based on a workshop
13-15 June 2012
U.S. National Science Foundation

US GEOTRACES Arctic Implementation Plan

1.0 Introduction to Arctic GEOTRACES

GEOTRACES is an international research program designed to characterize the marine biogeochemical cycles of trace elements and their isotopes (TEIs). The guiding mission of GEOTRACES is:

> **"To identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions".**

Three overriding research themes are pursued in support of this mission:

1) Quantifying TEI fluxes and the processes that regulate them at ocean interfaces, such as air-sea and sediment-water boundaries.
2) Understanding internal cycling of elements, including their uptake and removal from surface waters, regeneration in the subsurface ocean, and transport by physical circulation.
3) Testing and improving geochemical tracers (proxies) used to infer ocean conditions in the past; understanding the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

The GEOTRACES program is global in scope, consisting of ocean sections where the above themes are explored as dictated by characteristics relevant to each ocean basin. Transects are chosen to cross regions of prominent sources and sinks (such as dust plumes, major river discharges, hydrothermal plumes and continental margins), sampling principal end-member water masses, and transecting major biogeographic provinces.

Establishing the sensitivity of TEI distributions to changing environmental conditions, a key component of the GEOTRACES mission, is particularly relevant to the Arctic, where *rapid climate change* and *accompanying biogeochemical responses* are occurring. TEI distributions in the Arctic Ocean are expected to evolve with climate change, for example under influence by increased runoff from land and by reduced transport by sea ice. Evolving TEI distributions, in turn, likely will impact the biogeochemical cycles of carbon and major nutrients through, for example, their role as micronutrients that are essential for marine organisms. These motivating factors pervade all aspects of the planning and implementation of the Arctic GEOTRACES initiative.

2.0 Historical Developments

This implementation plan builds upon a decade-long planning effort that is summarized briefly here to provide a context for the Arctic initiative.

2.1 International GEOTRACES Planning: International planning for GEOTRACES was launched in 2003 at a workshop in Toulouse, France. Research priorities and scientific goals identified at that workshop were embodied in the GEOTRACES Science Plan, published in 2006, and available at <http://www.geotraces.org/science/science-plan>. Priorities and goals defined in that document guide the global implementation of GEOTRACES research, including the Arctic initiative.

The global GEOTRACES program consists of a federation of individual national and multi-national efforts. Critical enabling activities were completed prior to the main research field program to ensure 1) internal consistency among data generated by participating labs and 2) that GEOTRACES results are available to the international oceanographic community. Policies and procedures to ensure data quality <http://www.geotraces.org/science/intercalibration> were developed by the GEOTRACES Standards and Intercalibration Committee and approved by the GEOTRACES Science Steering Committee. Every GEOTRACES cruise is expected to comply with these procedures. Key features of intercalibration include: crossover stations where different cruises collect dissolved and particulate TEI samples at a common location; collection of replicate samples to be analyzed by collaborating laboratories; and analysis of GEOTRACES standard reference samples for those TEIs for which consensus values are available <http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials>.

A GEOTRACES Data Assembly Centre <http://www.bodc.ac.uk/geotraces/> was established at the British Oceanographic Data Centre to make the global suite of

GEOTRACES data available in a uniform format. The GEOTRACES Data Policy <http://www.bodc.ac.uk/geotraces/data/policy/> is based on the policy in place at NSF, so it is not repeated here. The leaders of each GEOTRACES cruise are expected to submit information about planned cruises as soon as it is available, and to submit a cruise report together with complete hydrographic data upon completion of the cruise. Individual investigators are expected to comply with the GEOTRACES data policy by submitting meta data for planned measurements prior to a cruise, and by submitting final data within two years of their generation.

2.2 Arctic GEOTRACES Planning: Research objectives for Arctic GEOTRACES were defined in 2009 at an international workshop held in Delmenhorst, Germany. Arctic planning was informed by preliminary information derived during GEOTRACES-related cruises conducted as part of the International Polar Year (IPY). Results from the IPY cruises were used to target specific processes and specific regions of the Arctic Ocean for more detailed investigation, as described in the workshop report <http://www.geotraces.org/images/stories/documents/workshops/Artic/Arctic_report.pdf>. The following year, in a workshop held at the National Science Foundation, members of the US oceanographic community, with invited international colleagues, identified a subset of Arctic GEOTRACES goals that are particularly relevant to US Arctic research, and used these as a basis for scientific planning of a US Arctic GEOTRACES cruise <http://www.usgeotraces.org/documents/arcticDOC/ArcticWorkshopRpt.pdf>. These reports constitute the scientific planning documents that outline the research goals of GEOTRACES in the Arctic (see Section 3 below). Subsequently, GEOTRACES has focused on implementing a field program to meet those goals.

Early in the planning process the international community recognized the extreme challenges of implementing a pan-Arctic GEOTRACES initiative. The high costs and complex logistics inherent in Arctic research require collaboration. To achieve a comprehensive understanding of the geochemical processes within the Arctic and their effect on the global ocean, pan-Arctic coverage would require a multi-national, multi-icebreaker effort of historical precedence. Based on discussions at several national and international meetings, the complexity of such an undertaking (multi-national, multi-icebreaker) suggested that a timeframe for implementation would be on the order of 3-5 years and that planning discussions will be ongoing. Year 2015 was targeted for a likely major field effort.

To formalize potential cruise tracks within an international framework, an Arctic workshop, entitled "An Interdisciplinary Assessment of Climate Change Impacts on the Arctic Ocean", was held in Vancouver, Canada during 2 - 4 May 2012, where the expectations of participating nations were presented. A principal goal of the meeting was to coordinate international Arctic oceanographic expeditions under the auspices of the GEOTRACES program. Representatives from several nations expressed their expectations of Arctic expeditions in, or around, year 2015. Tentative national plans were drawn up for the Arctic (see Section 4) with the understanding that these plans would evolve as each country refined its priorities and capabilities. A report from the workshop is available on the web <http://www.geotraces.org/images/stories/documents/workshops/Artic/2012_Arctic_Workshop_Canada/Arctic_report_June12.pdf>.

The main outcomes of the workshop were (1) the development of an international GEOTRACES research program in the Arctic Ocean, (2) the coordination of this program with other relevant Arctic projects (e.g., “Arctic Great Rivers Observatory” and “Arctic in Rapid Transition” (ART), and (3) initiation of the organization of a follow-up workshop in Moscow.

The international implementation workshop in Vancouver was followed by a workshop at NSF (13-15 June, 2012) to refine the research objectives for a US GEOTRACES cruise in the western Arctic Ocean and to devise an implementation strategy to meet those objectives. Approximately 80 scientists, NSF program managers and representatives from the USCG and NOAA participated in the meeting. The results of the deliberations, synthesized below, will serve to prepare a set of priorities to guide the submission of the US Arctic GEOTRACES management proposal (due October 18, 2012), the submission of individual PI proposals (due 15 February 2014), and the evaluation of those proposals.

3.0 Motivation and Scientific Goals

The research goals for Arctic GEOTRACES are consistent with those of the global program, as defined in the Science Plan. In addition, the research goals for Arctic

GEOTRACES contain aspects that are unique to this extreme polar environment, including the expansive continental shelves, the relatively large inputs from rivers, sea ice, and the rapidly changing environmental conditions. With these factors in mind, specific research goals (defined below) were motivated by the following concerns:

- Understanding current biogeochemical processes. There have heretofore been few comprehensive studies of the chemical nature and biogeochemical processes of the Arctic Ocean. The first transect was in 1994 (Arctic Ocean Section Study) and there has been only intermittent submarine sampling (SCICEX); both ventures encompassed relatively few TEIs. Only relatively recent attempts at systematic sampling and coordinated process studies have occurred in the Arctic (e.g. POLARSTERN, 2007).
- Establishing baseline levels of TEIs, micro-and nano-nutrients, water mass tracers and aerosol chemistry with which to compare future change in the Arctic.
- Providing insights into the Arctic's future. TEI distributions provide insight into processes required for model development, and the data are used in model verification to constrain the trajectory of change.

Unique characteristics of the Arctic Ocean, and scientific issues related to them, include the following, which is by no means an exhaustive list:

- The presence of sea ice as a platform for retaining and transporting TEIs derived from various sources; partitioning of TEIs between water, snow, ice, melt ponds, and how this will change within a changing Arctic; the ecological effects of such change.
- Shelf-Basin exchange; chemical and sediment flux from the extensive Arctic shelves; chemical transformations across shelf areas.
- The seasonality and long-term trends of atmospheric deposition; pathways of contaminants to the Arctic from lower latitudes and possible change.
- The coupling of TEIs (e.g., Pb, Hg) to the health and sustainability of subsistence communities of the Arctic.
- Fluxes of TEIs through key Arctic "choke points".

These issues are described in detail in the Arctic workshop reports identified above.
These topics are discussed briefly in this document to provide a context for the

implementation strategy described in Section 4. Broad areas of study relevant to these issues include:

3.1 Aerosols: Aerosol deposition represents an important transport mechanism of contaminants from industrial nations bordering the region (Figure 1). This includes for example, Arctic Haze, which is a mixture of sulfate and particulate organic matter; ammonium, nitrate, black carbon, and mineral dust. US Arctic GEOTRACES aims to measure aerosol concentrations and characterize their deposition rates, with a view toward evaluating the contributions of natural and anthropogenic aerosols to surface-ocean and sea ice chemistry.

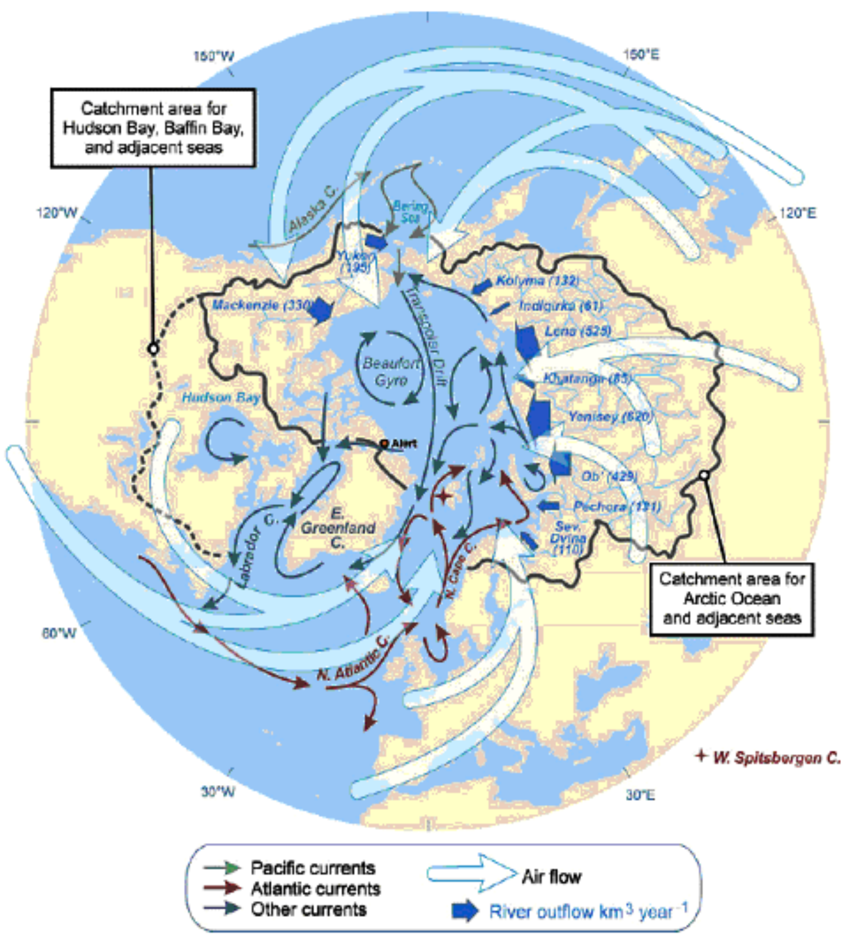


Fig 1. Transport pathways (atmospheric, rivers, ocean currents) bringing contaminants into the Arctic Ocean (from Macdonald et al., 2005).

3.2 Sea Ice: The cycling of TEIs in the Arctic Ocean is affected by sea ice, as ice retains and transports TEIs (e.g. Meese et al., 1997; Cota et al. 2006), releasing them seasonally into the water column during melting (Measures, 1999; Aguilar-Islas et al., 2008). Sources of TEIs to Arctic sea ice include entrained sediment (e.g. Measures, 1999), atmospheric deposition and brine inclusions. An important component of the Arctic program, therefore, is sampling for TEI concentrations in ice, snow, melt ponds and water from the ice-water interface. The US GEOTRACES Arctic cruise will provide the opportunity to study TEIs in and around the sea ice environment with the goal to determine:

1. The range of concentrations of various TEIs (dissolved and particulate).
2. Tracers that can identify the provenance of the entrained sediment.
3. Tracers that can be used to constrain atmospheric deposition.
4. Biological influences on sea ice TEI cycling; the effect of TEIs on the sea-ice ecosystem.

Studies of organic matter/TEI interactions in sea ice are a special opportunity, as unique biological communities occupy the ice. Organic ligands with unique compositions may be produced by sea ice algae. Through their regulation of TEI speciation, these ligands may play a role in TEI biogeochemistry and bioavailability that is not found in ice-free waters. Using a common set of analytical methods to determine the characteristics of metal-ligand complexes, investigators can test for the importance of ligands produced by ice algae by comparing results from sea ice with results from the underlying waters, and by further comparing these results with those from ice-free systems.

3.3 Water Column: Sampling of the water column on a US GEOTRACES Arctic cruise will be designed to evaluate the fluxes of TEIs through the Bering Strait choke point, to identify sources of TEIs and TEI-binding organic ligands delivered by Arctic rivers, to quantify shelf-basin exchange including, for example, TEIs mobilized by diagenetic processes in continental shelf sediments, and to define the chemical evolution of deep waters as they mix from the Atlantic into the Canada Basin. Diagenetic mobilization on continental shelves will be discussed in Section 3.4.

Pacific water transported into the Arctic Ocean through the Bering Strait is distinguished by low nitrate to phosphate ratios as a consequence of denitrification in continental shelf sediments. By analogy with the major nutrients, Pacific water may also have unique TEI characteristics. However, other than a distinct Pacific source that has been identified in the isotopic composition of dissolved Nd carried by water transported through the Bering Strait (Andersson et al., 2008), little is known about the impact of Pacific inflow on TEI cycles in the Arctic Ocean. Constraining the fluxes of TEIs through the Bering Strait is a goal of the US Arctic GEOTRACES program.

Off the shelf, over the Canada Basin, the polar mixed layer holds large contributions of both freshwater and terrigenous organic matter. More than 10 m of fluvial water resides in the layer and up to 25% of the dissolved organic matter (DOM) there is delivered by rivers. Marine and terrigenous-sourced DOM will likely display distinct interactions with the TEI's of the mixed layer. Diagnostic tracers of freshwater sources (e.g. Ostlund and Hut, 1984; Macdonald et al*.,* 1995; Bauch et al., 1995; Ekwurzel et al., 2001; Schlosser et al., 2002), in conjunction with TEI measurements, will be used to evaluate riverine supply of TEIs to the Arctic Ocean (e.g., Middag et al., 2009; Klunder et al., 2012; Roeske et al., 2012). In addition, following the protocols recommended for sea ice studies (Section 3.2), TEI-binding characteristics of terrestrial organic matter delivered by rivers will be compared with that of marine ligands to assess the impact of terrestrial compounds on TEI bioavailability and biogeochemical cycles.

Sampling across water mass fronts in the deep basins will characterize the chemical composition of Atlantic, Pacific and transpolar drift waters. Long sections will also identify sources (Section 3.4) and sinks (e.g., boundary scavenging) of TEIs at the basin margins. Historical studies of radiocarbon in the deep Arctic basins indicate a time scale of about 200 years (Schlosser *et al.,* 1994; 1997; Mauldin *et al.,* 2010) for water to mix from the Atlantic into the deep Canada Basin. Stoichiometric relationships among individual TEIs, as well as between TEIs and hydrographic variables, will be used to identify the processes contributing to the supply and removal of TEIs during the chemical evolution of deep water in the Arctic Ocean.

3.4 Sediments: Measurements of TEIs within sediments collected during the US Arctic GEOTRACES expedition are motivated by understanding geochemical processes in the sediments and their relationship to the water column, as well as providing tracers of physical transport mechanisms in the Arctic Ocean. Study of shelf sediments and pore waters will complement water column studies (Section 3.3) of TEI mobilization by organic regeneration and redox chemistry within sediments (e.g. Gobeil et al. 1997; Kuzyk et al., 2011). Shelf sediments also contain organic tracers of riverine sources of material, as well as short-lived radionuclides that are diagnostic of rapid delivery of sediment by sea ice (Baskaran et al., 2005). Deep basin sediments also contain tracers of circulation pathways and diagnostic provenance (e.g. Gobeil et al., 2001), while serving as the ultimate repository for TEIs scavenged from deep waters. Dissolved iron and manganese are more abundant in the Arctic than in other oceans (Macdonald and Gobeil, 2011), and studies of deep basin sediments will reveal the contribution to TEI scavenging and removal by formation of authigenic coatings of Fe-Mn oxides on suspended particles (e.g. Edmonds et al., 1997; Trimble et al., 2004; Moran et al., 2005).

The broad continental shelves of the Arctic Ocean are of particular interest because of the intense sediment diagenesis that mobilizes TEIs. The continental shelf of the Bering/Chukchi system has extremely high biological productivity due to the shoaling of nutrient-replete Pacific water onto the shallow (<50 m) shelf. These waters are held in the euphotic zone during a several hundred-kilometer transit to the Chukchi Sea from the Bering Strait, with a large fraction of the production exported to the seabed. Consequently, the underlying sediments are anoxic, particularly in the basins immediately north of St. Lawrence Island and north of Bering Strait. The combined effects of benthic regeneration of biogenic material together with diagenetic mobilization of authigenic inorganic phases are expected to release a substantial flux of TEIs from shelf sediments. Sediment studies will complement water column measurements to identify the processes responsible for these TEI fluxes while also quantifying the fluxes.

In the eastern Bering/Chuckchi system, the shelf is strongly impacted by fluvial inputs of terrigenous organic matter. Oxic sediments in the east hold the $\delta^{13}C$ signature of land plants, while in the west a marine signal dominates. Comparing TEI fluxes from these contrasting sedimentary regimes will aid in establishing the sensitivity of TEI fluxes to the nature and origin of organic material delivered to shelf sediments.

4.0 Implementation of the US GEOTRACES Arctic Expedition

The US GEOTRACES Arctic expedition was designed both to support the unprecedented international collaboration inherent in the pan-Arctic GEOTRACES initiative and to benefit from it. The workshop in Vancouver (May, 2012) provided the foundation for an international pan-Arctic GEOTRACES research program involving simultaneous use of multiple platforms from several countries to provide the broad synoptic coverage essential for fully characterizing the Arctic Ocean and establishing a baseline for quantifying future changes.

Figure 2 shows the tentative cruise tracks. Investigators from each country are seeking funding to complete the individual legs shown on the map. The overall sampling program includes the Pacific inflow through Bering Strait (US), the Arctic outflow to the Atlantic through the Canadian Arctic Archipelago (Canada), exchange between the Arctic and the Atlantic through Fram Strait and the Nordic Seas (Germany & UK), interactions with the Russian shelves and rivers (Russia), and a comprehensive coverage of the deep Canada and Eurasian basins (US, Sweden, Germany, and Canada). Crossover stations will be occupied by more than one country for the purpose of thorough intercalibration between national programs to provide data quality control. If fully implemented, these sampling expeditions would involve the simultaneous deployment of ice breakers or ice-reinforced research vessels from 6 different countries (US, Canada, Germany, Sweden, UK, and Russia) across different parts of the Arctic Ocean in 2015, and application of state of the art geochemical tracers to unravel the complex biogeochemical dynamics of the Arctic Ocean and surrounding continental shelf. Numerous scientists from countries without icebreaker capability will also be included in this endeavor. The program would be unprecedented in scope and scientific breadth.

4.1 US GEOTRACES Proposed Cruise Track: Within the context of international planning, and building on historical US research programs in the Arctic Ocean (e.g., Shelf-Basin Interaction, SHEBA), the US GEOTRACES Arctic expedition will focus on the western Arctic Ocean. Two viable options for a US cruise track have been developed, one (Figure 3A) that assumes a German presence in the Amundsen Basin (Figure 2) and one (Figure 3B) that presents a modified US cruise plan in the case that the German cruise is not funded. The former affords a more highly resolved deep basin transect to the southwest while the latter necessitates a more northerly extent of the US cruise track. Both tracks share common features: a Pacific end member station, a shelf-basin interaction segment, and a deep basin transect that resolves features of physical circulation. In addition, two "two crossover" stations (Canada Basin, Makarov Basin) are built into the plan for intercalibration among participating labs.

It is anticipated that the cruise starting point will be Dutch Harbor, with most equipment preloaded in Seattle. Disembarkation will likely be Barrow. Sampling of the most southern stations will begin immediately, continuing across the shelf-break transect and into the Beaufort gyre until significant ice is encountered. Plowing north to the northern-most stations, a coarsely resolved distribution of regular, super stations, and ice sampling will occur. This will assure maximum northward penetration, and allow fill-in of regular, super stations and ice sampling on the way back. This will also allow occupation of stations during "freeze-up" conditions on the southbound transect.

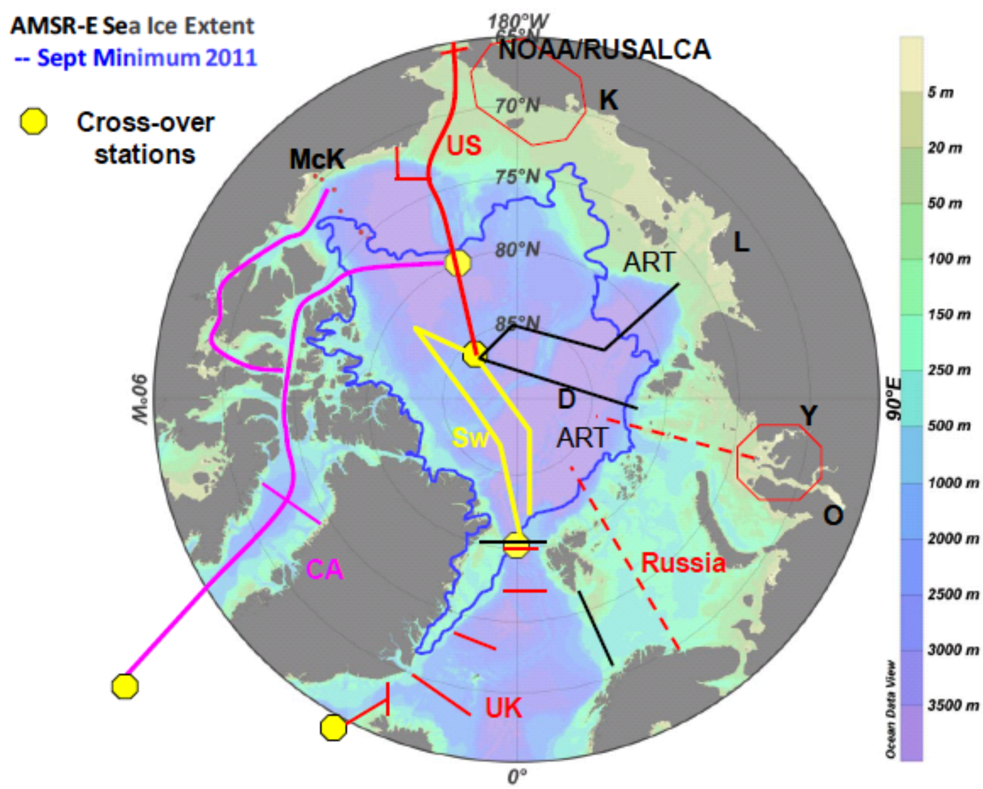


Figure 2. Tentative cruise tracks for the proposed 2015 international Arctic GEOTRACES program. Proposed national contributions are show in red (US, UK, Russia), magenta (Canada), yellow (Sweden), and black (Germany). Regions of interest for the ART program are also shown. Yellow dots denote cross-over stations to be occupied by more than one national program for cross-calibration. Mackenzie (Mck), Kolyma (K), Lena (L), Yenisei (Y), and Ob (O) show the location of the major rivers discharging in the Arctic Ocean. From workshop report (Vancouver, May 2012 "An Interdisciplinary Assessment of Climate Change Impacts on the Arctic Ocean).

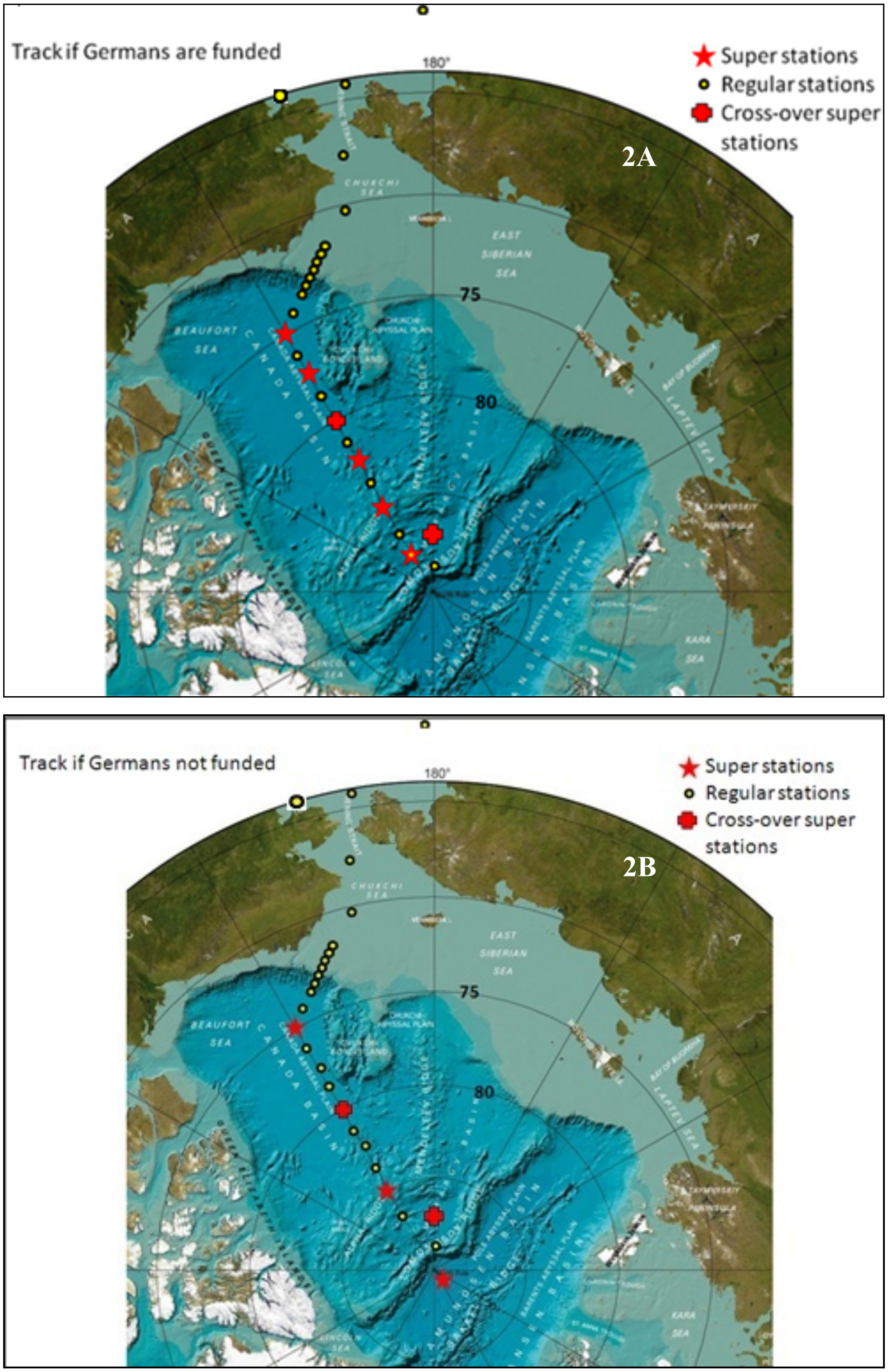


Figure 3. A) The most likely cruise track which assumes German presence in the Amundson Basin (see Fig 2) and affords a more highly resolved deep-basin US transect. B) The case if the Germans are not funded which would necessitate a more northerly extent of the US track.

This cruise plan will permit sampling important sites upstream of the Chukchi shelf break and the Canada Basin, including:

- a Pacific end-member station located off the shelf-break of the Bering Sea;
- a station in Norton Sound (near 63.5°N, 165°W), which is a site highly impacted by (terrigenous) outflow of the Yukon River;
- a station in the highly productive Chirikov Basin, located north of St. Lawrence Island and south of Bering Strait (centered near 65°N, 169°W); and
- a station within the highly productive southern Chukchi Sea (centered near 67.5°N, 168.5°W).

These latter two locations are bathed by nutrient-enriched Pacific waters and, hence, they are highly productive. Being located downstream of the Anadyr and Bering Straits, they are also regions of relatively reduced turbulence, such that particulate organic matter sinks to the shallow seafloor in great amounts, supporting a highly productive benthic ecosystem in organic-rich sediments.

D. Forcucci of the USCG will request clearance for the HEALY to sample across Bering Strait, into Russian waters, to complete the transect of the Bering Strait choke point. Contingency plans are bring made in case that clearance is denied (Section 5).

A transect of 6-8 stations are planned across the Chukchi shelf and shelf-break (Figure 3) to investigate shelf diagenesis signals, off-shelf plume dispersion, boundary scavenging, and TEI mobilization by carbon transformation processes. The spatial scale of sampling required to resolve water mass structures is illustrated in Figure 4.

A deep basin transect will start off with a super station (defined in the next section) at the end of the Shelf-Basin transect, and continue northward along 150° W. There will be 6-8 regular and 6-8 super stations depending on time available, which will be dictated by factors such as ice extent and the role of German participation (Figures 2 and 3). Figure 5, showing the September sea ice extent for two recent years of minimal ice coverage, illustrates the range of sea ice variability that can be expected. The number of stations along the deep-basin transect will be adjusted as needed to complete the section within the time frame allowed by sea ice conditions at the time of the cruise.

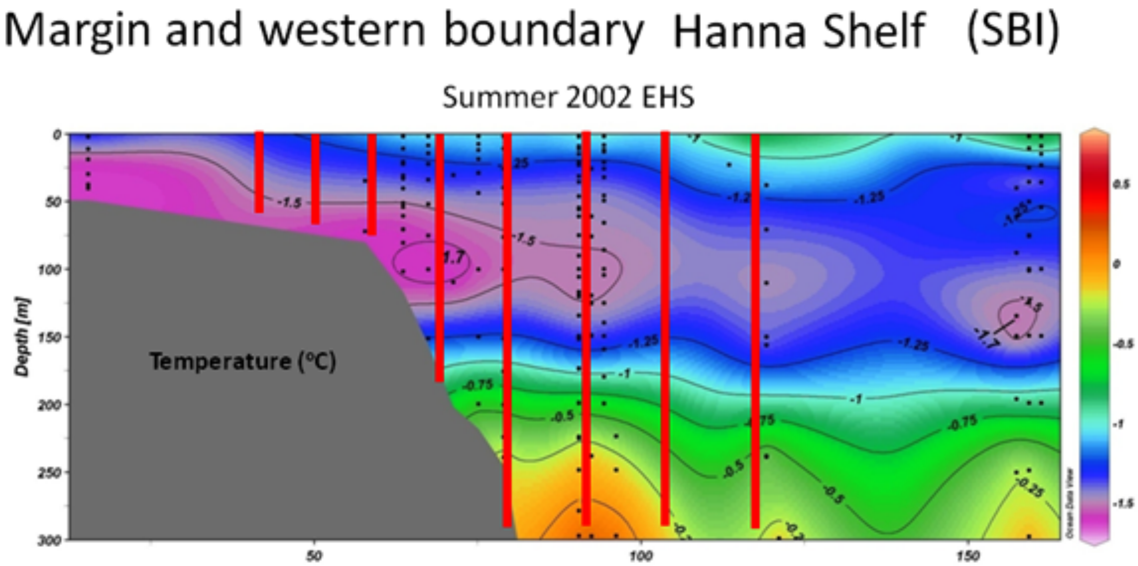


Figure 4. High resolution transect across the shelf and shelf break. The spatial scale of sampling required to resolve water mass structures is illustrated. Shown above is temperature contoured across the East Hannah Shoal (EHS) during the Shelf-Basin Interaction Program (SBI).

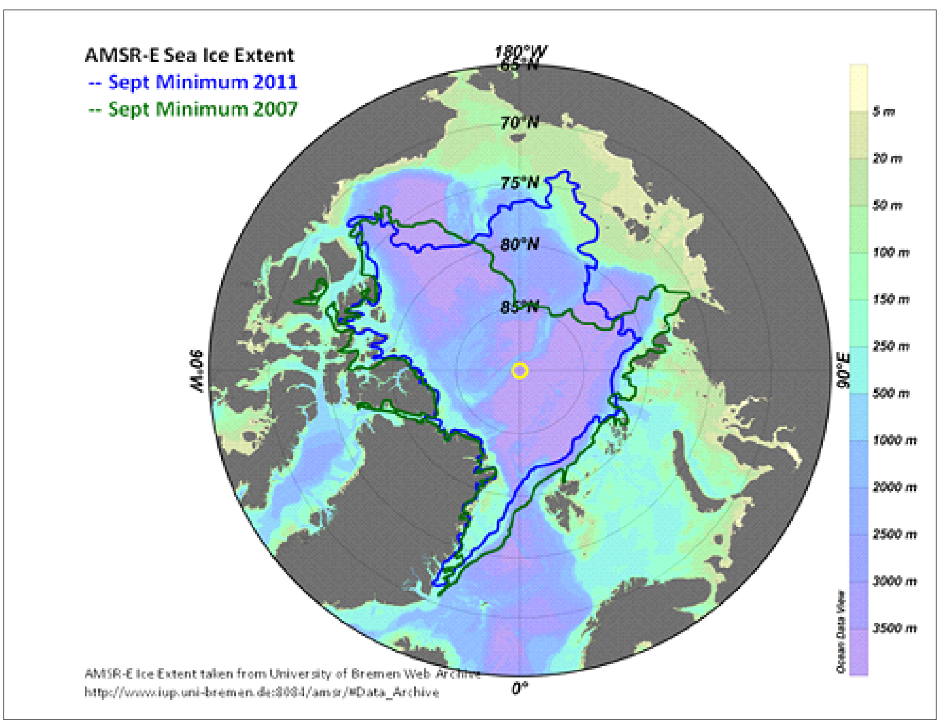


Figure 5. September sea ice extent for two "minimal" years, 2007 and 2011. Data collected by the Advanced Microwave Scanning Radiometer – Earth Observing System (AMSR-E) instrument on the NASA Earth Observing (EOS) Aqua satellite.

4.2 Station Plan: Aerosol sampling (Section 4.2.1) will run continuously, so this component of the sampling program is not explicitly part of the station plan. Four sampling devices will be deployed at each station:

- The US GEOTRACES trace-element "clean" carousel
- A standard rosette equipped with Niskin bottles
- In-*situ* pumping systems to collect surface water and suspended particles
- Sediment sampling with a Multicorer (shelf only), and Monocorer (deep stations), as part of the rosette deployment.

Additional sampling of snow and ice will take place in ice-covered regions.

Shallow stations, on the continental shelf and upper slope, will consist of one deployment of each of the four devices. There is no plan for a dedicated cast of a coring device at deep-water stations (Section 4.3.4). Two deployments of each of the rosette systems will be required at deep stations.

The strong stratification characteristic of the upper Arctic Ocean necessitates high sampling resolution in upper 500 m (e.g., one cast of 12 depths for 0-500 m). In addition, highly resolved near bottom sampling is required for investigation of bottom scavenging processes (e.g., nepheloid layer).

At selected stations, designated "super" stations, additional casts will be scheduled to collect water and particulate material. Consistent with GEOTRACES station operations on the 2010/2011 US North Atlantic GEOTRACES cruise, these casts will be dedicated to those parameters that require samples too large to be accommodated in the sampling routine of the standard station plan. The number of super station casts of each device will be determined by the needs of individual proposals that are funded to participate in the Arctic expedition. As an example, for the US GEOTRACES Atlantic section, super stations typically required three additional casts to meet the sample needs for artificial radionuclides, ^{210}Pb-^{210}Po, and Si isotopes.

Arctic sampling will also have unique aspects not encountered in prior US GEOTRACES cruises, including snow, ice, melt pond and sediment collection. Logistics pertaining to these sampling activities are described in the following subsections.

4.2.1 Aerosol and Precipitation Sampling: Dry and wet deposition will be collected with the US GEOTRACES aerosol and rainfall sampling equipment (Figure 6).

Aerosols: The high-volume total suspended particle (TSP) aerosol samplers (Tisch 5170V-BL) will be equipped with different filter holders and substrates appropriate for the planned number of replicates and analyses. Two samplers will be deployed with adaptor plates that hold 12 acid-washed Whatman 41 filters (47mm). These will collect bulk aerosols to be used for TEI analysis. A third sampler will be deployed with an 8 x 10-inch filter holder loaded with a pre-combusted (550^{o}C, >4 hours) quartz micro fiber (QMA) filter that will also collect bulk aerosols for the analysis of organic species, nitrogen compounds and isotopes, and Hg. The fourth sampler will be equipped with a 5-stage Sierra-style slotted cascade impactor loaded with acid-clean-washed Whatman-41 slotted filters to collect size-fractionated aerosols (>7 µm to <0.49 µm) for TEI analysis. Contamination from ship's exhaust will be avoided by positioning the samplers as high and forward as possible on the ship, and by using an automated wind speed and sector control system receiving input from an anemometer and weather vane to restrict collection to predetermined wind speed (>0.5 m/s) and direction (±60^{o} from the bow of the ship). This control system shuts off power to the aerosol samplers immediately when the wind falls outside of these pre-set limits. Aerosol samples will be collected on a 24 hour integrated basis. When aerosol loads are very low, filters from consecutive days can be analyzed in combination.

The provenance of sampled air masses will be modeled using the back trajectory feature of the NOAA HySplit model (http://ready.arl.noaa.gov/HYSPLIT_traj.php). A 5-day back trajectory will be computed for each collection period.

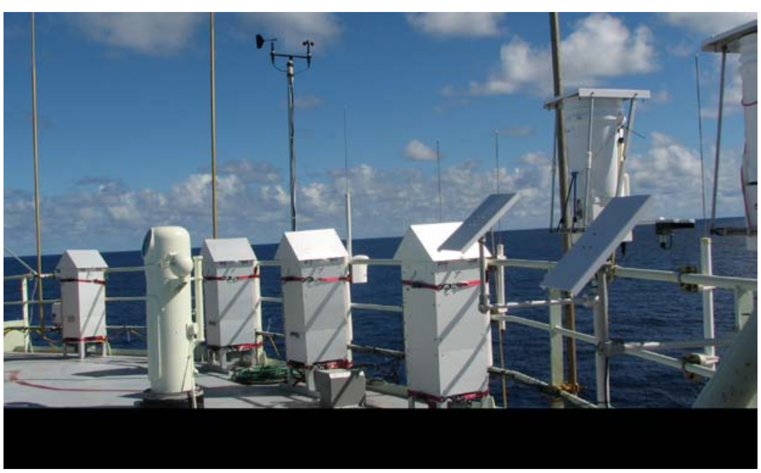


Figure 6. Aerosol and rain samplers deployed on the *R/V Knorr* during the US GEOTRACES Atlantic Zonal Section cruise.

Precipitation samples: Unfiltered rainwater will be collected with two N-CON automated rain samplers, equipped with acid-cleaned funnels (700 cm^2) and 2 liter receiving bottles. Rain samples will be collected on an 'event' basis (minimum 1 mm of rain). The samples will be collected and processed immediately upon completion of the rain event. Subsamples (25-100mL) will be filtered within 30 minutes of collection (described below).

Snow samples can be collected from the ship using a set of pre-washed wide-mouth polyethylene bottles mounted horizontally (into the wind) on a pole mounted on the "flying bridge" next to the rain samplers. This has been successfully tested using polyethylene condiment squeeze bottles; the dispensing spout (pointed aft) allows air to flow easily through the bottle, and the snow is impacted on the bottle walls as the air passes through. The bottles will be collected after the snow event and allowed to melt in the ship's lab. If more than 50mL of melted snow is collected, at least 25 mL will be filtered using the method described below for rain samples.

Fog sampling methods for TEIs will be investigated, and utilized if it can be determined that they are appropriate for the low concentrations of TEIs that are expected. A passive fog sampler that seems to be appropriate for our needs has been described by Beiderwieden et al. (2005). This sampler would be deployed on the flying bridge on an event basis, and the samples would be preserved for various TEI measurements.

Sample Storage: Size-fractionated aerosol samples and bulk samples collected on QMA filters will be placed inside individual zipper-seal bags and stored frozen until processing. Bulk aerosols collected onto 47mm Whatman 41 filters will be placed in plastic petri dishes after collection. Filters to be leached the day of collection will be stored refrigerated; others will be stored frozen, or as required by the collaborating PI. Rain samples and leachates will be acidified (to 0.024M Q-HCl) in LDPE bottles, or as required by the collaborating PI.

Onboard Sample Processing: Sample collection, processing and analysis will follow rigorous trace metal clean (TMC) procedures. Filter subsampling will take place under Class-100 conditions using ceramic (Zr-oxide) scissors. Depending on particle loading, QMA filters will be cut into 14 (or fewer) equal fractions, and slotted filters used with the impactor will be separated into 9 strips (to take advantage of the existing strips in these filters). The 47 mm Whatman 41 filters will not be subdivided.

On the day of collection, ultra-high purity water (≥18 MΩ.cm) and filtered surface seawater will be used to leach bulk aerosols to estimate the fractional solubility of aerosol-derived TEIs using the "instantaneous leaching" method described below. Surface seawater leaches can also be used to determine the amount of colloidal Fe and Fe(II) in the leachate, and to provide aerosol leach solutions to collaborators. We will obtain filtered surface seawater from the GEOTRACES trace-metal clean towed-fish pumping system or from the shallow GO-Flo bottles on the trace metal rosette.

Collection Blanks: Sets of filter blanks will be collected (2-3 times during the cruise) by placing loaded filter holders in the samplers without turning the motors on. Filter blanks will be subsampled in the same manner as the samples. Whatman 41 filters will be acid washed using the same protocol that was employed during the Atlantic GEOTRACES cruise. This protocol has been reported to dramatically reduce blank levels and improve detection limits (Baker et al., 2006).

Aerosol solubility treatment: We will utilize an "instantaneous leach" protocol (Buck et al., 2006) with 100 mL volumes of ultra-high-purity water (UHP water) and filtered surface seawater (SW) as the leaching solutions. A suite of 30-40 TEIs will be analyzed directly on the UHP water leaches by ICP-MS. TEIs from the SW leaches will be analyzed back in the lab using a chelating resin for pre-concentration and ICP-MS detection (Milne et al., 2010, Biller and Bruland, 2012). A 20 mL subsample from the UHP leach is stored frozen for the analysis of major ions (potassium, chloride, nitrate, sulfate, and oxalate) using ICPMS and ion chromatography. Blank filters will be used to generate leach blanks.

Size-fractionation of soluble Fe in aerosol leaches: Two replicate 47 mm Whatman aerosol filters will be leached with seawater as described above. The leachate will be filtered through 0.02 μm Anodisc filters membranes (Whatman) to determine the truly soluble Fe fraction, and the colloidal fraction (by difference). These samples will be analyzed back in the lab using $Mg(OH)_2$ coprecipitation-isotope dilution (Wu and Boyle, 1998) and ICP-MS detection.

Redox speciation of soluble Fe in aerosol leaches: Two replicate 47 mm Whatman 41 aerosol filters will be leached with seawater as described above. The leachate will be immediately acidified to ~ pH 1.8 and passed through an NTA Superflow (Quaigen) column. This resin binds Fe (III), but does not bind Fe (II) at this pH (Lohan et al., 2005). Freshly made acidified Fe (II) standards will be passed through the same column. These samples and standards will be analyzed back in the lab using $Mg(OH)_2$ coprecipitation-isotope dilution (Wu and Boyle, 1998) and ICP-MS detection to determine the efficiency of the column.

Aerosol filter digestions: Whatman 41 aerosol filters will be digested by sequential treatments with heated mixtures of ultrapure HNO_3 and HF as described by Morton et al. (in press). TEIs in these digestions will be quantified using the method of standard additions with ICP-MS analysis. Collection filter blanks (described above) and reference materials (Arizona Test Dust, HISS-1 and MESS-3) will also be digested and analyzed.

Rain and snow sample processing: Immediately after each rain or snow event, the unfiltered samples will be brought quickly into the clean lab on the ship and a portion will be filtered through a pre-cleaned 47mm 0.2 µm polysulfone filter. Filtered and unfiltered aliquots in 125 mL polyethylene bottles will be acidified to 0.024M HCl using ultrapure HCl. These samples will be stored for TEI analysis in the shore lab using ICP-MS. Subsamples can be provided to the Hg team for ship-board analysis of total Hg. Subsamples (20mL) of filtered rain and snow are also taken into small polyethylene bottles, and frozen, for shore-based analysis of major cations and anions using Ion Chromatography (Dionex 4500i). When the sample volume exceeds the analytical needs for the GEOTRACES TEIs, aliquots will be provided to other collaborators.

Natural radio-isotope analyses: Aerosol and precipitation samples for ^{7}Be and $^{232/230}$Th isotopes will also be collected to take advantage of the recently developed research methods that allow quantification of the total atmospheric deposition of those isotopes from their water column profiles (Landing et al., 2012; Anderson et al., 2012). The atmospheric deposition of other soluble and particulate TEIs can be calculated by multiplying the deposition estimates (derived from the radio-isotope profiles) by the ratios of TEIs to ^{7}Be and ^{232}Th on aerosols.

Additional aerosol sensors: Additional aerosol sensors can be deployed on the ship to quantify, for example, cloud-condensation nuclei (CCN), aerosol black carbon (aethalometer), and aerosol optical properties (absorption and scattering coefficients). The suite of sensors to be deployed will be comparable to the sensors that are used at ground-based stations around the Arctic Ocean (Tiksi, Barrow, and Alert).

Ground-based measurements: Discussions are continuing with the operators of aerosol monitoring stations surrounding the Arctic Ocean (Tiksi, Barrow, and Alert) in order to collect samples comparable to those that will be collected on the ship for TEI analysis. It is hoped that samples will be collected from 2014-2016 (3 years) to bracket the 2015 ship-board sampling in order to place those analyses in context with longer-term patterns in aerosol concentration and chemistry. Sampling at the ground-based stations may require additional funding support.

4.2.2 Sampling water for contamination-prone TEIs: Depth profiles for dissolved and suspended particulate TEIs will be obtained using the GEOTRACES carousel sampling system (Cutter and Bruland, 2012) operated by Greg Cutter's group in combination with those from a conventional rosette (below) following the GEOTRACES cruise protocols (http://www.geotraces.org/libraries/documents/Intercalibration/Cookbook.pdf). The US GEOTRACES carousel is a Seabird aluminum frame with polyurethane powder coating that holds twenty four, 12 L GO-Flo bottles capable of firing up to 3 at once. The carousel uses a Seabird 9+ CTD with dual temperature and conductivity sensors, SBE 43 oxygen sensor, a Seapoint fluorometer, and a Wet Labs transmissometer; all of the pressure housings and pylon are titanium, eliminating the need for zinc anodes and resulting contamination. The carousel itself is attached to a 14 mm OD, 7800 m long Kevlar conducting cable spooled onto a Dynacon traction winch with slip rings. The bottles are fired (up to 3) on the upcast while moving into clean water at ca. 3 m/min in order to minimize contamination from the frame and sensors (Cutter and Bruland, 2012). Thus, carousel sampling can acquire 11.5 – 34.5 L of water per depth for determinations of contamination-prone TEIs.

The GO-Flo bottles are immediately transferred into the HEPA-filtered, positive pressure clean lab van where they are sub-sampled for dissolved and particulate TEIs.

Assuming two GO-Flo bottles will be fired at each depth, one GO-Flo will be pressurized (<8 psi) with filtered, compressed air and the water directly passed through a 0.2 µm Acropak-200 capsule filter and into sample bottles (low density polyethylene, Teflon, etc depending on the analyte) for contamination-prone elements (e.g., Fe, Zn). In addition, if a TEI cannot be filtered due to contamination (e.g., perhaps Pb isotopes), unfiltered samples can be taken from this GO-Flo. The second GO-Flo will be devoted to particulate samples where the entire volume (ca. 11.5 L) is passed directly through a 0.45 µm polysulfone Supor filter membrane filter under <8 psi pressure (not vacuum). The filtrate from this membrane filter is then used for TEIs that are not as prone to contamination (e.g., Al, Mn), and the filter used for total metal determinations via acid digestion and ICP-MS analysis. All water samples from the carousel system are completely processed in the Class 100 clean van, including acidification under a HEPA laminar flow bench if desired.

To assess the integrity and representativeness of the TEI samples, salinity and nutrient samples, and aliquots for shipboard determinations of dissolved Zn, are taken from each GO-Flo. Comparisons of salinity and nutrients concentrations with those from the conventional rosette (with bottles that are not prone to leaking) allow leaking or misfiring to be easily identified (e.g., Cutter and Measures, 1999).

4.2.3 Sampling water for noncontamination-prone TEIs: Work on the two Intercalibration cruises, and the US GEOTRACES North Atlantic cruises show that a conventional CTD/rosette can be used for all the radionuclide and most of the radiogenic isotopes. For these and water column hydrography, we will use the 12 position, CTD rosette operated by the SIO Ocean Data Facility (ODF) and overseen by Jim Swift. This unit has 30 L Niskin-like bottles that have coated stainless steel springs and Viton o-rings, and will also be equipped for direct, inline filtration (0.45 µm Acropak-500 capsule filters). Sensors on this system include a transmissometer, Seabird SBE-43 oxygen probe, and fluorometer. As far as the need for quality hydrography, not only can GO Flo bottle leaking be identified, the data are crucial for identifying the water masses being sampled. In this respect, shipboard measurements of micromolar inorganic nutrients (nitrate, silicate, and phosphate), salinity and dissolved oxygen will be made on the standard rosette and the trace-metal clean rosette both for identification of water masses and diagnosis of bottle performance issues. Such measurements will be done to WOCE/CLIVAR standards.

4.2.4 *Sampling sea ice and snow*: The sea ice environment presents GEOTRACES with new sampling challenges related to access, specialized equipment, and sea ice heterogeneity. Sampling of sea ice, snow, melt ponds, and the water layer immediately under the ice has to take place off-board with light-weight, portable equipment, and in relatively rapid fashion. Heterogeneity among and within ice floes needs to be addressed by the sampling scheme, and efficient sampling protocols to provide homogenized sea ice (dissolved and particulate) samples to interested labs remain to be established.

Sea Ice Access: A straightforward way to access a sea ice site is to lower personnel and equipment onto an ice floe next to the ship while occupying a water column station, if concurrent operations are allowed. Access by helicopter or by small boat are additional possibilities. It is not known at this time if the project budget can accommodate a helicopter.

Sampling Sea Ice: We will request that sea-ice sampling be run concurrently with CTD sampling from the ship. If the request were denied, then a minimum of ten sea ice stations (8hrs/station) would have to be included in the station time budget for the cruise. Samples collected at each of these stations will include ice cores, snow, melt ponds, and the water layer immediately under the ice. Collection of ice cores will follow the protocols employed by the few studies of trace metals in sea ice, which have obtained samples by extracting cores of small diameter with electrically operated corers, rather than cutting away large sea ice blocks. The small diameter cores are easy to handle and can be kept clean. Collecting small diameter cores is recommended for GEOTRACES. A corer with materials appropriate for trace metal sampling is currently being investigated. An electro-polished stainless steel corer (Lannuzel et al., 2006), used to collect trace metals from Antarctic sea ice, is thought to provide clean cores avoiding laborious post-cleaning steps. A Kovacs fiberglass ice corer, used to collect trace metals from Bering Sea ice (Aguilar-Islas et al., 2008), requires post-cleaning of the cores. Corers used to obtain glacial ice with trace element sampling in mind are available from Icefield Instruments, Inc (http://www.icefield.yk.ca/ice-coring-drills.html). These use titanium and carbide in the cutting head and polyethylene (PE) tube inserts in the shaft for minimum core handling, and could be adapted for GEOTRACES purposes.

Depending on the volume of melted sea ice requested by groups characterizing the sea ice, an individual sample may require more than one ice core. The protocol to homogenize and distribute sea ice samples to individual PIs without contamination will be determined after testing. To address the heterogeneity of a given sea ice floe, subgroup of ice cores (making an individual homogenized sample) will be collected at several locations from each station. The number of these subsamples is yet to be determined, but at least 3-5 subsamples from each ice flow should be considered.

A method for the collection of particles from homogenized sea ice samples is yet to be determined, but will be developed with appropriate testing.

Sampling snow: Snow studies in the Arctic are traditionally from terrestrial or coastal environments, but enhanced deposition of aerosol TEIs over marine areas is expected due to the nucleating effects of sea salt, and the increased rates of fog-related deposition within marine ice fog. At each ice station, snow accumulated on top of the sea ice will be sampled from each of the sea ice subsample locations, and these subsamples will be combined to obtain a large enough homogenized snow sample per sea ice station. Snow will also be collected opportunistically during snow events, either from the ship or from ice floes.

Sampling snow cleanly is straightforward, and does not require specialized equipment. Pre-cleaned PE shovels and Teflon bags are used for collecting snow over sea ice.

Sampling melt ponds: At the time of the cruise melt ponds will be present on ice floes. Melt ponds will be sampled opportunistically from sea ice stations. Melt pond water will be pumped with a Teflon diaphram pump (Cole Parmer), or a peristaltic pump, and Teflon tubing into pre-cleaned bottles/carboys.

Sampling seawater under the ice: The thin layer of seawater immediately below sea ice is an important part of the water column that cannot be sampled with the GEOTRACES rosette. The upper 1 m is expected to display strong gradients in salinity and dissolved

TEIs (e.g. Kadko and Swart, 2004), and will be characterized and sampled once per ice station. These samples will be distributed to a subset of researchers interested in under-ice gradients. Additionally, large homogenized samples should be collected to complete water column profiles (at least to the mixed layer depth) for most TEIs.

To collect seawater under the ice an auger is used to drill an access hole. Kovacs Enterprises (http://www.kovacsicedrillingequipment.com/) has stainless steel augers (2") that can be used for this purpose. Access holes are drilled in advance of sampling to allow the potentially contaminated seawater to be renewed, and any eroded gradients to be reestablished. Sampling from nearby open leads is of course another option. A miniature CTD or a thermistor chain can be used to characterize the upper 10-20m. Water will be pumped with a Teflon diaphram pump (Cole Parmer), or a peristaltic pump, through Teflon tubing into pre-cleaned bottles/carboys. In-line filtered (Pall Acropak Supor capsule filters (0.2 µm) and unfiltered samples are collected.

Processing ice and snow samples: All post-sampling processing of sea ice and snow will be carried out in the ship's temperature-controlled labs under ISO conditions. Other samples can be post-processed in a "bubble" (a space enclosed by plastic sheeting and supplied with filtered air) or a trace metal clean van. The sampling scheme for ice stations outlined above represents considerable amount of work on the ice floe as well as back in the ship's labs. A dedicated "super tech" will be requested in the management proposal to support this work.

4.2.5 Sediment sampling: Sediment sampling on the shelves will be accomplished by deploying a Multicorer device. As the water depths will be quite shallow (<500 m and often <100 m) this process will use minimal ship time. The Multicorer will be deployed from the fantail to avoid interference with the collection and processing of water column samples (rosettes and *in situ* pumps). Following the protocols developed on UK GEOTRACES cruises, coring will be the last operation at each shelf station to avoid resuspending particles in the water column prior to other sampling activities. Operation of the Multicorer will require a dedicated coring tech supplemented by assistance from investigators who plan to use sediment samples.

Sediment sampling in the deep ocean will be accomplished using the NIOZ mono corer (Figure 7) hung below the Niskin rosette on the deep cast at each station. This requires no additional ship-time. The mono corer deployment strategy has been tested on the Dutch GEOTRACES South Atlantic cruise and its use is planned for the US GEOTRACES Pacific cruise scheduled for 2013. Thus, the US GEOTRACES community will have experience using this device prior to the Arctic expedition.

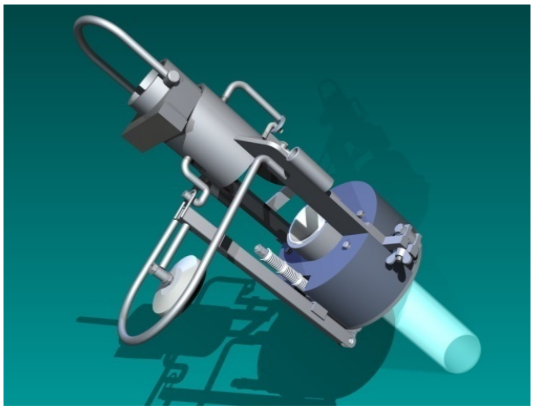


Figure 7. NIOZ mono corer

Processing sediments aboard GEOTRACES cruises is a concern as it represents a potential source of contamination for water samples. Steps to reduce the potential for contamination include:

- Sampling from the fantail to isolate coring from rosette and pump operations.
- Coring as the last activity at shelf stations to avoid resuspended sediments in the water column.
- Handling core tubes in an isolated space (e.g. van, lab).

On board processing is essential for time-sensitive parameters, including those affected by chemical transformations caused by exposure of sediments to oxygen. Recommended on-board processing includes:

- Redox chemistry would be compromised with storage, so it is suggested to use "Jahnke squeezers" (Figure 8) that have proven to get pore waters from multicore tubes without the need for sectioning and processing of individual sediment samples. If porewater fluxes are needed, the whole core squeezer described by Bender et al., (1987) can be employed to get high resolution samples in the upper 1 cm of the sediment.
- Splitting cores to allow XRF characterization.

o Sectioning cores allow subsamples for organic proxies to be frozen for later analysis on land.

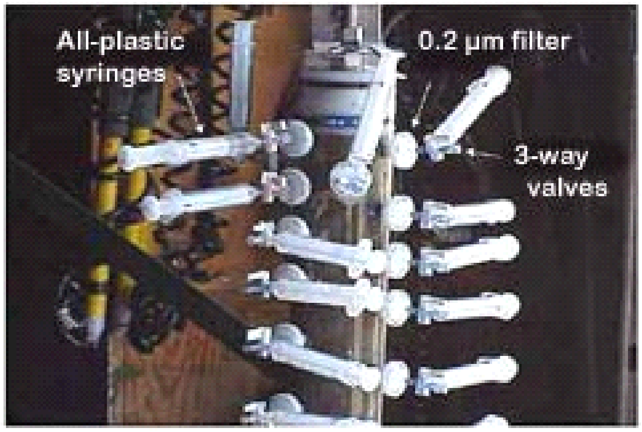


Figure 8. A "Jahnke squeezer" (Jahnke, 1988) sediment core barrel pressurized to extract pore water. Image from <http://www.glwi.uwm.edu/research/biogeochemistry/hydrothermal/yellowstone/pwYNP0

4.2.6 Analyses to support interpretation of TEI data: In addition to standard hydrography and nutrients, additional parameters are traditionally measured aboard GEOTRACES cruises to aid in interpreting TEI distributions. Supporting measurements that are expected to be of particular value for the Arctic expedition include:

o Nutrients, hydrography, oxygen.: As for other US GEOTRACES cruises, it is recommended that the SIO-ODF facility be engaged to support this work.

o To provide a more highly resolved picture of the temperature and salinity regime of our samples, particularly for the more widely spaced deep basin stations, XCTD probes (Sippican Model 1) will be deployed along the cruise track, at approximately 10km intervals.

o Tracers of ocean circulation: Circulation tracers are used to interpret the transport and internal cycling of TEIs. Tracers that are expected to be useful in the Arctic include chlorofluorocarbons, tritium-helium, radiocarbon, and products of nuclear fuel processing.

o Diagnostic tracers of freshwater source: Rivers are thought to be a large source of TEIs to the Arctic Ocean. Tracers that aid in quantifying river contributions to freshwater include oxygen isotopes and selected TEIs (e.g., Ba).

o Organic compounds that affect TEI speciation and behavior: Continental runoff and shelf sediments each supply large amounts of organic material to the Arctic Ocean that may affect TEI biogeochemistry through the formation of metal-ligand complexes. A limited characterization of the organic material, and its source, will be needed to interpret TEI distributions. Minus 80° freezer space will also be required to preserve the organic samples.

5.0 Unresolved Issues

The finalized cruise track, and attainment of the research goals described above, will ultimately depend on the disposition of plans of two other nations: 1) obtaining permission from Russia to extend a track across the Bering Strait choke point, and 2) the nature of German participation. The latter offers no difficulty other than finalizing the northward extent of the US track, so it is not discussed further.

Completing a section across the Bering Strait choke point is desirable, as it allows the evaluation of TEI fluxes from the Pacific Ocean into the Arctic. Ideally, GEOTRACES would sample for TEIs aboard the HEALY in the vicinity of a mooring array across the Bering Strait that measures temperature, salinity, water velocity and transmissivity. These data are being generated through an ongoing project led by University of Washington investigators under the direction of R. Woodgate (http://psc.apl.washington.edu/HLD/Bstrait/bstrait.html).

Anticipating that Russia may not grant clearance for the HEALY to work in Russian waters, discussions with K. Crane of NOAA have begun regarding the possibility of sampling aboard a cruise of the Russian-American Long-term Census of the Arctic (RUSALCA) program < http://www.arctic.noaa.gov/aro/russian-american/>. The Russian research vessel, the Professor Khromov, has been used to support joint Russian-US research of the RUSALCA program since 2004. Leaders of the US GEOTRACES Arctic expedition will make inquiries concerning the possibility of incorporating a limited TEI sampling program into a RUSALCA cruise, and whether or not such a cruise could also be used to train Russian students in the use of a US trace metal-clean sampling system.

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