

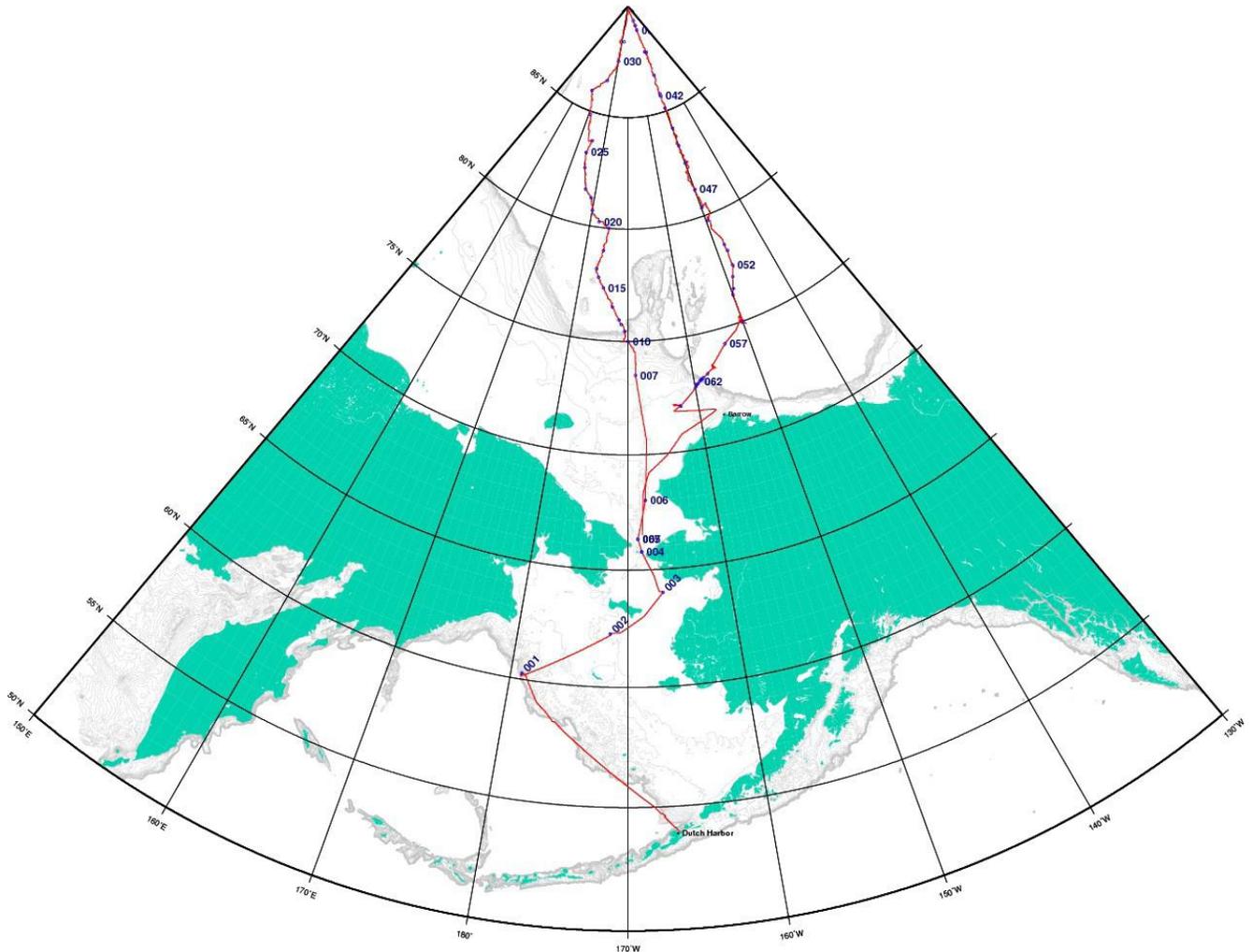
# U.S. Arctic GEOTRACES

USCGC HEALY (HLY1502)

09 August, 2015 - 12 October, 2015  
Dutch Harbor, Alaska - Dutch Harbor, Alaska

Chief Scientist: Dr David Kadko  
Florida International University

Co-Chief Scientist: Dr William Landing  
Florida State University



GEOTRACES Cruise Report

October 2015

## I. Cruise Narrative

The US Coast Guard icebreaker Healy left Dutch Harbor, AK, on schedule at 13:00 local time on 09 August, 2015. The cruise proceeded to the Rinse #1 station, then to Rinse #2 where we had a 'mini-station' to test out our various sampling systems. This proved useful as some kinks were worked out. Stations 3 through 6 went as scheduled, but we had bad seas and skipped Station 7 with the idea to return to it on the way back.

The original design of the expedition was to go counter-clockwise from station 7, up the Canada Basin, with the southward return through the Makarov Basin (figure 1). However, based on satellite imagery which indicated very heavy ice on the eastern (Canada Basin) leg of the expedition (figure 2), it was decided to do the reverse of our original plan, that is go north on the western (~ 180 W) leg and return south on the eastern (150 W leg). It was felt that the heavy ice conditions along 150 W would have led to a very inefficient use of time and fuel, potentially leading to a truncation of the expedition and its objectives. The revised plan is shown in Figure 3.

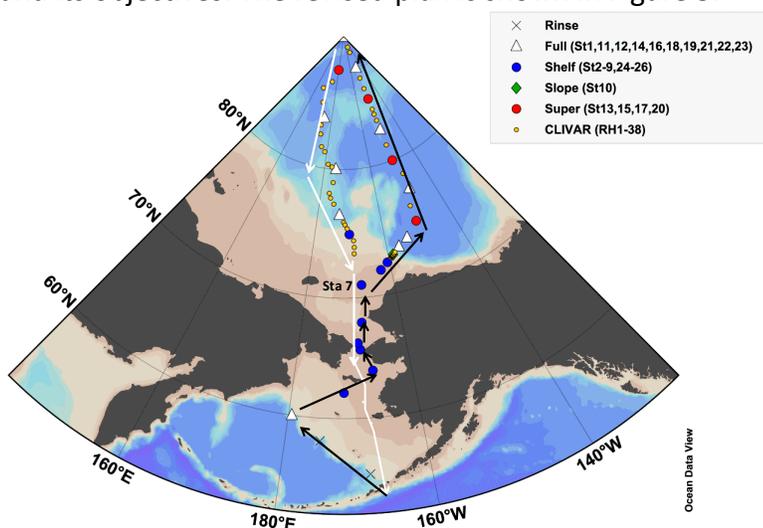


Figure 1. Original cruise plan

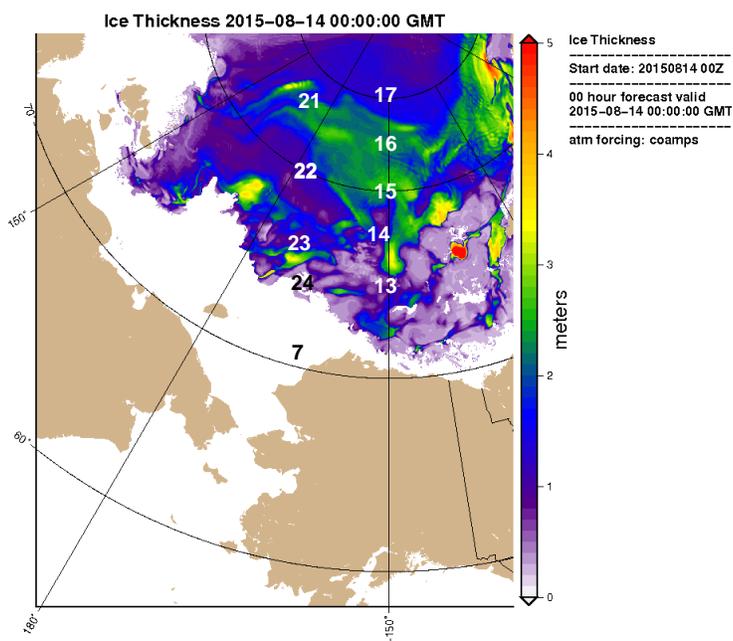
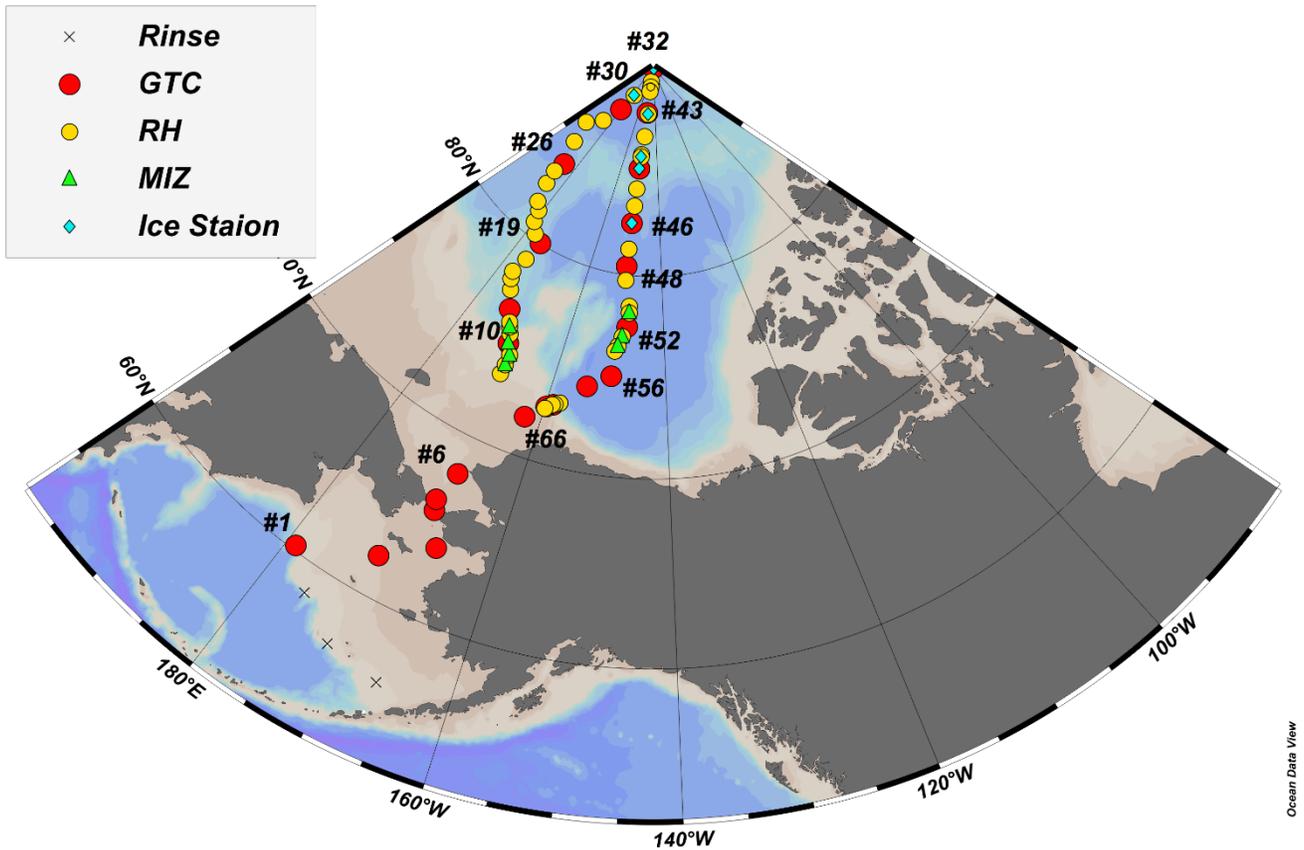


Figure 2.  
Ice thickness on Aug 14, 2015.  
Note ice thickness greater than  
3 meters on the eastern leg.

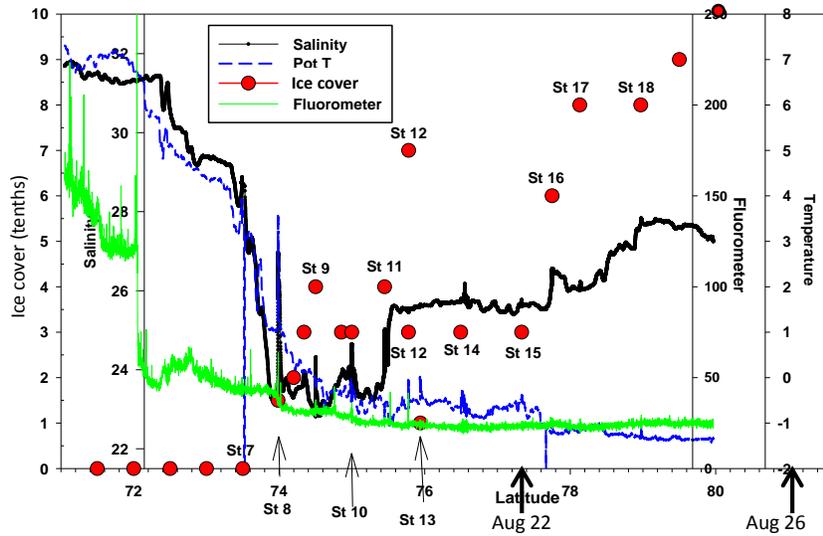


**Figure 3. Revised cruise track, heading north on the western, Makarov Basin leg, returning south along the eastern, Canada Basin leg.**

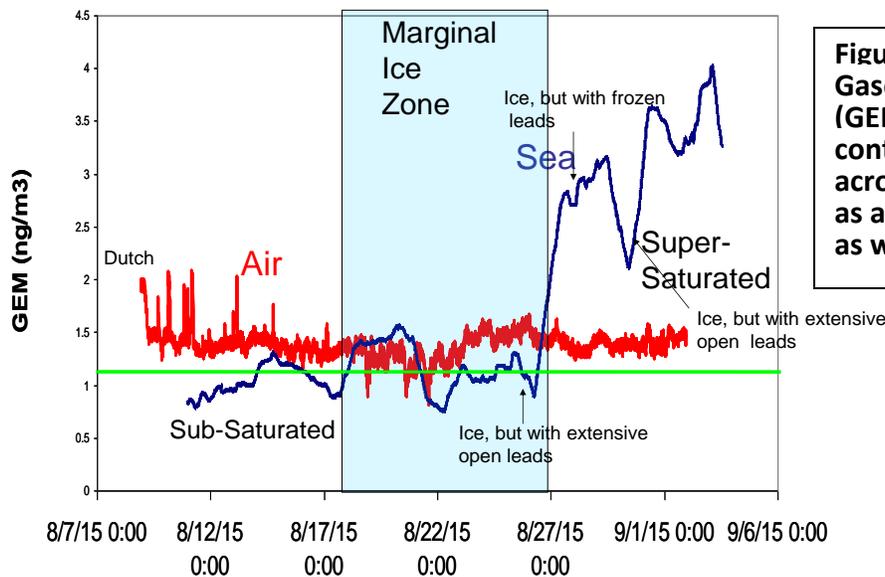
The trip north on the revised plan was very smooth. Ice conditions were surprising light. The marginal ice zone (MIZ) was encountered farther south than we anticipated, leading to the expectation of heavy ice northward. However only relatively thin ice was observed during our northward progress indicating that ice extent does not predict ice volume. For example, at 80 N and 175 W (original GT station 22) there was ~ 80% ice cover but it was thin and precluded an ice station occupation. While the lighter ice allowed us easy transit to keep on schedule, it prevented occupation of ice stations until almost the midpoint of the expedition.

The location of the MIZ corresponded to several repeat hydrography (RH) stations so we were able to utilize those locations to accomplish the MIZ station work that had been anticipated further north. The serendipitous overlap of these stations saved us further time.

The MIZ is a physically and chemically dynamic zone and we made the first ever systematic chemical measurements through it. Figure 4 shows data from the continuous seawater sampling system (from ~8m depth), illustrating the surface melt lens as the ice was approached from open water. Figure 5 shows continuous measurement of dissolved gaseous elemental Hg (GEM; Steve Brooks) through the MIZ. Clearly, ice acts as a barrier to Hg evasion after late winter and spring deposition. This was seen on large as well as local spatial scales.



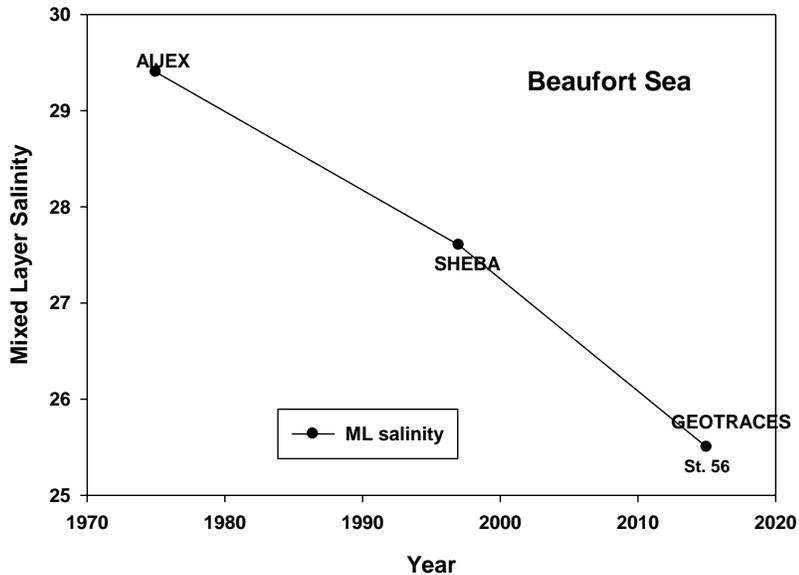
**Figure 4.** Salinity, temperature, and fluorometer readings from the continuous seawater sampling system. Red dots are the ice concentrations (in tenths) of the indicated station.



**Figure 5.** Gaseous elemental mercury (GEM) in the air and sea water via continuous seawater monitoring across the MIZ (S. Brooks). Ice acts as a barrier to Hg evasion on large as well as local spatial scales.

During the two weeks after GEOTRACES station 22 (80 N and 175 W) we continued north through the Makarov Basin. Along the way we completed 3 GEOTRACES “full” stations (an assortment of deep and shallow casts (water samples, Mclane pumps), 9 Repeat Hydrography sites (single casts) and one “Super” station (a full station with additional casts for other trace elements and isotopes). The ice along our route was surprisingly thin. Most of the ice encountered was first year ice, with the exception of some heavier ice over the Alpha Ridge. This was one of the significant observations of the expedition, and is consistent with decreasing Arctic ocean ice cover observed over recent decades and corresponding surface ocean freshening (Fig 6).

The lighter ice allowed us very fast progress, but we were unable to occupy the ice for a majority of the track. To accommodate the needs of folks who required ice for their projects, we chose to stop any place where there was ice sufficiently sturdy to occupy it. This happened on September 3, at a latitude of 88° 19.78N. This was an added station (Station 33) just for ice work (ice, snow and upper water column samples). The weather was easy to work in (about 0°C and light winds) and it was nice to get off the ship.



**Figure 6.**  
Mixed layer salinity in the area of the AIDJEX (1975) experiment, and subsequent occupations, including SHEBA (1997) and GEOTRACES station 56 (2015).

From there we proceeded to the North Pole. Approaching the pole we encountered Canadian vessels Louis S. St-Laurent and Terry Fox, on their way south. They reported light ice at the Pole which proved to be the case for us as well. There was thin ice, many leads (most refrozen) and recent snow. This required us to do some searching for a suitable ice floe for safely doing our North Pole station work.

At 11:47 (eastern time) Saturday, Sept 5, 2015 we arrived at the north pole. This was the first time a US ship arrived unaccompanied to the pole. A wonderful experience that will stay with us for a long time.

We occupied a full station at the pole. On Sept 7, we went on the ice. We had a great North Pole celebration. There was a recognition and awards ceremony led by the captain and XO. The chief scientist invited Phoebe Lam and Jessica Fitzsimmons to accept the science party awards on behalf of the science party and they performed admirably, saluting the captain smartly. Susan Becker presented Jim Swift a career polar service recognition award (this, his 3<sup>rd</sup> trip to the North Pole). This was followed by an ice liberty with Santa, football, cigars and more. Following our break, we went to work on the ice for ~10 hours. This was more difficult than the first ice station because it was colder (~ 17° F). Sampling the relatively freshwater under-ice lens was tricky because of freezing in the sampling hoses. This led to a long night (albeit in daylight).

If that wasn't enough shortly after our work we were visited by the German ship POLARSTERN, also a GEOTRACES venture. We had about a 5 hour exchange of folks and that was exciting. Our friend and colleague from POLARSTERN, Michiel Rutgers von der Loeff, afterwards wrote from his ship "The ship is still vibrating from the wonderful experience yesterday. What a chance that we finally managed to have this meeting and exchange, such a welcome happening for all on board. And a landmark for GEOTRACES. "

We departed the North Pole on September 7, 2015, to undertake our track south toward Alaska, across the Canada Basin, continuing our series of GEOTRACES and Repeat Hydrography stations. From

the North Pole to ~81.3 N, we completed another 2 full, and one super GEOTRACES stations. Four ice stations were occupied bringing the total to 6. Ice conditions and weather precluded us from doing any more ice station work for the remainder of the cruise. There were also 8 RH stations completed in this interval. Going south, we could sense a change of season, experiencing snowfall and losing daylight. The Coast Guard preferred to do our cast operations at night, and drive when there was better light to navigate ice ridges. The temperature dropped (~10° F, not counting wind chill), making work on the ice and deck less comfortable and taking a toll on equipment (e.g. CTDs, ship cranes). This is a harsh environment. Although things were breaking we were able to maintain our schedule. Remarkably, although we drove through the thickest ice of the expedition, there were extended leads, miles long, crisscrossing our route. We were able to follow these at a relatively rapid pace (7kts or more). This translated to a tremendous savings of time. On September 22, we occupied a planned superstation at 80 N, 148 W (station 48, originally GT station 15). Station work then preceded smoothly through September 28, where we finished our 54<sup>th</sup> station, the last of a series of MIZ stations which included a full station (station 52, originally GT 14).

Unfortunately weather conditions led to a truncation of station 56 (Sept 29, 2015), the cross-over station with the Canadian GEOTRACES program (originally GT 13). Several operations were accomplished, but ultimately the station was abandoned. Severe wire angle for the aft operations made continuation of work too problematic. The Vectran conducting cable for the GEOTRACES rosette had to be inspected but it was not damaged. The Vectran trawl wire for the Mclane pumps was damaged and some hundreds of meters were removed. The weather forced us to skip the next full station (original GT 12) but on October 2, we accomplished all tasks at station 57 (GT 11) and continued through 2 more RH stations and Station 60 (GT 10) which was a slope station (SBI 3) at ~900 m depth.

After Station 60, the weather forecast did not look good. As the RH stations required only a cast from the starboard winch, which was more manageable for the HEALY than aft operations, it was decided to shoot over to the more complex SBI 2 station, (depth = 80 m, station 61, old GT 9) and there do a concurrent RH cast. The plan was to return to the intervening RH stations as weather permitted. This we were able to do, with stations 62-65 being RH casts in depths of 290 m, 160 m, 520 m and 66 m respectively. On Oct 10 we proceeded to station SBI 1 (Station 66, old GT 8). We were able to accomplish all tasks under the worsening seas. With deteriorating weather, this was to be our last science operation. We never could get back to old GT 7, and did not re-occupy the 2 Bering Strait mooring sites that we had sampled early during the expedition.

### **Summary Statement and Acknowledgements**

Our original plan was a highly ambitious one. Thinner than expected ice allowed relatively rapid transit, which, when coupled with extremely efficient deck deployments, led to a fulfillment of nearly all our over-the-side operations, both from the GEOTRACES and Repeat Hydrography perspectives. Ironically those same ice conditions which facilitated smooth station progress hindered the ability to perform all the ice stations we had hoped for, although we did attain 60% of our most optimistic expectation in that regard. Deteriorating weather conditions near the expedition's end cost us only a small fraction of our intended goals. In the end we occupied 66 combined GEOTRACES, Repeat Hydrography, and ice stations. Given the highly complex nature of this expedition, which included the harsh environment, uncertainties of weather and ice, diversity of scientific operations, and working within an unfamiliar military framework, this expedition was an enormous success which all participants can be proud of.

This accomplishment is the result of extraordinary collaborative and cooperative actions by many.

We thank our international partners, the Chemical Oceanography Program and Office of Polar Programs of the National Science Foundation, our colleagues in the GEOTRACES community and the US Steering Committee, the Repeat Hydrography Program, and the crew of the USCGC Healy, including Capt. Jason Hamilton, and Cmdrs. Karl Lander and William Woityra.

## **2. Individual Science Programs**

### **GEOTRACES carousel sampling.**

The Cutter (ODU) group provided the GEOTRACES Clean Carousel sampling system (GTC), including the Dynacon winch with 7300 m of Vectran cable with conductors, clean lab, and Seabird carousel/CTD with 24 12L GO-FLO bottles (and 14 spares). Simone Moos (MIT) and Gabrielle Weiss (UH) were the “super technicians” in charge of the trace element sampling itself, while Lisa Oswald (ODU) oversaw the logistics and sample logging, including maintaining the HLY1502 cruise Event Log for the entire cruise. GO-FLO particulate sampling was covered under another grant and Peter Morton (FSU) and Sara Raushenberg (Bigelow) took care of this sampling effort. ODU graduate student Kyle McQuiggan and Greg Cutter ran the GTC sampling operations (data acquisition, winch operations), assisted by Bill Schmoker and Carl Lamborg.

In total, 39 GTC hydrocasts were conducted and 2 GO-FLOs per depth were triggered, one for filtration with Acropak capsules and one for 25mm membrane filtration (Supor, 0.4  $\mu\text{m}$ ). An average of 17 sample bottles were filled from each Acropak-filtered GO-FLO, and 6 from the membrane-filtered GO-FLO. The membranes were then stored for subsequent particle analyses by Ben Twining (Bigelow Lab) and Peter Morton (FSU). For the 27 stations occupied, which includes shelf, slope, MIZ, and Full and Super stations in the deep Makarov and Canada Basins, this represented the acquisition of over 5662 trace element samples. Shipboard analyses of Al, Mn, and Fe (UH), Hg (UCSC) and Zn (FSU) indicated intermittent contamination for some GO-FLOs, and these were replaced with a backup bottle upon discovery of a consistent contamination pattern. Most samples were taken from the GTC in support of shore-based analysis. Including these, the following groups received samples: Anderson (LDEO; colloidal Th); Boyle (MIT; Cr and Pb isotopes); Cutter (ODU; shipboard As and shore-based Se); Fitzsimmons (TAMU; colloidal TEIs); Hatta/Measures (UH; shipboard Al, Fe, Mn); John (USC; TEI isotopes); Lam/Heller (UCSC; Fe(II)); Lamborg (USCS; Hg); Landing/Wyatt (FSU; shipboard Zn); Saito (WHOI; Co); Shiller (USM; Ba, Ga, V). It should also be noted that bad weather and possible damage to the GTC cable did not allow us to use the GTC at the last Super Station (Station 56) that had been designated as the US/Canada crossover for GEOTRACES intercalibration. Thus, at the last Full station in the Canada Basin four replicate samples for the suite of TEIs were taken and will be distributed to relevant Canadian colleagues to facilitate intercalibration.

### **Shipboard As determinations**

Because the chemical speciation of arsenic is not stable with storage, ODU graduate student Zoe Wambaugh made shipboard determinations of dissolved arsenic speciation (As[III], As[V], monomethyl As, dimethyl As) at 17 stations, including all shelf stations and three ice stations. She

analyzed over 200 samples using a selective hydride generation, cryogenic trapping, and gas chromatography/photoionization detection method. As[III] ranged from 0-0.1 nM (except at Station 61 at the Canada Basin/Chukchi slope where it went from 0.05 nM in the surface to 0.3nM at the bottom) and usually between 0 and 0.1 nM when we were in the ice. Total As ([III]+[V]) ranged from 8-24 nM, while monomethyl As was 0.3-3 nM and dimethyl As ranged from 0.03-2 nM. In general, these concentrations are similar to other ocean basins with the exception of As[III], which was much lower and indicates far less biological uptake of As[V] and subsequent detoxification via reduction to As[III].

### **Th, Pa, Nd, and REE Sampling**

At each of the Arctic GEOTRACES stations there were dedicated casts for collecting three 5-liter samples for a) long-lived Th isotopes ( $^{232}\text{Th}$  and  $^{230}\text{Th}$ ) and  $^{231}\text{Pa}$ , b) Nd isotopes and the REEs, and c) an archive sample for future use. Sampling was carried out by Tim Kenna and Marty Fleisher. Initially, the ODF 12-place 30 liter Niskin bottle rosette was used to collect the water samples. Fairly early on, it was decided that there were advantages to using the ODF 36-place 10 liter Bullister bottle rosette instead, tripping three bottles/depth to get to the desired 30 liter volume required for dissolved gases, tracers, carbon parameters, nutrients, salts and dissolved oxygen, as well as our three 5-liter samples and other filtered samples mentioned below. At select stations, the 10 liter bottles allowed us the flexibility to combine our sampling with that of the Th, Ra, pigment casts and/or the artificial radionuclide casts. We were well supported and assisted by the ODF and STARC crew throughout the cruise.

The Th/Pa/Nd/REE group collected more than 1100 5-liter cubitainers of water. Samples were filtered by gravity through Teflon-lined Tygon tubing and Supor Acropak 500 capsule filters (0.8/0.4  $\mu\text{m}$  pore size). Immediately after collection, the samples were acidified to pH=2 with 20 ml of distilled 6 Molar HCl, caps were parafilmed, and then samples were double-bagged, then stored in pallet boxes. One-third of the samples will be analyzed by the Th/Pa groups (Bob Anderson Lab at Lamont and Larry Edwards Lab at UConn), one-third will be analyzed by the Nd/REE groups (Brian Haley at OSU, Steve Goldstein at Lamont and Howie Scher at U. South Carolina). The archive sample is kept at Lamont, for distribution to the above labs for reanalysis of questionable samples or for future analysis of non-contamination prone trace elements.

Along with the above-mentioned sampling by others, we also collected unfiltered 200 ml samples for Lignin Phenols (~125 samples for Rainer Amon, Texas A&M) at specified stations. Other Acropak capsule filtered samples collected were 1) duplicate 60 ml samples for  $^{15}\text{N}$  in Nitrate analyses (~350 samples for Julie Grainger, UConn) at all stations, as well as duplicate samples for  $^{15}\text{N}$  in Nitrite at shelf stations, 2) 4 liter samples for Silicon isotope measurements (~200 samples for Mark Brzezinski, UCSB), and 3) 100ml Hg Thiol samples (~100 for Carl Lamborg, UCSC).

At selected stations, 125 ml subsamples were taken from the 5 liter Th/Pa cubitainer for measuring colloidal  $^{232}\text{Th}$ . Four 15 ml aliquots were filtered through a 10 kDa Amicon centrifugal filtration unit. The Amicon filtered solution and the remainder of the initial subsample were acidified to pH=2 with 200 $\mu\text{l}$  of distilled 6M HCl.

### **Total $^{234}\text{Th}$ (Particulate and Dissolved) Collection and Analyses**

Total  $^{234}\text{Th}$  samples were collected at 31 stations of 66 (combined Repeat Hydrography and

GEOTRACES stations). At full (9) and super (4) stations, total  $^{234}\text{Th}$  samples were collected from 30 L Niskins on mid-water and deep McLane pump casts and from the ODF rosette on the (shallow) Ra/Th/pigment cast. At shelf and slope stations (7), total  $^{234}\text{Th}$  samples were collected from the shallow ODF cast. In two instances where a depth was missed on the McLane pump casts, the ODF rosette was used to retrieve samples from the missing depths. At Station 32, the makeup cast was given a new station number (Station 34). Eight samples were typically retrieved from per pump cast, and 12 samples per Ra/Th/Pigment cast. Of the 12 samples collected on Ra/Th/Pigment casts, 8 matched the pump depths from the shallow pump cast and the remaining 4 depths were chosen based on features observed in the station's CTD data. Samples at the MIZ (8) and Ice (2) stations were collected using a combination of the ODF shallow cast and  $^7\text{Be}$  pumping. At these stations 1-4 depths were sampled from the upper 70 m of the water column.

For each sample, approximately 4 liters of seawater were collected from each Niskin using volumetrically pre-calibrated bottles. A 50.39 dpm/g  $^{230}\text{Th}$  spike was added to each sample for recovery calculations. Total  $^{234}\text{Th}$  was then precipitated using additions of  $\text{KMnO}_4$  and  $\text{MnCl}_2$ . Preliminary sample processing and analyses using RISO Laboratory Anti-coincidence Beta Counters were completed on board. In summary, 337 total  $^{234}\text{Th}$  samples were collected and processed by Erin Black and Steven Pike.

#### **CFC Sampling** (on board personnel Hickman and Gorman).

The Lamont CFC group measured F12, F11, F113, and SF6 on US Arctic Geotraces 2015. A total of 1140 samples were collected from a 12 place rosette and a 36 place rosette. A total of 66 stations were sampled. The samples were collected in 500 ml bottles and were measured on a purge-and-trap sampling system in tandem with a gas chromatograph. Underway CFC and SF6 sampling was done with an automated flow through system. Water samples were taken from the uncontaminated seawater line and analyzed at approximately 15 minute intervals. The automated system strips CFCs and SF6 gasses from the water sample and sends them to a gas chromatograph for analysis. Processing and analysis of the chromatograms will be done ashore.

#### **Zn Sampling**

Over 300 sub-samples for dissolved zinc (dZn) determination were collected from 25 GTC casts (Neil Wyatt). All sub-samples were filtered (0.2  $\mu\text{m}$  AcroPak Supor), acidified (0.024 M q-HCl) and then analyzed shipboard for dZn using flow-injection analysis, as first described by Nowicki *et al.* (1994). In addition, dZn sub-samples were collected and analyzed during 6 ice stations and 19 small-boat operations using the same procedures. Data generated onboard served a dual purpose: 1) to validate the sample collection methods by highlighting any potential contamination sources in real-time and 2) to determine the distribution and biogeochemistry of dZn in the Western Arctic Ocean. The accuracy of the method was assessed by repeat quantification of dZn in SAFe and GEOTRACES reference seawater samples. The data generated onboard was reported to the shipboard data assembly system and each measurement assigned a data quality flag. A series of shipboard contamination tests were performed to test individual GO-FLO bottles for potential Zn contamination. Finally, in addition to the shipboard determinations, sub-samples were collected from a single GTC cast by Wyatt and Fitzsimmons to assess the adsorption and recovery of trace metals when using low-density

polyethylene sub-sample bottles. These sub-samples were collected and stored for shore-based ICPMS determinations of dissolved trace metals at Florida State University.

### **Particulate Analysis (Morton/Twining/Rauschenberg)**

Samples for Synchrotron X-ray Fluorescence (SXRF) and ICP-MS analyses were collected at **18 vertical profile stations, 7 marginal ice zone stations, and 6 ice stations** during the GEOTRACES Arctic Section cruise.

**SXRF:** Unfiltered water samples were taken for SXRF analysis from select depths of the GEOTRACES GO-FLO rosette, small boat, melt ponds, ice and under-ice water. Samples were preserved with 0.25% trace metal clean buffered glutaraldehyde and centrifuged onto C/formvar-coated Au TEM grids and SiN windows. Using an inverted Leica microscope, transmitted light (differential interference contrast) and chlorophyll autofluorescence images of the cells were collected along with X,Y,Z coordinates on the grids. One hundred and eighty four grids were prepared for analysis.

**Bulk particulate samples:** Four hundred and five suspended particulate matter (SPM) samples are being stored for analysis via HR-ICP-MS, including: 328 water column and small boat samples, a variety of ice samples (including under ice, melt pond, and snow), and associated process blanks. Using the GEOTRACES GO-FLO rosette, SPM samples were collected at each depth sampled (3-24 depths per station) directly from 6 psi pressurized GO-FLO bottles onto membranes (25mm Supor 0.45 $\mu$ m polyethersulfone) which were mounted in Swinnex polypropylene filter sandwiches. An average of 6 L of water was filtered through each membrane. Water from the small boat was collected in a 4-L acid-washed carboy, and pressurized with 0.2- $\mu$ m filtered air to force water through a 25-mm Supor 0.45 $\mu$ m membrane held in Swinnex polypropylene filter sandwiches. Unfiltered under-ice and melt pond samples were filtered shipboard using a similar set-up (4-L carboy through 25-mm Supor 0.45  $\mu$ m filter). Snow was collected in a 2-L polycarbonate tub, melted shipboard to a liquid volume of 600-900 mL, and filtered using the 4-L carboy/25-mm Supor filter set-up.

### **Ultrafiltration (Fitzsimmons)**

Two ultrafiltration methods were used to separate the truly dissolved (“soluble”) metal fraction from the colloidal fraction in various samples: a 10 kDa (3 nm, Pellicon XL) cross flow filtration system and a 20 nm membrane filtration system (Anodisc). Ultrafiltered samples will be analyzed in the Fitzsimmons laboratory at Texas A&M University using ICP-MS techniques for Fe, Mn, Cu, Cd, Zn, and Ni concentrations along with the <0.2  $\mu$ m “dissolved” samples collected using the GTC rosette; all three samples analyzed together from a single depth will reveal the relative contributions of small (3-20 nm) and large (20-200 nm) colloids to the dissolved metal fraction. 387 total dissolved (<0.2  $\mu$ m) samples were collected in 250mL volumes. 381 x 60mL samples were collected through the Anopore membrane (<20 nm), including 337 seawater samples from the GTC rosette, 18 samples from the ice hole, 6 snow samples, 16 sea ice samples (including 10 from two sectioned ice cores in collaboration with Ana Aguilar-Islas and Rob Rember), and 4 meltpond samples. 362 x 60mL samples were collected through the cross flow filtration system - one permeate (<10 kDa) and one retentate 60mL bottle from each of 181 sampling events – including 137 seawater samples from the GTC rosette, 18 samples from the ice hole sampling, 6 snow samples, 16 sea ice samples (including 10 from the sectioned ice cores), and 4 meltpond samples.

In addition, ultrafiltered samples were provided collaboratively to several other groups. 102 x 60mL <20 nm filtered seawater samples and 54 x 1L cross flow filtered (<3 nm) samples from the Super stations and the SBI transect were provided to Marty Fleischer and Bob Anderson in order to calculate the partitioning of Th isotopes into soluble and colloidal fractions. 130 x 1L cross flow filtered

samples were provided to Seth John in order to determine whether soluble and colloidal Fe have variable Fe isotope ratios in seawater, which would suggest different sources or different controlling processes for soluble and colloidal Fe. 62 x 250mL cross flow filtered samples were provided to Katlin Bowman in order to calculate the relative contribution of soluble and colloidal Hg fractions to total dissolved mercury in seawater. Finally, a collaboration with Chris Marsay and Cliff Buck investigated the partitioning of solubilized aerosols into soluble and colloidal fractions by ultrafiltering aerosol leachate with Anopore (<0.02 µm) filters and also completing aerosol leaches using ultrafiltered (<3 nm) seawater. These experiments were completed at odd-numbered aerosol deployments (n=7) in triplicate.

### **Shipboard trace metal analysis: Dissolved Al, Fe, and Mn**

Sampling for dissolved Al, Fe, and Mn was accomplished using the dedicated GEOTRACES trace-element rosette with 24 Teflon-coated, 12 L General Oceanics GO-FLO bottles. The University of Hawaii group (Hatta and Measures) performed shipboard determinations on subsamples of water taken from these bottles and filtered using a 0.2 µm Acropak filter by the subsampling team. Subsamples were collected into acid-washed 125 mL PMP bottles, acidified to 0.024M HCl and analyzed shipboard for dissolved Al, Fe & Mn using flow injection analyses (Resing and Measures, 1994; Measures et al., 1995, Resing and Mottl, 1992 respectively). A total of 411 trace metal samples were collected at 28 GEOTRACES water column stations. Included in this total were samples collected at nominal depths of 1, 5 and 20m from under the sea ice at 6 stations, using a portable pumping system. At these same stations samples of melted snow (6 samples), sea-ice (5 samples), and where available melt ponds (5 samples) were also obtained. These latter samples were also filtered through the 0.2 µm Acropak filter. The precision of each of the methods was established by replicate determination of the same sample at the beginning of a day's run the values were typically: 2.1% for Al at 12.8nM; 0.67% for Fe at 2.97 nM, and 1.16% for Mn at 2.7 nM.

### **<sup>7</sup>Be measurements**

Samples of water, snow, ice, aerosols and particles were collected for <sup>7</sup>Be analyses (Kadko, Stephens, Aguilar). Water for <sup>7</sup>Be was pumped into barrels on deck (500-700L) with a submersible pump to depths as great as 50m. At first, a self-recording profiling CTD (Seabird 37) was attached to the pump to determine exact depths, but after the fact it was observed that wire angles at times caused us to miss intended target depths chosen by prior CTD casts at the station. Subsequently, we switched to a cabled CTD system (Seabird 19plus) which enabled real-time determination of depth, temperature and salinity. The water was then pumped out of the barrels through Fe-coated acrylic fibers. On the ice, water was pumped through a hydrohole directly into the fibers. Typically, water was taken from 0.5, 1.5m and 5m depth below the ice-water interface, determined with the self-recording profiling CTD. Snow and ice cores were melted and <sup>7</sup>Be was collected by Fe-hydroxide precipitation in the presence of a stable Be carrier. Aerosols will be provided by C. Buck, and particulate samples on filters by P. Lam. All samples will be counted by high resolution, low background gamma spectrometry.

### **Mercury in the Air and Seawater**

Mason, Brooks and Moore were responsible for monitoring dissolved gaseous mercury (DGM) in the seawater, its equivalent, gaseous elemental mercury (GEM) in the air, oxidized mercury species in air, oxidation precursors in air, and aerosols.

In the absence of sea ice, the surface waters were, on average, slightly sub-saturated. Within the marginal ice zone the water was a mix of sub-saturated and super-saturated. In the contiguous ice the

water was strongly super-saturated (Figure 5). The reverse occurred on the return leg North Pole to Dutch Harbor. Ice appears to act as a barrier to evasion after late winter and spring deposition (Feb-June). This has obvious ramifications for a future ice-free seasonal Arctic, and predicted decrease in maximum annual ice coverage.

Concurrent measurements of oxidized mercury species, and their atmospheric radical precursors indicated that during this period of the year (Aug-Oct) the production and deposition of oxidized mercury species is negligible. This lack of summer/fall chemistry has been noted at Barrow and Alert, and now appears to be pan-Arctic.

### **Ocean Mercury**

On-board: Alison Agather, Dr. Katlin Bowman, Dr. Carl Lamborg

On-shore: Dr. Chad Hammerschmidt

Activities:

- 1) Received samples from GEOTRACES Clean Rosette (GTC) for on-board analysis of dissolved total mercury, dissolved elemental mercury, dissolved dimethylmercury and dissolved monomethylmercury. Analytical problems prevented most of the samples for dissolved monomethylmercury to be analyzed at sea. Thus, we archived as many samples as possible for later on-shore analysis. A lack of adequate containers meant that some depths and stations were skipped for this one parameter. We also participated in the GEOTRACES Clean Rosette deployment. Number of samples: dissolved total, dimethyl, elemental mercury: 364; dissolved monomethylmercury: 249
- 2) Received samples from the McLane in-situ pumps for particulate total mercury and particulate monomethylmercury. Samples were stored frozen on-board for later analysis. Number of samples: 266
- 3) Received samples from the ODF Rosette for dissolved thiol analysis. Samples stored frozen for on-shore analysis. Number of samples: 152
- 4) Received samples from the McLane in-situ pumps for particulate thiol analysis. Samples were stored frozen on-board for later analysis. Number of samples: 266
- 5) Deployed Sterivex filter cassettes on McLane in-situ pumps for genomic analysis on-shore. Number of samples: 200
- 6) Participated in on-ice sampling of snow, ice cores and under-ice seawater. Seawater samples received and analyzed on-board as with the GTC samples (numbers included in categories above).
- 7) Processed ice cores for Mason/Brooks/Moore team collected at the ice stations. 8 cores.
- 8) Received and stored samples of melt ponds and precipitation generated by Landing/Buck team for the Mason/Brooks/Moore team.
- 9) Sampled ODF rosette and received samples from surface water (Aquilari/Remember team) for pigment analysis (analysis coordinated by Cutter team).
- 10) Participated in outreach activities through on-board blogging (Bowman and Agather).
- 11) Participated in science communication/education on-board at science meetings (Bowman), through seminar to Coast Guard and science audiences (Lamborg) and by lecturing in the coast guard oceanography class (Agather).
- 12) Collected water for Arctic Ocean intercomparison with international collaborators.

Preliminary findings: The range in mercury concentrations were not dramatically different than other basins studied, but the distribution is quite different. For example, total Hg concentrations are enhanced in the surface and quite low at depth (Figure 7), in contrast to our findings elsewhere. This is perhaps due to the age of the water (intermediate/deep waters along the transect are of Atlantic origin and hundreds of years old) and the relative weakness of Arctic Ocean productivity, resulting in little injection of Hg into deeper waters via either the biological pump or transport of pollution

mercury from the solubility pump associated with deep water formation in the North Atlantic. We also had tantalizing results from a few stations suggesting sea ice might be a location for the production of dimethylmercury.

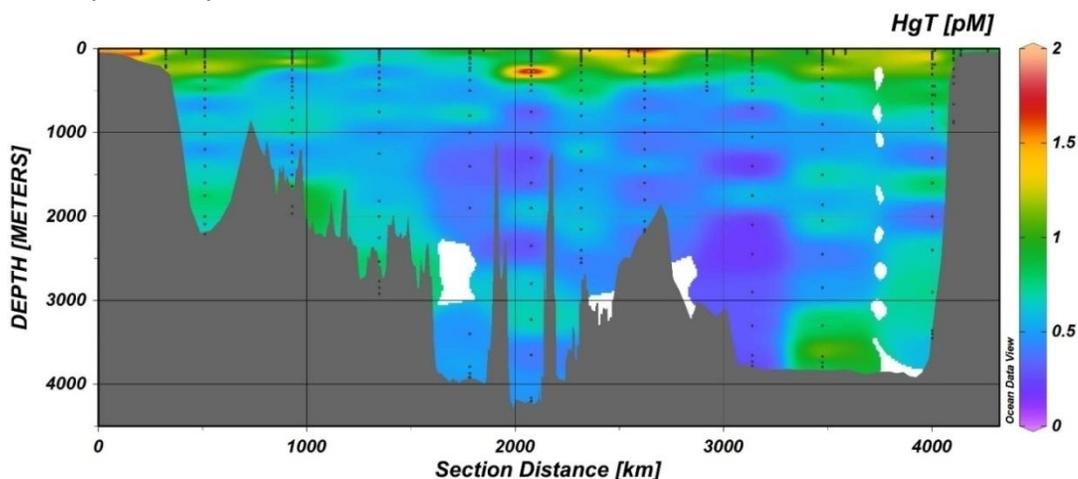


Figure 7. Total Hg across the HLY-1502 section

### Dissolved Inorganic Carbon Isotopes (L. Whitmore)

Dissolved Inorganic Carbon ( $^{13}\text{C}/^{12}\text{C}$ ,  $^{14}\text{C}$ ) samples (for Quay lab) were collected at 64 stations (Repeat Hydrography and Geotraces stations). There were 66 total stations, and one Repeat Hydrography station was omitted (Station #7/66), and station 34 did not have DIC operations. At Repeat Hydrography stations two surface samples were collected. At Geotraces 'shelf' stations (6 total), four depths were sampled one time each. At Geotraces 'slope' stations (3 total), the number of samples varied depending on the depth – one sample was collected at each depth. At Geotraces 'basin' stations (12 total), regardless of full or super designation, 24 depths were sampled once each.

Exceptions occurred on stations 14 and 56. Station 14, a basin station, had a niskin run out of volume before a sample could be collected. Station 56, due to weather, was cut short and only the deep section (12 samples) was collected.

At each ice station (6 total) a sample was collected from the '1 m Ice Hole' and the 'Bulk Snow.'

All samples were 250 mL total volume and were poisoned with 100  $\mu\text{L}$   $\text{HgCl}_2$ . Total, 418 DIC-isotope samples were collected throughout the duration of the expedition. Samples will be processed at University of Washington and other institutes.

### Dissolved Gases ( $\text{N}_2/\text{Ar}$ ) and $\text{N}_2\text{O}$ (L. Whitmore)

Sixty milliliter dissolved gas samples were collected for Altabet in duplicate at 25 Geotraces stations (no ice stations) and some Repeat Hydrography Stations (3 total). Samples from Repeat Hydrography stations were collected from 12 depths of the surface 500 m. The Repeat Hydrography samples should enable improved slope characterization for the Beaufort Shelf – Canada Basin region. Each sample was poisoned with 500  $\mu\text{L}$   $\text{HCl}$  in the sampling bay. In total, 742 dissolved gas samples were collected.

One hundred sixty milliliter  $\text{N}_2\text{O}$  samples were collected at all Geotraces 'shelf' and stations 57, 60, and 61. These samples were poisoned with 200  $\mu\text{L}$   $\text{HgCl}_2$  in post. A total of 61  $\text{N}_2\text{O}$  samples were collected.

### **Dissolved Methane (L. Whitmore)**

Methane (Shiller/Whitmore) was monitored in the HLY1502 transect by two distinct methods. The first method is the continuous surface seawater system. A Weiss-type equilibrator was used to generate an equilibrated headspace that was measured every 13 seconds on a Picarro methane analyzer (G2301). Bow air was also measured every hour for a duration of 2-5 minutes. These measurements combined with ship windspeed data will enable flux calculations for the bulk of the ship's transit. The second method for monitoring dissolved methane was a discrete system. Samples were collected at 25 Geotraces stations (7 'shelf', 3 'slope', and 15 'basin'/'MIZ'). In the early stages of the expedition, duplicate samples were taken when available, primarily on the shelf. Due to water budget constraints, duplicate samples were cut from the cruise plan. Across the Beaufort Shelf – Canada Basin seven Repeat hydrography stations were sampled to allow for a better defined SBI transect. Seventy milliliter samples were collected into 140 mL syringes with 3-way gas-tight Leur-Lock valves. In post, a 70 mL methane-free headspace was generated. Samples equilibrated for approximately 30 minutes. The equilibrated headspace was then measured on a Picarro methane analyzer (G2301).

In total, 501 discrete seawater samples were collected and processed aboard ship.

Shiller – other:

In addition, the GEOTRACES Super-techs collected subsamples for Ba, Ga, and V.

### **Po-210/Pb-210 Analysis (K. Krupp onboard)**

Samples for Po-210/Pb-210 analysis were collected from 4 super stations, 3 shelf stations, 1 full station, 1 pacific end member station, 6 ice stations, 2 dirty ice events, and from 14 aerosol deployments. The number of water samples ranged from 16-24 depths for super stations and 3-6 depths for shelf/end member stations. These samples were collected from the ODF rosette and filtered using 0.2um Acropack filters. Two additional filtered water samples were taken from 8L niskins attached atop the multicorer instrument at two separate shelf stations. Four unfiltered water samples were collected for intercalibration between the Dr. Baskaran and Dr. Maiti laboratories (collected from 1 full station and 1 super station (original GT 15)). The particulate samples collected by McLane pumps for associated dissolved water samples will be sent to the participating labs for analysis upon completion of the cruise. Samples collected at ice stations included snow, melt pond water, under ice water, and ice cores. All samples were collected unfiltered and subsequently filtered in the onboard lab for analysis of both particulate and dissolved phases. The 2 dirty ice events were conducted between stations using a man basket and each event included a community sample which was divided among seven groups. Aerosol deployments were conducted every three or four days, depending on the total run time of the pumps.

Dissolved water samples from the shelf stations and 2 of the 4 super stations (original GT13, 15) were acidified and stored for shipment to Dr. Maiti's laboratory where they will be processed. All of the remaining samples were processed onboard by Katie Krupp. Dissolved seawater/melted ice station samples were processed by co-precipitation using an iron carrier followed by electroplating to silver planchets. Particle samples and aerosols were leached with acids and plated in the same manner. A known amount of Po-209 spike was added to each sample for determination of Po-210 recovery. These planchets and sample solutions will be brought back to Wayne State University for alpha counting and further processing in order to measure Pb-210 and thus determine the Po-210/Pb-210 ratio for each sample collected. In summary, approximately 310 samples were collected for polonium-210 and lead-210 analysis on the 2015 Arctic GEOTRACES cruise.

## **Meltpond sampling**

Melt ponds were sampled at Stations 33, 38, 42, 43 and 46 (Landing/Marsay/Wyatt). A battery-powered peristaltic pump and silicone tubing were used to fill a carboy for shipboard filtration (Acropak-200, <0.2  $\mu\text{m}$ ) and subsampling for numerous contamination prone TEI samples inside the main lab bubble (subsampling carried out by Morton/Weiss). Carboys were also filled for analysis of non-contamination prone TEIs. At each station, the melt ponds were frozen over, so a hole was drilled using the TM-clean corer. Salinity was measured at each melt pond following sampling.

## **Aerosol and precipitation sampling:**

Aerosol samples were collected over periods of three to five days using five high-volume aerosol samplers. Three samplers were used to collect aerosols on acid-cleaned Whatman-41 (cellulose) filters for analysis of inorganic trace elements and isotopes (TEIs) and a fourth was fitted with pre-combusted glass-fiber filters (GFF) or quartz microfiber (QMA) filters for analysis of organic species, Hg and nitrogen compounds. The fifth sampler was equipped with a five-stage Sierra-style slotted cascade impactor to collect size-fractionated aerosols (from >7  $\mu\text{m}$  to <0.49  $\mu\text{m}$ ). All aerosol samples will be analyzed for ultra-high purity (UHP) water-soluble, seawater soluble and total TEIs at Skidaway Institute of Oceanography and Florida State University. Replicate sample filters will be shared with collaborators for analysis of a large suite of TEIs and organic compounds. Air mass back-trajectories for all sampling times will be modeled using the NOAA HYSPLIT program.

In total, 14 aerosol filter deployments/collections were made, resulting in:

- 14  $\times$  36 Whatman-41 filters (frozen for storage)
- 14  $\times$  12 GFF/QMA filters (frozen for storage)
- 9  $\times$  5 impactor filter stages and backing filters (frozen for storage)

Unused filters of each type were also set aside for blank analysis.

UHP-water and filtered seawater leaches were carried out on aerosol-laden W41 filters while at sea. In collaboration with Jessica Fitzsimmons (Texas A & M), leaches were also carried out with seawater that had been filtered through Millipore filters (0.025  $\mu\text{m}$  pore-size), Anopore filters (0.02  $\mu\text{m}$  pore size) and with ultra-filtered seawater (<10 kDa), in order to study the importance of colloidal ligands in aerosol Fe solubility. These leaches included:

- UHP-water – 30  $\times$  100ml sample leaches and 9  $\times$  100ml blanks; 95ml acidified to 0.024M HCl for TEI analysis; 5ml frozen for major anion analysis.
- Filtered seawater – 39  $\times$  100ml sample leaches and 12  $\times$  100ml blanks; acidified to 0.024 M HCl.
- Filtered seawater (Anopore) – 21  $\times$  50ml sample leaches (blanks as for filtered seawater); acidified to 0.024 M HCl.
- Filtered seawater (Millipore) – 36  $\times$  50ml sample leaches and 10  $\times$  50ml blanks; acidified to 0.024 M HCl.
- Ultra-filtered seawater – 21  $\times$  50ml sample leaches and 9  $\times$  50 ml blanks; acidified to 0.024 M HCl.

Additional aerosol sample collection was carried out using three samplers provided by Yuan Gao (Rutgers). These included:

1. A 10-stage MOUDI (Micro-Orifice Uniform Deposit Impactor) sampler to collect size-segregated aerosol samples on Teflon filters (8 sets of samples and 2 sets of deployment blanks collected).
2. A Chemcomb portable bulk aerosol sampler to collect aerosol particles for Fe speciation (14 samples and one deployment blank collected).
3. A “streaker” sampler to collect aerosols for individual particle analyses to study aerosol composition and morphology (19 samples and one deployment blank collected).

Two automated rain samplers were used to collect rain/snow (one dedicated to samples for analysis of multiple TEIs and the second designated for samples for Hg analysis) and two cut-off 2L polycarbonate bottles were used to collect falling/blowing snow. Due to low rainfall, all but one sample from the rain samplers consisted of an UHP-water rinse of the collection funnel/bottle, with the rinse recovered for analysis. In total, precipitation samples resulted in:

- 9 UHP-rinse samples and 2 deployment blanks collected using the rain samplers (multiple TEIs, Hg, major anions).
- 1 large rainfall event using the rain samplers (80ml for filtered and unfiltered TEIs, major anions, particulate TEIs; 70ml unfiltered for Hg).
- 6 snow samples collected using cut-off 2L bottles (6 for unfiltered TEIs and major anions, 3 samples for filtered TEIs, major anions and particulate TEIs, 1 sample for water soluble organic matter (WSOM) and black carbon particulates).

#### **Small Boat operations** (A. Aguilar-Islas and R. Rember)

A surface seawater sample (1 m) was collected from a small boat at open water stations (except those where weather did not allow small boat operations). This sample was taken to complete the vertical profiles from the GT rosette which had its shallowest sample at 20 m. Samples were collected using a battery powered pump and Teflon-lined PVC tubing. Filtered (0.2  $\mu$ m supor) and unfiltered samples were collected at 11 stations along the northward transect (Stns. 1-4, 6, 8-10, 12, 14, 17), and at 8 stations along the southward transect (Stns. 51-54, 57, 60-61, 66). At each station a homogenized 25L carboy sample was filtered on board the small boat, and subsampled into community provided bottles inside the main lab bubble. At station 10 due to issues with the pump an unfiltered carboy sample was collected by submerging the carboy into the water from the small boat. On-board analysis determined this sample was grossly contaminated for Zn. At station 51 to reduce the time spent on the small boat during rough weather conditions, an unfiltered carboy sample was collected with the pump and filtered on board. Carboy subsampling was done by super techs or by J. Fitzsimmons, P. Morton, C. Marsay or N. Wyatt. Approximately 30 subsamples were taken at each station for a total of about 570 community subsamples (See Appendix II).

#### **Sea Ice operations** (A. Aguilar-Islas, R. Rember and K. Dilliaine)

Snow, ice cores and water under the ice was collected from the six sea ice stations (Table 1). The strategy to position sea ice station locations alongside water stations for concurrent operations was not always possible, and Stations 31, 33, 39 and 42 were not in the immediate vicinity of water stations, while stations 43 and 46 were associated with the water stations of the same number. Ice stations were constricted north of 88.4° N on the northward leg, and north of 82.5° N on the southward leg of the cruise. This narrow latitudinal range resulted from a combination of ice conditions, weather conditions, and available time.

**Table 1 – Ice station Summary**

| Ice Station | Longitude | Latitude | Nearest station |
|-------------|-----------|----------|-----------------|
| 31          | 183.33W   | 88.42N   | Station 30      |
| 33          | 3.529E    | 89.96N   | Station 32      |
| 39          | 149.61W   | 87.78N   | Station 38      |
| 42          | 150.54W   | 85.74N   | Station 43      |
| 43          | 150.00W   | 85.16N   |                 |
| 46          | 149.83W   | 82.49N   |                 |

**Bulk Snow.** Bulk snow for contamination prone elements was collected with an acid clean high density polyethylene shovel into a low density polyethylene drum liner. Discrete snow samples were also collected in community provided containers. The bulk snow was melted on board, filtered through a Supor 0.2 um filter membrane and subsampled into community provided bottles by A. Aguilar-Islas and R. Rember. Twenty subsamples were taken at each station for a total of 120 snow subsamples (See Appendix II).

**Bulk Sea Ice.** A homogenized melted bulk sea ice sample was generated from 4 cores collected with the TM-clean ice corer at each ice station. The four cores were melted on board, filtered through a supor 0.2 um filter membrane into a 25 L carboy, and subsampled into community provided bottles by A. Aguilar-Islas and R. Rember. Fourteen subsamples were taken at each station for a total of 84 bulk sea ice subsamples (See Appendix II).

**Community Sea Ice Cores.** Discrete ice cores were collected for individual PIs at all stations. Cores were collected with the TM-clean corer for the Hg group (Mason), and with the Kovaks corer for all others. Twelve to fifteen cores were taken at each station for a total of 85 sea ice community cores (See Appendix II).

**Sea Ice Characterization.** Discrete ice cores were collected to characterize the sampled ice floe. This included 10 cores for addressing the heterogeneity of trace metal distribution in sea ice, and 6 cores for characterizing physical and biological parameters. In total 16 ice cores were taken at each station for a total of 96 characterization cores. Other ice station work consisted of snow and ice thickness surveys, visually recording above and under ice conditions, obtaining data on light penetration through the snow/ice column and on air temperature changes during station occupation, and conducting a vertical plankton tow.

**Collection of Seawater under the Ice.** Seawater samples were collected from under the ice at three depths with the same pumping system used for small boat operations. The first depth was approximately 0.5 to 1 m under the ice, and collected samples at this depth are considered surface water column samples. The second depth was from 5 m below the water surface to match the shallowest ODF rosette sampled depth. The third depth was from 20 m below the water surface to match the shallowest GT rosette sampled depth. Filtered (0.2 um Supor) and unfiltered samples were collected from these depths. Similar to small boat ops, a homogenized 25 L carboy sample was collected and subsampled into community provided bottles inside the main lab bubble. The carboy from stations 33 and 46 were filtered onboard. Carboy subsampling was done by super techs or by P. Morton, N. Wyatt, or W. Landing. To reduce the time spent on the ice, non-contamination prone samples were collected unfiltered, and were filtered (Acropak 500) on board by M. Fleisher. The suite of subsamples distributed to the community from seawater collected at ice stations vary depending on location. Approximately 75 subsamples were taken at each station for a total of about 450 seawater subsamples (See Appendix II). Several cruise participants helped during sea ice operations. In

particular C. Lamborg, S. Rauschenberg, J. Fitzimmonds., K. Bowman and K. McQuiggan assisted during sample collection at all ice stations.

**Summary:** In total distributed community subsamples include; 1,070 seawater, 120 snow, 84 melted sea ice, and 85 frozen ice cores.

**Conservative tracers (3He/3H, Oxygen isotopes)**

A total of 356 water samples for measurement of <sup>3</sup>H, He, and <sup>3</sup>He/<sup>4</sup>He ratios were collected at GT stations. An additional 74 water samples were collected at CLIVAR stations 58, 59, 62-65 along the Canadian Basin Slope. An additional 6 water samples for tritium measurements have been obtained at every ice station from the Ice Hole, 1m depth events.

**3He-3H** - Water samples for the measurement of <sup>3</sup>H were collected in 1000 ml glass bottles. The bottles were rinsed in water from the Niskin bottle to be sampled, filled, and sealed using polypro-lined caps and electrical tape. The samples for helium and its isotopes were collected in crimped copper tubes, fixed to aluminum channels. Tritium and helium measurements will be made at the Lamont Doherty Earth Observatory’s Environmental Tracers Laboratory. Tritium and helium can add valuable information to the basic hydrography on mean pathways and regions of vertical or horizontal mixing. Non-tritogenic <sup>3</sup>He enters the ocean as a dissolved gas at geothermally active spots. It is used as a tracer for deep waters, which have been in contact with hydrothermal vents. Finally, the <sup>3</sup>H/<sup>3</sup>He ratio is used to estimate the apparent age of water masses that have been in contact with the surface within the past several decades.

**Oxygen isotope ratios** - A total of 1022 water samples were collected for measurement of <sup>18</sup>O/<sup>16</sup>O ratios at all depths (GT stations), and in the upper 500m (CLIVAR stations). Additional samples were obtained from Small Boat events (15 samples), and selected ice floe sampling events (total of 28; See Table 2).

Water samples for the measurement of oxygen isotope ratios were collected in 50 ml glass bottles. The bottles were rinsed in water from the Niskin bottle to be sampled, filled, and sealed using polypro-lined caps and electrical tape. Oxygen isotope ratios will be measured at Lamont Doherty Earth Observatory using a Picarro L2130-I Analyzer. Combined with salinity and nutrients, oxygen isotope ratios are useful in distinguishing freshwater components in the upper Arctic Ocean.

| Event        | <sup>3</sup> H | <sup>18</sup> O |
|--------------|----------------|-----------------|
| Ice Hole 1m  | 6              | 6               |
| Ice Hole 5m  | 6              | 0               |
| Ice Hole 20m | 6              | 0               |
| Ice Bulk     | 6              | 0               |
| Melt Pond    | 4              | 0               |

**Pumping Operations**

Phoebe Lam, Steve Pike, Erin Black, Lauren Kipp

**I. Sample collection by McLane In Situ Pumps**

**Sampling overview**

Modified dual-flowpath battery-powered McLane in-situ pumps (McLane WTS-LV) were used to collect size-fractionated small (<51 μm) and large (>51 μm) particles and short lived dissolved radium and thorium isotopes using a Mn-coated cartridge during the HLY1502 Arctic GEOTRACES voyage. At most stations and depths, a second Mn-coated cartridge was used to collect actinium isotopes. Where the second Mn-coated cartridge was not deployed, a second cartridge coated with

FeCuCN was deployed to collect cesium isotopes. Finally, small Sterivex cartridges were deployed at select stations through a third, unmetred flowpath to collect samples for mercury genomics.

### By the numbers

In-situ pump samples were collected at a total of 20 stations (6 shelf, 1 slope, 9 full, 4 super) over 33 casts (1 cast/shelf station, 1/slope, 1-2/full; 1-3/super). At full stations, a shallow cast of 8 pumps covered the upper 500-750m, and a deep cast of 8 pumps covered the rest of the water column. At 2 super stations (stations 30, 48), a third pump cast of 8 pumps increased sampling resolution to 24 from the typical 16 depths to match the resolution sampled by the ODF and GTC rosettes. **A total of 233 depths were sampled by the various pump media (various filter and cartridge types). Filter subsamples and cartridges will be analyzed for over 25 parameters by 19 groups** (see Table 3 for PI and parameter information).

### Operational overview

Up to eight pumps were clamped onto a 0.322" OD Hytrel-jacketed, non-conducting Vectran hydrowire from the "3/8" " winch deployed off the stern A-frame of the USCGC Healy. Pumping time was typically four hours, but was reduced to three hours at some of the final shelf stations because of concerns with drifting into shallower waters during pumping. Deployment and recovery took 2-6 hours depending on water column depth. A typical shelf station took a total of 5 hours; a shallow cast took ~6 hours, and a deep cast took ~9-10 hours.

Shallow McLane pump casts were followed by a dedicated ODF rosette cast to collect water for pigments,  $^{234}\text{Th}$ , and  $^{226}\text{Ra}$  to determine efficiency of the  $\text{MnO}_2$ -coated cartridges for Ra. In lieu of a dedicated ODF cast for all mid-water and deep pump casts, a 30 liter Niskin bottle was hung above each pump to collect water for  $^{234}\text{Th}$  and  $^{226}\text{Ra}$ . Bottles were tripped by Teflon-coated messenger at mid-cast, with large lanyards to allow bypass of the pumps. The calm but cold conditions of Arctic waters presented challenges for both the pumps and the messenger-tripped Niskin bottles. The motor cable on the pump frequently shorted out, halting pumping soon after starting. This problem was mostly alleviated by using silicone sealant in the cable connections. The cold, calm conditions also led to problems with messengers not always releasing, and getting caught on extremely small edges. This was solved by making lanyard loops smaller and filing down edges on which the lanyards could be caught.

A self-recording profiling CTD (SeaCAT 19plus) with WETLabs ECO-FL-NTU fluorometer/turbidity sensor, SBE43 oxygen sensor, and WETLabs C-star transmissometer, was shackled to the end of the line for 12 of the 33 casts in the early part of the cruise. The CTD developed increasingly severe problems, partially exacerbated by freezing temperatures that damaged sensors, and was no longer deployed after station 32. An RBR Deepwater D Virtuoso pressure sensor was attached on a pump on every cast: on casts in which the CTD was at the end of the line, the RBR pressure sensor was usually attached on a pump about halfway up the line to provide additional depth control; on casts in which the CTD was not deployed, the RBR pressure sensor was attached to the bottom-most pump. The CTD and/or RBR pressure sensors were used to correct for the actual depth of the pumps, making the assumption that the wire angle was constant for the entire length of deployed cable. A 12 kHz pinger was attached to the CTD at the beginning of the cruise, but the ship's 12 kHz transducer could only pick up a faint signal to ~500m water depth, and was unable to pick up its signal deeper than that. The pinger was no longer deployed after the first couple of full water column stations.

Target pump sampling depths were chosen to match a subset of the ODF and GTC sampling depths. At ice-covered stations, a good, vertical wire angle was generally maintained during pumping, so target and actual pump depths were very similar. At open water stations, significant wire angles

(>20°) during pumping were a consistent problem, and actual depths were sometimes several tens of meters off of the target GEOTRACES depths.

#### Wire damage incident

Half an hour before the end of pumping at station 56, the wire tended to port and got caught on the aft side of the A-frame, abrading through the protective Hytrel jacket and fraying a few strands of the Vectran strength member. The wire out was 643m. The wire was released from the A-frame by A-framing out, but then tended hard outboard (>70° outboard wire angle), and the pump string was towed for ~half an hour before commencing recovery. The damaged section was recovered while the wire tended hard outboard, and an Amsteel safety line was attached above and below the ~4' damaged section at the 01 deck to complete recovery of the pumps. All pumps were recovered safely. The >51um size fraction particles were likely lost during the half hour of towing. Hopefully, the 1-51um particle samples and cartridge samples will be ok. This station was subsequently aborted due to continued bad weather. The next day, the wire was unspooled on deck and the bottom 650m was cut. The line was re-terminated with a stopper line.

#### Filter Holder Configuration

Two sets of filter holders were deployed on each pump: the “QMA side” consisted of a 51um polyester prefilter, backed by a 150um polyester support filter (not analyzed), followed by a pair of 1um (nominal) Whatman quartz fiber (“QMA”) filters, backed by a 150um polyester support filter (not analyzed); the “Supor side” consisted of a 51um polyester prefilter, backed by a 150um polyester support filter (not analyzed), followed by a pair of 0.8um polyethersulfone filters (“Supor800”) filters. Paired filters increase the collection efficiency of particles beyond the nominal pore size of a single filter. The top and bottom QMA filters together collect ~0.8um (approximate, and depends on particle type). The top and bottom Supor filters together collect ~0.6um (approximate, and depends on particle type) (Bishop et al., 2012 Limnology and Oceanography Methods).

The median volumes pumped through the “QMA”-side filter holder, the “Supor”-side filter holder, and the Mn-coated cartridges were 928L, 396L, and 1382L, respectively. A total of 286,868 liters was filtered over the entire cruise.

After primary filtration, the QMA and Supor flowpaths combined and passed through MnO<sub>2</sub>-impregnated acrylic cartridge filters to scavenge dissolved Ra/Th and Ac or Cs isotopes. Both the primary QMA and Supor flowpaths and the combined pump outflow were flow-metered independently to determine volumes collected.

A set blank filters was deployed on every cast for each of the primary QMA and Supor filter holders. These “dipped blank” filters were complete filter sets wrapped in a 1um polyester mesh, and sandwiched in a perforated polypropylene container that was zip-tied to a pump in or near the clear water minimum. Dipped blank filters were handled and processed identically to active filters.

## **II. Surface sampling for Ra isotopes**

At all GEOTRACES and Repeat Hydrography stations, ~280 L of surface water was collected and filtered through Mn-oxide coated acrylic fibers to collect Ra isotopes. In total, 69 samples were collected. At stations when Be-7 was sampled, water was collected using the pump used by the Kadko lab; at all other stations water was collected using a submersible pump deployed over the starboard side of the ship to ~2 m depth. At sea, these surface samples were processed in a similar manner to the MnO<sub>2</sub> pump cartridge samples. They were analyzed for short-lived Ra isotopes on the ship-board RaDeCC system by Lauren Kipp.

**Table 3: List of samples distributed from McLane Pumps**

| <b>PI</b>                               | <b>What</b>                             |
|---|---|
| <b>SUPOR--0.8-51um particles</b>        |   |
| Ed Boyle                                | Pb isotopes                             |
| Mark Brzezinski                         | Si isotopes                             |
| Brian Haley                             | Nd isotopes                             |
| Seth John                               | Fe isotopes leach                       |
| Seth John                               | Fe isotopes total                       |
| Bob Anderson                            | 230Th, 231Pa                            |
| Phoebe Lam                              | pTM, lithogenic particles               |
| Phoebe Lam                              | biogenic silica (bSi)                   |
| Greg Cutter                             | Se, As                                  |
| Ben Twining/Pete Morton                 | bioTM                                   |
| <b>QMA--1-51um particles</b>            |   |
| Chad Hammerschmidt                      | Hg species                              |
| Carl Lamborg                            | Thiols                                  |
| Mak Saito                               | proteins                                |
| Phoebe Lam                              | PIC, POC, d13C                          |
| Ken Buesseler                           | 234Th                                   |
| David Kadko                             | 7Be                                     |
| Matt Charette                           | 228Th, Ra                               |
| Julie Granger                           | d15N                                    |
| Kanchan Maiti                           | 210Pb/210Po                             |
| Mark Baskaran                           | 210Pb/210Po                             |
| Tim Kenna                               | 239Pu, 240Pu, 237Np, 137Cs,<br>and 90Sr |
| <b>SP &gt;51um prefilter over Supor</b> |   |
| Ken Buesseler                           | 234Th                                   |
| Julie Granger                           | d15N                                    |
| Phoebe Lam                              | POC, d13C                               |
| <b>QP &gt;51um prefilter over QMA</b>   |   |
| Phoebe Lam                              | pTM, lithogenic particles               |
| Phoebe Lam                              | PIC                                     |
| Phoebe Lam                              | bSi                                     |
| Kanchan Maiti                           | 210Pb/210Po                             |
| Mark Baskaran                           | 210Pb/210Po                             |
| Bob Anderson                            | 230Th, 231Pa                            |
| Mark Brzezinski                         | Si isotopes                             |
| <b>Cartridges</b>                       |   |
| Matt Charette                           | Ra isotopes                             |
| Doug Hammond                            | Actinium isotopes                       |
| Tim Kenna                               | Cs isotopes                             |
| Carl Lamborg                            | Hg genomics                             |

## **Pumping Appendix: sample processing notes**

### Size-Fractionated Particle Sample Processing

After each pump was recovered, seawater in the filter holder headspaces was drawn down on deck when temperatures were  $>-3^{\circ}$ , or in the bubble if temperatures were colder because of seawater freezing in the lines. All handling was conducted using trace-element handling techniques and acid-cleaned plastic equipment. Wedge-shaped subsamples of 51 $\mu$ m prefilters and paired Supor filters were cut using a ceramic rotary blade on a clear, acrylic plate on a light-box. Sub-samples of paired QMA filters were removed using acrylic and/or stainless steel circular punches. Sub-sampled filters and pre-filters were photographed under a fixed light source/camera rig for archival purposes. The QMA-side prefilter ("Qp") and Supor filters ("S") were dried at room temperature under a HEPA-filtered hood. The Supor-side prefilter ("Sp") QMA filters ("Q") were handed to the Buesseler group (Erin Black and Steve Pike): the "Sp" filter was rinsed onto a 25mm 1 $\mu$ m Ag filter using filtered seawater and dried in a 59 $^{\circ}$ C oven. The QMA filters ("Q") were also dried in a 59 $^{\circ}$ C oven. After  $>6$  hours, dried "Qp" and "S" filters were transferred into cleanroom bags. All primary filter processing and sub-sampling was conducted by Phoebe Lam with help from Maija Heller and Yang Xiang.

### Large Volume Ra/Th/Ac Sample Processing and At-Sea Radium Counting

MnO<sub>2</sub>-impregnated sample cartridges for Ra/Th/Ac radionuclide collection were removed from the pumps after cast recovery and rinsed with radium-free freshwater to remove salt. Cartridges were dried to dampness prior to shipboard measurement of short-lived radium isotopes. <sup>224</sup>Ra ( $t_{1/2} = 3.7$  d) and <sup>223</sup>Ra ( $t_{1/2} = 11.4$  d) were measured on the Radium Delayed Coincidence Counter (RaDeCC) system and typically counted within 24 h of sample collection. All cartridge filter processing and counting for radium was conducted by Lauren Kipp. Scavenging efficiencies of the cartridge filters for Ra and Th is validated by a discrete seawater sample taken in parallel with every pump depth sampled. For shallow pump cast depths, this calibration sample was collected by the ODF Niskin rosette; for mid-water and deep pump casts, a 30 L Niskin bottle was hung next to each pump and bottles were triggered by messenger at mid-cast. For <sup>226</sup>Ra, 20-25 L seawater was passed over a column of MnO<sub>2</sub> impregnated acrylic fiber on deck, which removes radium at 100% efficiency. These filter samples were bagged and will be analyzed for <sup>226</sup>Ra through its daughter, <sup>222</sup>Rn back in land-based laboratories. Efficiency filter samples were collected by Erin Black and processed by Lauren Kipp.

## **Pigments**

Pigment samples were collected during the cruise from the ODF rosette (on casts shared with the radium/thorium group), from the surface by small boat and from below sea ice at three depths at ice stations. In all, 117 samples were collected at 23 stations. In most cases, the samples consisted of 2-L of seawater filtered through glass fiber filters and then folded into cryovials, wrapped in tin foil and wet frozen at -80 on board. Analysis of the pigments will be done at Oregon State University.

**Dissolved Fe(II):**

Shipboard measurements were performed by Dr. Maija Heller for Fe(II) following a method by King et al. (1995). Selected profiles are presented in Figures 8-9. The required PMT for analysis was borrowed on board of FS Polarstern (Germany) at the North Pole from NIOZ scientist (Micha Rijkenberg, Netherlands), since the PMT owned by UCSC (USA) was damaged at the very beginning of the cruise, likely by a bad power supply.

- 117 samples were analysed from the Geotraces carousel from Stn 38-66 (see table 1),
- 5 ice samples from Stn 43 /46; , (operated by Ana Aguilar, Rob Rember)
- 3 small boat surface samples from Stn 60,61,66, (operated by Ana Aguilar, Rob Rember)
- 1 Multicorer niskin sample from Stn 66; (operated by Greg Cutter)

**Table 4: Stations sampled for dFe(II)**

| Station |                          | Number of samples |
|---------|--------------------------|-------------------|
| 38      | Full station             | 24                |
| 43      | Super Station+ Ice       | 26                |
| 46      | Full Station+ Ice        | 15                |
| 48      | Super Station            | 24                |
| 51      | MIZ Station              | 3                 |
| 52      | Full station             | 24                |
| 53      | MIZ Station              | 3                 |
| 54      | MIZ Station              | 3                 |
| 57      | Full station             | 24                |
| 60      | Full station             | 12                |
| 61      | Full station             | 3                 |
| 66      | Full station+ Multicorer | 4                 |

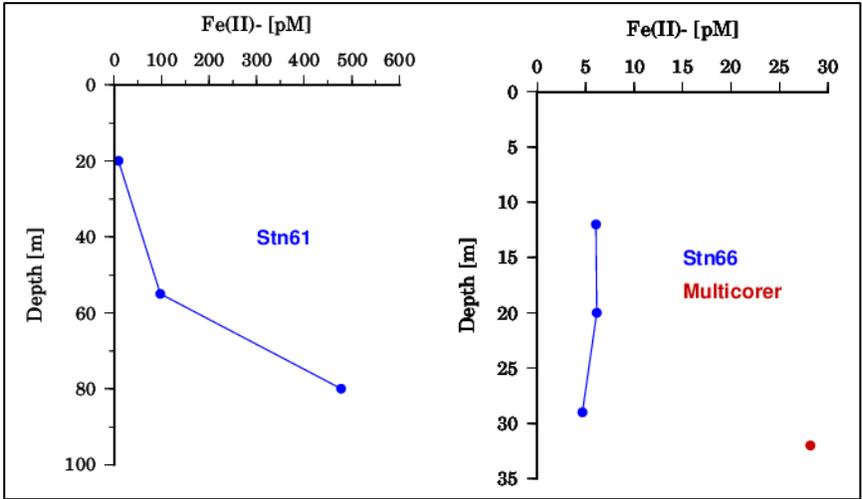
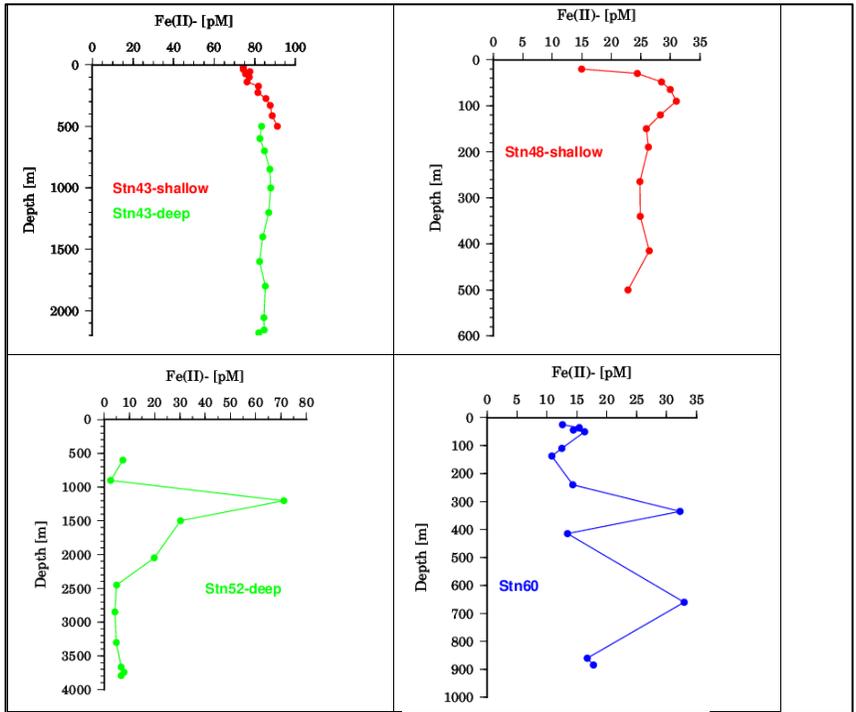


Fig. 8: Selected dFe(II) profiles obtained from the GTC and one Multicorer niskin sample at Stn66

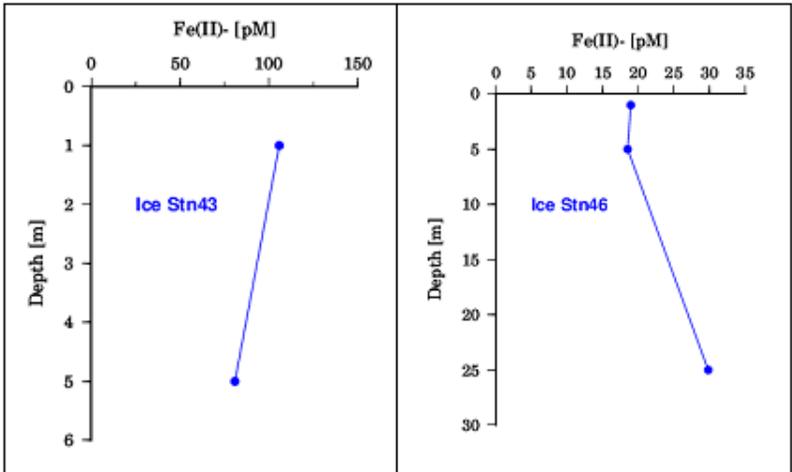


Fig 9: dFe(II) values obtained from ice samples at Stn43 & 46.

### **3. Outreach Efforts from the ship for Arctic GEOTRACES**

Significant effort was invested in outreach for the US Arctic GEOTRACES program. We had a number of ongoing cruise “blogs” as well as significant representation at home university web sites and the ship’s shore-based web site.

1. Bill Schmoker, our on-board PolarTREC science teacher, posted over 65 blogs (with descriptive text and photos) to the PolarTREC web site:

[www.polartrec.com/expeditions/us-arctic-geotraces/journals](http://www.polartrec.com/expeditions/us-arctic-geotraces/journals)

2. Dr. Peter Morton’s blog: <http://SeaPeteRun.tumblr.com>;

3. Dr. Katlin Bowman’s blogs: <http://hginthesea.wordpress.com>; [www.huffingtonpost.com/katlin-bowman/](http://www.huffingtonpost.com/katlin-bowman/)

4. Alison Agather’s blog: <http://alisonsarcticadventure.wordpress.com>

5. Laura Whitmore’s blog: <http://healy-polar-usm.tumblr.com>

6. Dr. Jim Swift: <http://ushydro.ucsd.edu/outreach>

7. Andrew Margolin’s blog: <http://arctic-andy-usaos2015.blogspot.com>;

[http://instagram.com/arctic\\_andy/](http://instagram.com/arctic_andy/); [http://twitter.com/arctic\\_andy](http://twitter.com/arctic_andy); <http://rsmas.miami.edu/blog/>

8. Dr. Tim Kenna’s blog: TRACES of Change in the Arctic:

<http://blogs.ei.columbia.edu/tag/traces-of-change-in-the-arctic/>

9. Dr. Dave Kadko, Florida International University news release:

<http://news.fiu.edu/2015/08/fiu-professor-to-lead-historic-arctic-research-expedition>

10. Dr. Bill Landing’s home web site: <http://www.eoas.fsu.edu/>;

11. Dr. Ana Aguilar-Islas, University of Alaska Fairbanks news release:

<https://web.sfos.uaf.edu/wordpress/news/?p=1953>

12. Healy cruise track:

<http://icefloe.net/uscgc-healy-track-map>

13. Daily pictures from the aloft conning tower:

[http://icefloe.net/Aloftcon\\_Photos/index.php?album=2015](http://icefloe.net/Aloftcon_Photos/index.php?album=2015)

In addition, there were other outreach efforts:

14. Kawerak Conference

As part of the US Arctic GEOTRACES outreach effort, Dave Kadko, Bill Landing, Ana Aguilar-Islas put together a package for presentation at the recent Kawerak Conference in Nome. This was a meeting for rural Alaska natives and other rural Alaska residents. Ana kindly agreed to go to the meeting and make a presentation for GEOTRACES, pass out a brochure we constructed, and was available for interviews and discussions with attendees. The local radio station did a story, and it was picked up by Alaska Dispatch News.

<http://www.knom.org/wp/blog/2015/06/05/over-50-arctic-researchers-on-coast-guard-cutter-healy-preparing-north-pole-voyage/>

<http://www.adn.com/article/20150609/arctic-researchers-prepare-voyage-north-pole-aboard-coast-guards-healy>

<https://web.sfos.uaf.edu/wordpress/news/?p=1973>

15. We participated in a novel outreach project designed and coordinated by Dave Forcucci (US Coast Guard Marine Science Coordinator) to involve students and the public with an Arctic research cruise on Healy. GEOTRACES was a perfect match for the inaugural kick off of "Float your Boat". One thousand 8" long cedar boats, were commissioned (funded by GEOTRACES with 1,300 boats being the final number) from the Center for Wooden Boats (CWB.org) in Seattle, WA and distributed to school groups, scout troops, and science open-house events around the country. Students personalized their boats with bright colors and after returning to Seattle the boats were branded with floatboat.org and packed into the hold of Healy for journey to the North Pole. During the Geotraces cruise, four groups of boats were deployed on ice floes between 87.5 N and 80N on the 150 W meridian each with a small satellite buoy which were deployed by UW/APL to study ice movement. The iridium satellite-linked buoys provide an opportunistic chance for high resolution, real-time tracking of the boats for at least the short term (1 year or so). After drifting with the Arctic ice, the boats will eventually be free of its grasp and float to a distant shore to be discovered and reported. This was documented by our on-board PolarTREC teacher, Bill Schmoker, on his PolarTREC web site blog: [9-16-15 Float Your Boat](http://www.polar-trec.org/2015/09/16/float-your-boat/). The "Float Your Boat" wooden boat project: [https://urldefense.proofpoint.com/v2/url?u=http-3A\\_floatboat.org\\_&d=AwIFAg&c=1QsCMERiq7JOMEnKpsSyjg&r=ooN6\\_yXa23lQoVNTupdxFw&m=-s9xFtUQ7TpdvKaytFKJXqw2rnY1pWVDLGV22bn3xY&s=N1SpRSIb3fIsAC3VhFuB784\\_Y07IITiYXmyUxdcp\\_rDU&e=](https://urldefense.proofpoint.com/v2/url?u=http-3A_floatboat.org_&d=AwIFAg&c=1QsCMERiq7JOMEnKpsSyjg&r=ooN6_yXa23lQoVNTupdxFw&m=-s9xFtUQ7TpdvKaytFKJXqw2rnY1pWVDLGV22bn3xY&s=N1SpRSIb3fIsAC3VhFuB784_Y07IITiYXmyUxdcp_rDU&e=) ; and [https://urldefense.proofpoint.com/v2/url?u=https-3A\\_www.facebook.com\\_explorethearctic&d=AwIFAg&c=1QsCMERiq7JOMEnKpsSyjg&r=ooN6\\_yXa23lQoVNTupdxFw&m=-s9xFtUQ7TpdvKaytFKJXqw2rnY1pWVDLGV22bn3xY&s=BLrHMPzEhZLB\\_L-DIUtzozg7xwRD9txtULZVAg5Jag&e](https://urldefense.proofpoint.com/v2/url?u=https-3A_www.facebook.com_explorethearctic&d=AwIFAg&c=1QsCMERiq7JOMEnKpsSyjg&r=ooN6_yXa23lQoVNTupdxFw&m=-s9xFtUQ7TpdvKaytFKJXqw2rnY1pWVDLGV22bn3xY&s=BLrHMPzEhZLB_L-DIUtzozg7xwRD9txtULZVAg5Jag&e)

16. The coastguard offered an oceanography course to its crew for college credit. Kadko, Swift, Measures, Lam, Landing, Becker, Aguilar-Islas, and Cutter contributed lectures to this and it was a rewarding experience. Two students, Alison Agather and Lauren Kipp also did a nice job with this.

17. We presented science lectures every Wednesday night geared to the Coast Guard crew. Numerous scientists and students contributed to this activity.

#### **4. Ancillary programs**

##### **XCTD and XBT deployments**

A series of 76 combined XBTs and XCTDs were deployed by the STARC team on behalf of D. Kadko to better resolve the hydrography between sampling stations.

##### **Buoy Deployment**

As a service to the oceanographic community, we deployed buoys for outside investigators. This was handled by Paul Aguilar.

UpTempO buoys, Mike Steele, Polar Science Center, Applied Physics Laboratory, University of Washington.

1) deployed 18 Aug 2015, at 05:30 local time. Location, 79 29.35N, 168 50.89W. This is a free floating buoy with a 25m long thermistor string. Buoy records and transmits location and temperature data from the top 25m of the water column.

2) deployed 19 Aug 2015 at 14:00 local time. Location 74 59.960N, 170 39.319W. This is a free floating buoy with a 60m thermistor sting. Buoy records and transmits location and temperature data

from the upper 60m of the water column. These buoys were actuated by removing a magnet. Removal of the magnet turned the buoy on, at which point the buoy was ready to deploy. The thermistor string was gently uncoiled and hand deployed over the stern of the ship followed by the lowering of the float and instrument portion of the buoy into the ocean using a slip line.

SIMB2 Allen Float Lagrangean float, Eric D'Asaro Ocean Physics Department, Applied Physics Laboratory, University of Washington.

Deployed 22 Aug 2015, at 03:30 local time, location 77 33N, 175 10W

The deployment of the float was made more difficult than it should have been due to a problem with the rs232 to usb adapter not working. Problem was solved by using an adapter that had software built into it. The float was turned on by magnetic switch and then needed to be set up using a laptop. Once all of the parameters checked out it was deployed off the stern again using a slip line. The float remained on the surface momentarily and then sank as it was programmed to do. We were informed by email the next day that the instrument was performing as intended.

SVP Surface Velocity Profiler. These were small white floats deployed with the Float Boats, Ignatius Rigor, Polar Science Center, Applied Physics Laboratory, University of Washington.

The SVP buoys were actuated by removing a magnet approximately a day before deployment so that buoy operation could be confirmed by email with the Polar Science Center. The buoy down loads its data using a Iridium satellite link.

1) deployed 12 Sept 2015, at 15:00 local time. Location 86 084N, 149 48W. Buoy placed on the ice with float boat boxes 1 and 2 using the ships man basket and crewman with Tim Kenna.

2) deployed 16 September 2015. Time not recorded. Location 85 16N, 150 36W. The buoy and float boat boxes 3 and 4 were left on the ice at the end on an ice station.

3) deployed 19 Sept 2015. Time not recorded. Location 82 49N, 149 83W. The buoy and float boat boxes 5 and 6 were left on the ice at the end of an ice station.

4) deployed 24 Sept 2015. Time not recorded. Location 80 41N 148 58W. The buoy and the contents of float boat box 7 were deposited on the ice using the man basket from the aft port crane. Float boats were scattered on the ice and the cardboard box was returned to the ship for disposal.

### **PolarTREC Teacher- Bill Schmoker**

Bill Schmoker served as a PolarTREC teacher on the expedition. He helped out where he was needed, in particular volunteering as a bottle Sherpa for all GEOTRACES rosette casts. On ice stations he participated with coring and ice characterization efforts along with <sup>7</sup>Be pumping. He also helped with loading and unpacking operations in Seattle including aerosol sampler set-up and re-organizing the holds. He lent a hand with changing aerosol filters throughout the cruise. The bulk of his efforts centered on photography and outreach. He posted a new blog entry every day of the cruise along with entries detailing Seattle operations (<http://polartrec.com/expeditions/us-arctic-geotraces/journals>), with 70 journals posted as of 10 October. To accompany these posts he published 371 photos, which were also made available to the science team on the shared public drive during the cruise. He also edited 64 videos of different expedition aspects which will be published on the PolarTREC YouTube channel. Looking ahead, he anticipates follow-up blog posts and the creation of lesson plans to share on the PolarTREC resources page. He will explore possible speaking opportunities to present the trip to school groups, teacher organizations, and wider public audiences. He has offered the use of his roughly 5700 archived expedition photos and videos to anyone with a desire to use them.

## Appendix I Cruise Participants

| Last Name     | First Name | Institution                    | Position   | GROUP                      |
|---------------|------------|--------------------------------|------------|----------------------------|
| Agather       | Alison     | Wright State                   | student    | Hg (water)                 |
| Aguilar       | Paul       | UW, APL                        | technician | APL                        |
| Aguilar-Islas | Ana        | UA, Fairbanks                  | scientist  | Sea Ice TM                 |
| Barna         | Andrew     | Scripps                        | technician | ODF                        |
| Black         | Erin       | WHOI                           | student    | pump group                 |
| Becker        | Susan      | Scripps                        | technician | ODF                        |
| Bowman        | Katlin     | UC Santa Cruz                  | scientist  | Hg (water)                 |
| Brooks        | Steven     | Univ Tennessee Space Inst.     | scientist  | Hg (air)                   |
| Carlin        | Croy       | OSU                            | technician | STARC                      |
| Cummiskey     | John (Ted) | Scripps                        | technician | ODF                        |
| Cutter        | Greg       | ODU                            | scientist  | GTCmetalloidTM             |
| Dilliplaine   | Kyle       | UA, Fairbanks                  | technician | Sea Ice TM                 |
| Fitzsimmons   | Jessica    | TAMU                           | scientist  | micro-nut TM               |
| Gorman        | Eugene     | LDEO                           | technician | CFC, SF6 (Smethie)         |
| Gum           | Joeseph    | Scripps                        | technician | ODF                        |
| Fleisher      | Martin     | LDEO                           | technician | ODFsupertech               |
| Hatta         | Mariko     | Univ Hawaii                    | scientist  | TM,ice                     |
| Heller        | Maija      | UC Santa Cruz                  | scientist  | particles (Lam)            |
| Hembrough     | Brett      | Scripps                        | technician | STARC                      |
| Hickman       | Ben        | Univ Hawaii                    | technician | CLIVAR CFC, SF6 (Ho)       |
| Huang         | Fen        | U. Miami, RSMAS                | technician | CLIVAR carbon              |
| Kadko         | David      | FIU                            | scientist  | ChfSci, 7Be                |
| Kenna         | Tim        | LDEO                           | technician | ODFsupertech               |
| Kipp          | Lauren     | WHOI                           | student    | pump group                 |
| Krupp         | Katie      | Wayne St. Univ                 | student    | 210Pb (Baskaran)           |
| Lam           | Phoebe     | UC Santa Cruz                  | scientist  | particles (Lam)            |
| Lamborg       | Carl       | UC Santa Cruz                  | scientist  | Hg (water)                 |
| Landing       | William    | FSU                            | scientist  | Co-chief, aerosols         |
| Margolin      | Andrew     | U. Miami, RSMAS                | student    | CLIVAR carbon              |
| Marsay        | Chris      | Skidaway Inst. Ocean           | scientist  | aerosol group              |
| McQuiggan     | Kyle       | ODU                            | student    | GTC CTD                    |
| Miller        | Melissa    | Scripps                        | technician | ODF                        |
| Measures      | Chris      | Univ Hawaii                    | scientist  | TM,ice                     |
| Moos          | Simone     | MIT                            | student    | GTC supertech              |
| Morton        | Peter      | FSU                            | scientist  | TM                         |
| Oswald        | Lisa       | ODU                            | technician | GTC Mgmt                   |
| Pasqualini    | Angelica   | LDEO                           | student    | CFC, SF6 (Smethie)         |
| Pike          | Steven     | WHOI                           | technician | pump group                 |
| Rauschenberg  | Sara       | Bigelow                        | technician | particles                  |
| Rember        | Rob        | UA, Fairbanks                  | scientist  | Sea Ice TM                 |
| Schatzman     | Courtney   | Scripps                        | technician | ODF                        |
| Schmoker      | William    | Centennial Middle School, Boul | teacher    | OUTREACH                   |
| Stephens      | Mark       | FIU                            | technician | 7Be (Kadko)                |
| Swift         | James      | Scripps                        | scientist  | CLIVAR                     |
| Wambaugh      | Zoe        | ODU                            | student    | metalloidTM                |
| Weiss         | Gabrielle  | U. Hawaii                      | student    | GTC supertech              |
| Winters       | Johna      | OSU                            | technician | STARC                      |
| Woosley       | Ryan       | U. Miami, RSMAS                | scientist  | CLIVAR carbon              |
| Whitmore      | Laura      | U. South. Miss.                | student    | Ba,Ga,V (Shiller)          |
| Wyatt         | Neil       | FSU                            | scientist  | aerosol group              |
| Xiang         | Yang       | UC Santa Cruz                  | student    | Particles (Lam)/pump group |

## Appendix II US Arctic GEOTRACES Sampling operations and analytes

| Small Boat           |                |   |            |                     |                             |
|----------------------|----------------|---|------------|---------------------|-----------------------------|
| Anderson             | Bob            | colloidal $^{232}\text{Th}/^{230}\text{Th}/^{231}\text{Pa}$ | filtered   | Acropak-200 (0.2um) | boba@ldeo.columbia.edu      |
| Boyle                | Ed             | Cr(III)   | filtered   | Acropak-200 (0.2um) | eaboyle@mit.edu             |
| Boyle                | Ed             | Cr isotopes   | filtered   | Acropak-200 (0.2um) | eaboyle@mit.edu             |
| Boyle/Rember         | Ed/Rob         | Pb isotopes   | filtered   | Acropak-200 (0.2um) | eaboyle@mit.edu             |
| Cutter               | Greg           | As  | filtered   | Acropak-200 (0.2um) | gcutter@odu.edu;            |
| Cutter               | Greg           | Se  | filtered   | Acropak-200 (0.2um) | gcutter@odu.edu;            |
| Hastings/Granger     | Meredith/Julie | N- isotopes   | filtered   | Acropak-200 (0.2um) | meredith_hastings@brown.edu |
| Fitzsimmons/Sherrell | Jessica/Rob    | TEIs  | filtered   | Acropak-200 (0.2um) | jessfitz@tamu.edu           |
| Fitzsimmons/Sherrell | Jessica/Rob    | TEIs  | filtered   | Acropak-200 (0.2um) | jessfitz@tamu.edu           |
| John                 | Seth           | TM isotopes   | filtered   | Acropak-200 (0.2um) | sethjohn@usc.edu            |
| John                 | Seth           | TM isotopes   | filtered   | Acropak-200 (0.2um) | sethjohn@usc.edu            |
| Lamborg              | Carl           | organo-Hg   | filtered   | Acropak-200 (0.2um) | clamborg@ucsc.edu           |
| Lamborg              | Carl           | total Hg  | filtered   | Acropak-200 (0.2um) | clamborg@ucsc.edu           |
| Measures/Hatta       | Chris/Mariko   | Al, Mn, Fe  | filtered   | Acropak-200 (0.2um) | chrism@soest.hawaii.edu;    |
| ODF                  |                | nutrients   | filtered   | Acropak-200 (0.2um) | sbecker@ucsd.edu;           |
| ODF                  |                | salinity  | filtered   | Acropak-200 (0.2um) | sbecker@ucsd.edu;           |
| Saito                | Mak            | archive   | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;            |
| Saito                | Mak            | Co-speciation   | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;            |
| Saito                | Mak            | Co  | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;            |
| Schlosser            | Peter          | $^{18}\text{O}$   | filtered   | Acropak-200 (0.2um) | schlosser@ldeo.columbia.edu |
| Shiller              | Alan           | V, Ga, Ba   | filtered   | Acropak-200 (0.2um) | alan.shiller@usm.edu;       |
| Wyatt                | Neil/Bill      | Zn  | filtered   | Acropak-200 (0.2um) | nwyatt@fsu.edu              |
|                      |                |   |            |                     |                             |
| Lam                  | Phoebe         | particulate TEIs  | unfiltered |                     | pjlam@ucsc.edu              |
| Mason                | Rob            | total Hg  | unfiltered |                     | robert.mason@uconn.edu;     |
| Morton/Twining       | Peter/Ben      | particulate TEIs  | unfiltered |                     | pmorton@fsu.edu;            |

| Snow (ice floe)      |                |                         |            |                     |                             |
|----------------------|----------------|-------------------------|------------|---------------------|-----------------------------|
|                      |                |                         |            |                     |                             |
| Aguilar-Islas/Rember | Ana/Rob        | key TEIs                | filtered   | Acropak-200 (0.2um) | amaguilarislas@alaska.edu;  |
| Buck/Gao             | Cliff/Yuan     | TEIs, major ions        | filtered   | Acropak-200 (0.2um) | Clifton.Buck@skio.uga.edu;  |
| Cutter               | Greg           | As                      | filtered   | Acropak-200 (0.2um) | gcutter@odu.edu;            |
| Cutter               | Greg           | Se                      | filtered   | Acropak-200 (0.2um) | gcutter@odu.edu;            |
| Hastings/Granger     | Meredith/Julie | N isotopes              | filtered   | Acropak-200 (0.2um) | meredith_hastings@brown.edu |
| Fitzsimmons          | Jessica        | colloial TEIs           | filtered   | Acropak-200 (0.2um) | jessfitz@tamu.edu           |
| John                 | Seth           | TM isotopes             | filtered   | Acropak-200 (0.2um) | sethjohn@usc.edu            |
| Measures/Hatta       | Chris/Mariko   | Al, Mn, Fe              | filtered   | Acropak-200 (0.2um) | chrism@soest.hawaii.edu;    |
| ODF Nutrient         |                | nutrients               | filtered   | Acropak-200 (0.2um) | sbecker@ucsd.edu;           |
| ODF Salinity         |                | salinity                | filtered   | Acropak-200 (0.2um) | sbecker@ucsd.edu;           |
| Saito                | Mak            | Co-speciation           | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;            |
| Saito                | Mak            | Co                      | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;            |
| Shiller              | Alan           | V, Ga, Ba               | filtered   | Acropak-200 (0.2um) | alan.shiller@usm.edu;       |
| Wyatt/Landing        | Neil/Bill      | Zn                      | filtered   | Acropak-200 (0.2um) | nwyatt@fsu.edu              |
|                      |                |                         |            |                     |                             |
| Buck                 | Cliff          | particulate TEIs        | unfiltered |                     | Clifton.Buck@skio.uga.edu;  |
| Hastings             | Meredith       | N-isotopes              | unfiltered |                     | meredith_hastings@brown.edu |
| John                 | Seth           | particulate TM isotopes | unfiltered |                     | sethjohn@usc.edu            |
| Lamborg/Mason        | Carl/Rob       | Hg                      | unfiltered |                     | clamborg@ucsc.edu           |
| Morton/Twining       | Peter/Ben      | particulate TEIs        | unfiltered |                     | pmorton@fsu.edu;            |

| Seawater (under Ice Floes; 1, 5, 20m) |              |   |            |                      |                               |
|---------------------------------------|--------------|---|------------|----------------------|-------------------------------|
| Aguilar-Islas/Rember                  | Ana/Rob      | Key TEIs  | filtered   | Acropak-200 (0.2um)  | amaguliarislas@alaska.edu;    |
| Anderson                              | Bob          | colloidal $^{232}\text{Th}/^{230}\text{Th}/^{231}\text{Pa}$ | filtered   | Acropak-200 (0.2um)  | boba@ldeo.columbia.edu        |
| Boyle                                 | Ed           | Cr isotopes   | filtered   | Acropak-200 (0.2um)  | eaboyle@mit.edu               |
| Boyle                                 | Ed           | Cr(III)   | filtered   | Acropak-200 (0.2um)  | eaboyle@mit.edu               |
| Boyle/Rember                          | Ed/Rob       | Pb isotopes   | filtered   | Acropak-200 (0.2um)  | eaboyle@mit.edu               |
| Brzezinski                            | Mark         | Si isotopes   | filtered   | Acropak-200 (0.2um)  | mark.brzezinski@lifesci.ucsb. |
| Cutter                                | Greg         | As  | filtered   | Acropak-200 (0.2um)  | gcutter@odu.edu;              |
| Cutter                                | Greg         | Se  | filtered   | Acropak-200 (0.2um)  | gcutter@odu.edu;              |
| Fitzsimmons/Sherrell                  | Jessica/Rob  | colloidal ??  | filtered   | Acropak-200 (0.2um)  | jessfitz@tamu.edu             |
| Granger/Altabet                       | Julie/Mark   | nitrate $^{15}\text{N}$                                     | filtered   | Acropak-200 (0.2um)  | julie.granger@uconn.edu;      |
| Heller                                | Majja        | Fe(II)  | filtered   | Acropak-200 (0.2um)  | majjaheller@gmail.com         |
| John                                  | Seth         | TM isotopes   | filtered   | Acropak-200 (0.2um)  | sethjohn@usc.edu              |
| Lamborg                               | Carl         | organo-Hg species   | filtered   | Acropak-200 (0.2um)  | clamborg@ucsc.edu             |
| Lamborg                               | Carl         | total Hg  | filtered   | Acropak-200 (0.2um)  | clamborg@ucsc.edu             |
| Measures/Hatta                        | Chris/Mariko | Al, Mn, Fe  | filtered   | Acropak-200 (0.2um)  | chris@soest.hawaii.edu;       |
| ODF                                   |              | nutrients   | filtered   | Acropak-200 (0.2um)  | sbecker@ucsd.edu;             |
| ODF                                   |              | salinity  | filtered   | Acropak-200 (0.2um)  | sbecker@ucsd.edu;             |
| Saito                                 | Mak          | Archive   | filtered   | Acropak-200 (0.2um)  | msaito@whoi.edu;              |
| Saito                                 | Mak          | Co speciation   | filtered   | Acropak-200 (0.2um)  | msaito@whoi.edu;              |
| Saito                                 | Mak          | Co  | filtered   | Acropak-200 (0.2um)  | msaito@whoi.edu;              |
| Shiller                               | Alan         | V, Ga, Ba   | filtered   | Acropak-200 (0.2um)  | alan.shiller@usm.edu;         |
| Wyatt/Landing                         | Neil/Bill    | Zn  | filtered   | Acropak-200 (0.2um)  | nwyatt@fsu.edu                |
| Anderson                              | Bob          | $^{232}\text{Th}/^{230}\text{Th}/^{231}\text{Pa}$           | filtered   | Acropak-500 (0.45um) | boba@ldeo.columbia.edu        |
| Haley/Goldstein                       | Brian/Steve  | Nd, REE   | filtered   | Acropak-500 (0.45um) | bhaley@coas.oregonstate.edu;  |
| Kenna                                 | Tim          | Pu, Np  | filtered   | Acropak-500 (0.45um) | tkenna@ldeo.columbia.edu;     |
| Kenna                                 | Tim          | $^{236}\text{U}$  | filtered   | Acropak-500 (0.45um) | tkenna@ldeo.columbia.edu;     |
| Aguilar-Islas/Rember                  | Ana/Rob      | particulate TM  | unfiltered |                      | amaguliarislas@alaska.edu;    |
| Amon                                  | Rainer       | total lignin phenols  | unfiltered |                      | amonr@tamug.edu               |
| Baskaran/Maiti                        | Mark/Kanchan | total Pb, Po  | unfiltered |                      | baskaran@wayne.edu;           |
| Kenna                                 | Tim          | $^{129}\text{I}$  | unfiltered |                      | tkenna@ldeo.columbia.edu;     |
| Lam                                   | Phoebe       | particulate TM  | unfiltered |                      | pjam@ucsc.edu                 |
| Millero                               | Frank        | ALK/DIC/pH  | unfiltered |                      | fmillero@rsmas.miami.edu      |
| Morton/Twining                        | Peter/Ben    | particulate TM  | unfiltered |                      | pmorton@fsu.edu;              |
| Quay                                  | Paul         | C-isotopes  | unfiltered |                      | pdquay@uw.edu                 |
| Schlosser                             | Peter        | tritium, $^{18}\text{O}$                                    | unfiltered |                      | schlosser@ldeo.columbia.edu   |

| ODF Rosette; Th-Nd cast |        |   |            |                      |                                   |
|-------------------------|--------|---|------------|----------------------|-----------------------------------|
| Anderson                | Bob    | $^{232}\text{Th}/^{230}\text{Th}/^{231}\text{Pa}$ | filtered   | Acropak-500 (0.45um) | boba@ldeo.columbia.edu            |
| Brzezinski              | Mark   | Si isotopes                                       | filtered   | Acropak-500 (0.45um) | mark.brzezinski@lifesci.ucsb.edu; |
| Granger                 | Julie  | $\text{NO}_2$ $^{15}\text{N}$                     | filtered   | Acropak-500 (0.45um) | julie.granger@uconn.edu;          |
| Granger                 | Julie  | nitrate $^{15}\text{N}$                           | filtered   | Acropak-500 (0.45um) | julie.granger@uconn.edu;          |
| Haley                   | Brian  | Nd, REE   | filtered   | Acropak-500 (0.45um) | bhaley@coas.oregonstate.edu;      |
| Hansell                 | Dennis | DOC   | filtered   | GFF (0.7um)          | dhansell@rsmas.miami.edu          |
| LDEO                    |        | archive   | filtered   | Acropak-500 (0.45um) |                                   |
| Altabet                 | Mark   | $\text{N}_2/\text{Ar}$                            | unfiltered |                      | maltabet@umassd.edu               |
| Altabet                 | Mark   | $\text{N}_2\text{O}$                              | unfiltered |                      | maltabet@umassd.edu               |
| Amon                    | Rainer | lignins   | unfiltered |                      | amonr@tamug.edu                   |
| Millero                 | Frank  | ALK/DIC/pH  | unfiltered |                      | fmillero@rsmas.miami.edu          |
| ODF                     |        | oxygen  | unfiltered |                      | sbecker@ucsd.edu;                 |
| ODF                     |        | salinity  | unfiltered |                      | sbecker@ucsd.edu;                 |
| ODF                     |        | nutrients   | unfiltered |                      | sbecker@ucsd.edu;                 |
| Smethie                 | Bill   | CFCs  | unfiltered |                      | bsmeth@ldeo.columbia.edu;         |
| Schlosser               | Peter  | $^{18}\text{O}$                                   | unfiltered |                      | schlosser@ldeo.columbia.edu       |
| Schlosser               | Peter  | tritium   | unfiltered |                      | schlosser@ldeo.columbia.edu       |
| Whitmore                | Laura  | methane   | unfiltered |                      | laura.whitmore@eagles.usm.edu     |

| ODF Rosette; Pu-Po casts |              |                  |            |                      |                           |
|--------------------------|--------------|------------------|------------|----------------------|---------------------------|
| Baskaran/Maiti           | Mark/Kanchan | Pb, Po           | filtered   | Acropak-500 (0.45um) | baskaran@wayne.edu;       |
| Kenna                    | Tim          | <sup>236</sup> U | filtered   | Acropak-500 (0.45um) | tkenna@ldeo.columbia.edu; |
| Kenna                    | Tim          | Pu, Np, Cs, Sr   | filtered   | Acropak-500 (0.45um) | tkenna@ldeo.columbia.edu; |
| Kenna                    | Tim          | <sup>129</sup> I | unfiltered |                      | tkenna@ldeo.columbia.edu; |
| ODF                      |              | oxygen           | unfiltered |                      | sbecker@ucsd.edu;         |
| ODF                      |              | salinity         | unfiltered |                      | sbecker@ucsd.edu;         |
| ODF                      |              | nutrients        | unfiltered |                      | sbecker@ucsd.edu;         |

| GTC clean carousel   |              |   |            |                     |                          |
|----------------------|--------------|---|------------|---------------------|--------------------------|
| Anderson             | Bob          | <sup>232</sup> Th/ <sup>230</sup> Th/ <sup>231</sup> Pa | filtered   | Acropak-200 (0.2um) | boba@ldeo.columbia.edu   |
| Boyle                | Ed           | Cr (total)  | filtered   | Acropak-200 (0.2um) | eaboyle@mit.edu          |
| Boyle                | Ed           | Cr(III)   | filtered   | Acropak-200 (0.2um) | eaboyle@mit.edu          |
| Boyle/Rember         | Ed/Rob       | Pb isotopes   | filtered   | Acropak-200 (0.2um) | eaboyle@mit.edu          |
| Fitzsimmons/John     | Jessica/Seth | Fe isotopes   | filtered   | Acropak-200 (0.2um) | jessfitz@tamu.edu        |
| Fitzsimmons/Sherrell | Jessica/Rob  | colloidal TM  | filtered   | Acropak-200 (0.2um) | jessfitz@tamu.edu        |
| Fitzsimmons/Sherrell | Jessica/Rob  | TM  | filtered   | Acropak-200 (0.2um) | jessfitz@tamu.edu        |
| John                 | Seth         | TM isotopes   | filtered   | Acropak-200 (0.2um) | sethjohn@usc.edu         |
| Lamborg              | Carl         | colloidal Hg  | filtered   | Acropak-200 (0.2um) | clamborg@ucsc.edu        |
| Measures/Hatta       | Chris/Mariko | Al, Mn, Fe  | filtered   | Acropak-200 (0.2um) | chrism@soest.hawaii.edu; |
| Saito                | Mak          | archive   | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;         |
| Saito                | Mak          | Co (labile)   | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;         |
| Saito                | Mak          | Co (total)  | filtered   | Acropak-200 (0.2um) | msaito@whoi.edu;         |
| Shiller              | Alan         | V, Ga, Ba   | filtered   | Acropak-200 (0.2um) | alan.shiller@usm.edu;    |
| Wyatt                | Neil         | Zn  | filtered   | Acropak-200 (0.2um) | nwyatt@fsu.edu           |
| ODF                  |              | salinity  | unfiltered |                     | sbecker@ucsd.edu;        |
| ODF                  |              | nutrients   | unfiltered |                     | sbecker@ucsd.edu;        |

|                         |       |                 |            |  |                    |
|-------------------------|-------|-----------------|------------|--|--------------------|
| Ra pumping              |       |                 |            |  |                    |
| Charette                | Matt  | Ra isotopes     | unfiltered |  | mcharette@whoi.edu |
| <sup>7</sup> Be pumping |       |                 |            |  |                    |
| Kadko                   | David | <sup>7</sup> Be | unfiltered |  | dkadko@fiu.edu     |

| McLane Pumps   |           |                                      |                               |                                     |                                   |
|----------------|-----------|--------------------------------------|-------------------------------|-------------------------------------|-----------------------------------|
| Particles      |           |                                      |                               |                                     |                                   |
|                |           |                                      | Filter Type                   |                                     |                                   |
| Anderson       | Bob       | 230Th, 231Pa                         | SUPOR--0.8-51um               |                                     | boba@ldeo.columbia.edu            |
| Boyle          | Ed        | Pb isotopes                          | SUPOR--0.8-51um               |                                     | eaboyle@mit.edu                   |
| Brzezinski     | Mark      | Si isotopes                          | SUPOR--0.8-51um               |                                     | mark.brzezinski@lifesci.ucsb.edu; |
| Cutter         | Greg      | Se,As                                | SUPOR--0.8-51um               |                                     | gcutter@odu.edu;                  |
| Haley          | Brian     | Nd isotopes                          | SUPOR--0.8-51um               |                                     | bhaley@coas.oregonstate.edu;      |
| John           | Seth      | Fe isotopes leach                    | SUPOR--0.8-51um               |                                     | sethjohn@usc.edu                  |
| John           | Seth      | Fe isotopes total                    | SUPOR--0.8-51um               |                                     | sethjohn@usc.edu                  |
| Lam            | Phoebe    | pTM, lithogenic particles            | SUPOR--0.8-51um               |                                     | pjam@ucsc.edu                     |
| Lam            | Phoebe    | biogenic silica (bSi)                | SUPOR--0.8-51um               |                                     | pjam@ucsc.edu                     |
| Maldonado      | Maite     | TM                                   | SUPOR--0.8-51um               | Canadian GEOTRACES intercalibration | mmaldonado@eos.ubc.ca             |
| Maldonado      | Maite     | biogenic Si                          | SUPOR--0.8-51um               | Canadian GEOTRACES intercalibration | mmaldonado@eos.ubc.ca             |
| Planquette     | Helene    | TM                                   | SUPOR--0.8-51um               | German GEOTRACES intercalibration   | Helene.Planquette@univ-brest.fr   |
| Twining/Morton | Ben/Peter | bioTM                                | SUPOR--0.8-51um               |                                     | btwining@bigelow.org;             |
| Twining/Morton | Ben/Peter | TM                                   | SUPOR--0.8-51um               |                                     | btwining@bigelow.org;             |
| Baskaran       | Mark      | 210Pb/210Po                          | QMA--1-51um                   |                                     | baskaran@wayne.edu;               |
| Buesseler      | Ken       | 234Th                                | QMA--1-51um                   |                                     | ken@dataone.whoi.edu              |
| Charette       | Matt      | 228Th, Ra                            | QMA--1-51um                   |                                     | mcharette@whoi.edu                |
| Geibert        | Walter    | POC,PIC                              | QMA--1-51um                   | German GEOTRACES intercalibration   | walter.geibert@awi.de             |
| Granger        | Julie     | 15N                                  | QMA--1-51um                   |                                     | julie.granger@uconn.edu;          |
| Hammerschmidt  | Chad      | Hg species                           | QMA--1-51um                   |                                     |                                   |
| Kadko          | David     | 7Be                                  | QMA--1-51um                   |                                     | dkadko@fiu.edu                    |
| Kenna          | Tim       | 239Pu, 240Pu, 237Np, 137Cs, and 90Sr | QMA--1-51um                   |                                     | tkenna@ldeo.columbia.edu;         |
| Lam            | Phoebe    | PIC, POC, d13C                       | QMA--1-51um                   |                                     | pjam@ucsc.edu                     |
| Lamborg        | Carl      | Thiols                               | QMA--1-51um                   |                                     | clamborg@ucsc.edu                 |
| Maiti          | Kanchan   | 210Pb/210Po                          | QMA--1-51um                   |                                     | kmaiti.lsu@gmail.com;             |
| Maldonado      | Maite     | POC,PIC                              | QMA--1-51um                   | Canadian GEOTRACES intercalibration | mmaldonado@eos.ubc.ca             |
| Saito          | Mak       | proteins                             | QMA--1-51um                   |                                     | msaito@whoi.edu;                  |
| Buesseler      | Ken       | 234Th                                | SP >51um prefilter over Supor |                                     | ken@dataone.whoi.edu              |
| Granger        | Julie     | N-15                                 | SP >51um prefilter over Supor |                                     | julie.granger@uconn.edu;          |
| Lam            | Phoebe    | POC, d13C                            | SP >51um prefilter over Supor |                                     | pjam@ucsc.edu                     |
| Anderson       | Bob       | 230Th, 231Pa                         | QP >51um prefilter over QMA   |                                     | boba@ldeo.columbia.edu            |
| Baskaran       | Mark      | 210Pb/210Po                          | QP >51um prefilter over QMA   |                                     | baskaran@wayne.edu;               |
| Brzezinski     | Mark      | Si isotopes                          | QP >51um prefilter over QMA   |                                     | mark.brzezinski@lifesci.ucsb.edu; |
| Lam            | Phoebe    | pTM, lithogenic particles            | QP >51um prefilter over QMA   |                                     | pjam@ucsc.edu                     |
| Lam            | Phoebe    | PIC                                  | QP >51um prefilter over QMA   |                                     | pjam@ucsc.edu                     |
| Lam            | Phoebe    | biogenic Si                          | QP >51um prefilter over QMA   |                                     | pjam@ucsc.edu                     |
| Maiti          | Kanchan   | 210Pb/210Po                          | QP >51um prefilter over QMA   |                                     | kmaiti.lsu@gmail.com;             |
| Charette       | Matt      | Ra isotopes                          | Cartridges                    |                                     | mcharette@whoi.edu                |
| Hammond        | Doug      | Actinium isotopes                    | Cartridges                    |                                     | dhammond@usc.edu;                 |
| Kenna          | Tim       | Cs isotopes                          | Cartridges                    |                                     | tkenna@ldeo.columbia.edu;         |
| Lamborg        | Carl      | Hg genomics                          | Cartridges                    |                                     | clamborg@ucsc.edu                 |

| Aerosol Sampling |              |   |        |                                      |  |   |                                |
|------------------|--------------|---|--------|--------------------------------------|--|---|--------------------------------|
|                  |              | Filter  | Filter | Impactor                             | Extracts                                     | Extracts  |                                |
|                  |              | W41   | GFF    | W41                                  | UHP  | Seawater  |                                |
| Anderson         | Bob          | <sup>232</sup> Th/ <sup>230</sup> Th/ <sup>231</sup> Pa |        |                                      |  | <sup>232</sup> Th/ <sup>230</sup> Th/ <sup>231</sup> Pa | boba@ldeo.columbia.edu         |
| Baskaran/Stewart | Mark/Jillian | <sup>210</sup> Pb/ <sup>210</sup> Po                    |        | <sup>210</sup> Pb/ <sup>210</sup> Po |  |   | baskaran@wayne.edu;            |
| Boyle            | Ed           | Pb isotopes   |        |                                      |  |   | eaboyle@mit.edu                |
| Buck             | Cliff        |   |        |                                      | TEIs   |   | Clifton.Buck@skio.uga.edu;     |
| Cutter           | Greg         | As, Se  |        |                                      |  |   | gcutter@odu.edu;               |
| Fitzsimmons      | Jessica      |   |        |                                      |  | soluble (Anopore) TEIs                                  | jessfitz@tam.u.edu             |
| Gao              | Yuan         |   |        |                                      | water soluble organic acids and major anions |   | yuangaoh@andromeda.rutgers.edu |
| Haley            | Brian        | Nd/REE  |        |                                      |  |   | bhaley@coas.oregonstate.edu;   |
| Hastings         | Meredith     |   |        |                                      | N isotopes                                   |   | meredith_hastings@brown.edu    |
| John             | Seth         |   |        |                                      |  | Trace metal isotopes                                    | sethjohn@usc.edu               |
| Kadko            | David        | <sup>7</sup> Be   |        |                                      |  |   | dkadko@fiu.edu                 |
| Landing          | Bill         | TEIs  |        | TEIs                                 |  | soluble (Millipore-VS) and dissolved TEIs               | wlanding@fsu.edu;              |
| Mason            | Rob          |   |        | Hg                                   |  | Hg  | robert.mason@uconn.edu;        |
| Wozniak          | Andrew       |   |        |                                      | Water soluble organic compounds              |   | awozniak@odu.edu               |

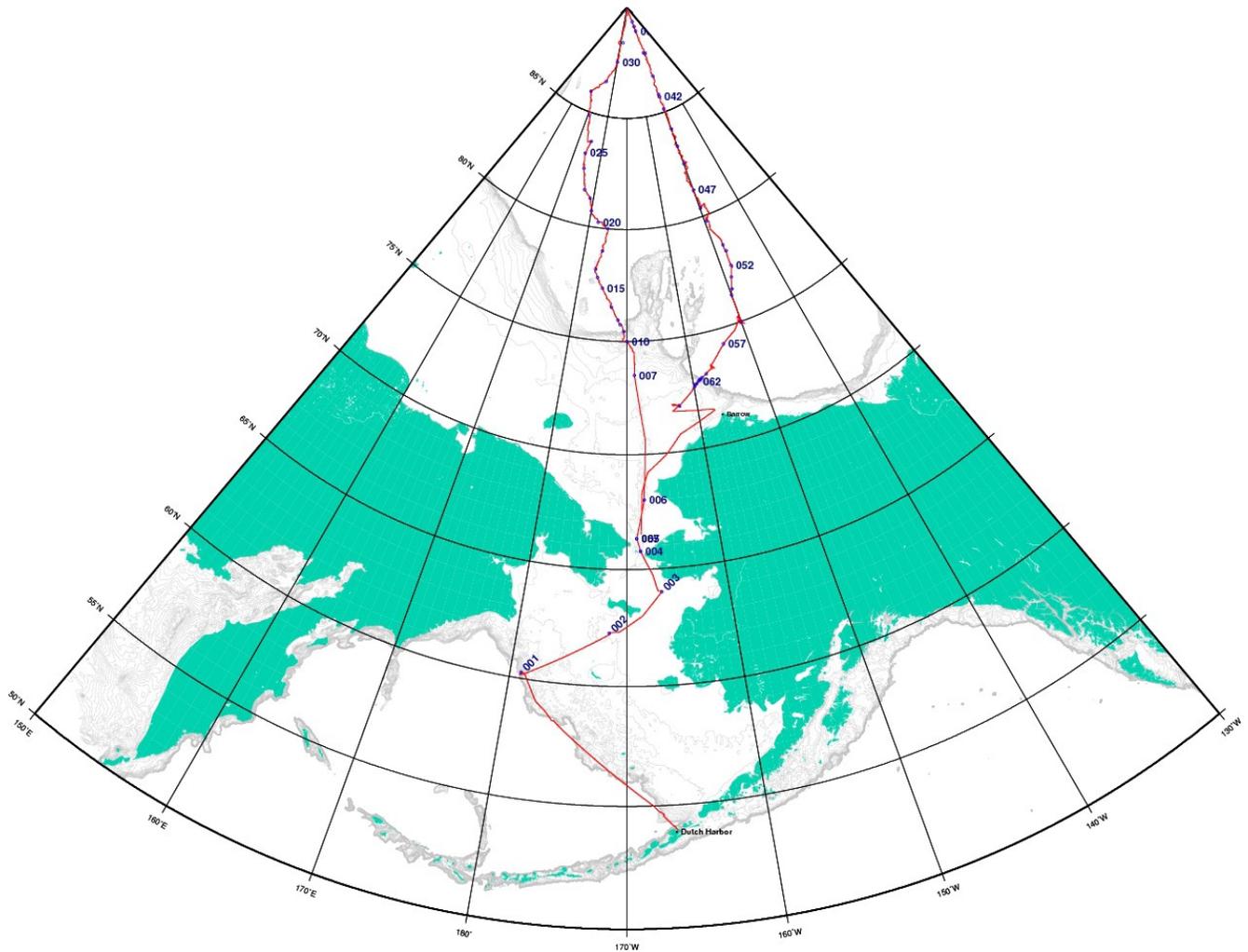
| Shipboard snow and Rain sampling |            |              |             |               |                            |
|----------------------------------|------------|--------------|-------------|---------------|----------------------------|
| Buck/Landing                     | Cliff/Bill | TEIs         | filtered    | 0.4um PCTE    | Clifton.Buck@skio.uga.edu; |
| Buck/Landing                     | Cliff/Bill | anions       | filtered    | 0.4um PCTE    | Clifton.Buck@skio.uga.edu; |
| Wozniak                          | Andrew     | WSOM; DOC    | filtered    | 0.7um GFF     | awozniak@odu.edu           |
| Buck/Landing                     | Cliff/Bill | TEIs         | unfiltered  |               | Clifton.Buck@skio.uga.edu; |
| Buck/Landing                     | Cliff/Bill | anions       | unfiltered  |               | Clifton.Buck@skio.uga.edu; |
| Mason                            | Rob        | Hg           | unfiltered  |               | robert.mason@uconn.edu;    |
| Wozniak                          | Andrew     | WSOM         | unfiltered  |               | awozniak@odu.edu           |
| Buck/Landing                     | Cliff/Bill | TEIs         | particulate | on 0.4um PCTE | Clifton.Buck@skio.uga.edu; |
| Wozniak                          | Andrew     | black carbon | particulate | on 0.7um GFF  | awozniak@odu.edu           |

| Underway Sampling    |         |                      |                   |                |                                   |
|----------------------|---------|----------------------|-------------------|----------------|-----------------------------------|
| Port passageway      |         |                      |                   |                |                                   |
| Brzezinski           | Mark    | Biogenic Si isotopes | particulate       | 0.8um Supor    | mark.brzezinski@lifesci.ucsb.edu; |
| Buesseler            | Ken     | Th-228               | particulate       | 51um mesh      | ken@dataone.who.edu               |
| Dilliplane           | Kyle    | plankton             | particulate       | >150um         | kbdilliplaine@alaska.edu;         |
| Kenna                | Tim     | Cs isotopes          | filtered          | 1um filtration | tkenna@ldeo.columbia.edu;         |
| Chem lab             |         |                      |                   |                |                                   |
| Smethie              | Bill    | CFCs                 | dissolved gaseous |                | bsmeth@ldeo.columbia.edu;         |
| Smethie              | Bill    | SF6                  | dissolved gaseous |                | bsmeth@ldeo.columbia.edu;         |
| Shiller              | Alan    | Methane              | dissolved gaseous |                | alan.shiller@usm.edu;             |
| Mason                | Rob     | elemental Hg         | dissolved gaseous |                | robert.mason@uconn.edu;           |
| Quay                 | Paul    | O2, Ar               | dissolved gaseous |                | pdquay@uw.edu                     |
| Atmospheric Sampling |         |                      |                   |                |                                   |
| Landing              | William | CO2                  | gaseous           |                | wlanding@fsu.edu;                 |
| Landing              | William | black carbon         | aerosol           |                | wlanding@fsu.edu;                 |
| Mason                | Rob     | Gaseous elemental Hg | gaseous           |                | robert.mason@uconn.edu;           |
| Mason                | Rob     | reactive gaseous Hg  | gaseous           |                | robert.mason@uconn.edu;           |
| Mason                | Rob     | aerosol Hg           | aerosol           |                | robert.mason@uconn.edu;           |

**U.S. GEOTRACES ARCTIC**  
USGS Healy (HLY1502)  
09 August, 2015 - 12 October, 2015  
Dutch Harbor, Alaska - Dutch Harbor, Alaska

Chief Scientist: Dr David Kadko  
Florida International University

Co-Chief Scientist: Dr William Landing  
Florida State University



STS/ODF Cruise Report  
09 October, 2015

## **Narrative - SIO Oceanographic Data Facility CTD/Hydrographic Support for the US Geotraces Arctic Ocean Expedition and Repeat Hydrography Program - J. Swift (SIO)**

A seven-person team from the Oceanographic Data Facility (ODF) of the Shipboard Technical Support group (STS) at the UCSD Scripps Institution of Oceanography carried out NSF-funded CTDO casts, salinity, oxygen, and nutrient analyses, data processing, and oceanographic interpretative activities on the US Geotraces Arctic Expedition on USCGC Healy, 09 August to 12 October 2015, Dutch Harbor, AK, round trip. The ODF team also supported extra casts at separate stations for an add-on repeat hydrography component which improved the horizontal resolution provided by the relatively sparse Geotraces stations alone. The extra casts were sanctioned by the US Global Ocean Carbon and Repeat Hydrography Program (now US GO-SHIP) and received supplementary NSF support; also, support for five additional days at sea was added. The budgets and work force for the CFC/SF6 and ocean carbon teams which were already part of the Geotraces work plan were also supplemented so that a more nearly complete repeat hydrography suite of measurements could be made at all stations.

The CTD/hydrographic group included: two nutrient analysts (Susan Becker - ODF team leader - and Melissa Miller), a data processor/analyst (Courtney Schatzman), an oxygen and data tech (Andrew Barna), a CTD and oxygen tech (Joseph Gum), a CTD/electronics/marine technician (John 'Ted' Cumiskey), and a scientist (James Swift), who was also the scientific leader for the repeat hydrography work. Gum and Swift ran the CTD console. Swift also assisted with data quality control and prepared data interpretation documents for use by the on-board Geotraces science team.

The CTD/hydrographic team provided at sea, in addition to basic CTD/hydrographic data collection: CTD and bottle data processing, oceanographic leadership of the CTD/hydrographic team, interpretation of the CTD/hydrographic data, and nutrient and salinity analyses for other Geotraces casts (e.g., from trace metal rosette casts, small boat casts, and ice samples). CTD/hydrographic data were processed and most documentation completed at sea, scientifically useful CTD/hydrographic data available to participants daily at sea, bottle data parameters analyzed at sea were merged with others at sea when provided in a timely manner to the ODF data specialist, and oceanographic interpretation of the CTD/hydrographic data was provided to the groups at sea.

The pre-cruise plan was that ODF would operate two CTD/rosette systems, one equipped with 12 30-liter bottles for all ODF casts at each Geotraces station and one equipped with 36 10-liter bottles for the single cast at each repeat hydrography station. This would provide the large

volumes per level needed on Geotraces casts, provide excellent single-cast vertical resolution at repeat hydrography stations, and avoid switching rosettes at any given station type. The original plan was to store one on deck, covered and with heaters, while the in-use rosette would be kept in the Healy's starboard staging bay. It was quickly realized both that it would be difficult to switch rosettes in and out of the staging bay, and also that there was adequate space and facilities in the staging bay to keep both in the bay in an inboard-outboard tandem, with just enough lateral (fore-aft in ship direction) space to pass one by the other to switch them. [There was also a trace metal clean rosette system with 24 10-liter Go-Flo bottles, kept on the fantail with a specialized UNOLS trace metal clean winch, operated by a team supervised by Greg Cutter, Old Dominion University, which provided Geotraces samples and CTD data which were part of the ODF data processing responsibilities on the cruise.]

There were no serious problems with this plan, but experience quickly showed that the 10-liter bottles were much less prone to leaking than were the 30-liter bottles, and that three 10-liter bottles delivered more water than did one 30-liter bottle. It was also determined that in nearly all situations a low-volume nutrient sample could be the only check sample needed when three 10-liter bottles were closed at one level and one of them had salinity, oxygen, and nutrient samples. The samplers also stated that they preferred the 10-liter bottles. Thus, at the cost of tripling the nutrient sample load for ODF casts at Geotraces stations, ODF switched to using only the 36x10-liter rosette. One remaining issue was that there were two Geotraces instruments on the 12x30-liter rosette that were not on the 36x10-liter rosette, which was already thought to be 'full up' on sensors, but the STARC techs, working with ODF and also the SIO/STS engineers in San Diego, worked out an installation plan that placed all instruments onto the 36x10-liter rosette, which was then used for the remainder of the cruise. (The 12x30-liter rosette was disassembled and the frame stored on deck.)

Overall, ODF CTD operations went well, especially considering some of the operational challenges the expedition faced. There was a sizeable deck and MST force which took care of pushing the rosette in and out of the staging bay (the rosette was kept on a platform which slid on 'railroad tracks'), launch preparations, launch, and recovery. [Although the rosette frame was nearly as large as the cart, it never slipped off (which could have damaged some of the instruments close to the frame bottom).] The STARC tech on watch and/or ODF tech was responsible for seeing that the water sample bottles were prepared for deployment and all equipment mounted on the rosette frame was ready for the cast. The ship supplied winch operators from the deck crew, and the CTD computer operator (Gum or Swift) ran each cast from a seat near the winch operator, who could see the deck crew, A-frame, and water from the aft control room. The USCGC Healy's bridge staff sometimes required significant time to come onto station. Before this was understood, during some stations early in the expedition the rosette sat on deck longer than desirable, especially so when air temperatures started to reach well below

freezing. Thus a procedure was developed to deal with this: the rosette was readied as usual, but the staging bay door was kept shut and deck crew did not open it to move the rosette out onto deck until permission to deploy had been received from the bridge. At that point the staging bay roll-up door was opened and subsequent deployment was as rapid as could be managed. In very cold conditions, the STARC tech blew air from a large heater-fan onto the rosette while it was on deck. One complication which affected a small group of stations roughly in the middle of the cruise was that the staging bay door motor ceased functioning, and the manual roll-up took about 10 minutes, during which time the CTD could become quite cold unless it was kept warm with the heater fan. Despite use of the heater fan there was some freeze damage to the CTD dissolved oxygen sensors and possibly a pump, but very little harm done to the CTD data. Warm air was ducted onto the rosette on recovery in an effort to keep any water sample freezing to the water in the spigots. As the ship worked south, air temperatures warmed a little and the engineers worked on the door mechanism - one way or the other the door began working again.

On the final deep ODF cast at many of the Geotraces stations, the rosette was equipped with a monocrorer device to capture a sediment sample. The monocrorer was attached via a 26-meter rope to the bottom of the rosette frame. The altimeter on the rosette would 'see' only the monocrorer - i.e. it would constantly report 26 meters 'height above bottom'. Based on past Geotraces experience a pyramidal device constructed from 4 plastic panels was attached above the monocrorer to deflect sound impulses instead of reflecting them upward. This device, nicknamed 'the cone of silence', worked well, enabling normal altimeter function. Special cast procedures were used - deploy no faster than 40 meters/minute, slow to 10-20 meters per minute before the monocrorer would hit the bottom, leave at bottom one minute, pull out slowly - were employed. Some monocrorer casts were successful, some were not. The device caused no problems other than the extra time for the slower down cast.

Water sampling was carried out in the starboard staging bay, with the roll-up door in the closed position. The staging bay was kept cold (but well above freezing) during gas sampling: heaters in the staging bay were regulated to avoid all but a small degree of warming of the water in the 10-liter ODF bottles.

There were relatively few mishaps during ODF rosette casts other than continual concerns regarding effects of sub-freezing temperatures as noted above. The most serious incident occurred near the start of work in the ice when the CTD cable was snagged by an ice floe drifting aft and carried more than 100 meters aft. Eventually it was freed, at the only cost of needing to cut off damaged cable and reterminate. Another serious incident, near the end of the expedition, arose when the winch operator lowered the rosette, rather than raising it, after bottom approach. With tension off the wire, the wire kinked, and a retermination was required - there were no effects on the data.

It bears noting that the Arctic Ocean sea ice Healy traversed appeared to be mostly first-year ice. Good progress was often made on one engine in the ice, though on the heavier stretches two

engines were sometimes used. Extra power appears to have been required remarkably few times for an expedition working in the central Arctic Ocean. Over the Alpha Ridge Healy traversed the heaviest ice overall encountered during the expedition, but the navigators in the aloft control station were always able to spot a feasible route, avoiding heavy, impassible pressure ridges. Sometimes it took some back-and-ram operations to get through a thicker, older ice floe, and there was one short instance when three engines were needed. In ice covered water during parts of the expedition where there was darkness the ship typically did not navigate the pack at night, but this affected only a small number of days of the expedition. Once the ship was south of the crest of the Alpha Ridge, there were many-miles-long, wide leads that Healy followed. Overall, progress through the ice was remarkable for a single icebreaker in this domain. For example, Healy made it solo through some areas that were too tough for Healy and Oden together in 2005, and was able to operate freely in areas out of the question during the 1994 expedition by two heavy icebreakers.

During the cruise there was a fair amount of snow, and the decks were often slippery. By mid-September there was some full darkness every night, and by the end of the month and early October there were beautiful aurora displays visible in open areas of the sky.

### **ODF Data Quality, Management and Availability**

The ODF rosette casts meet a similar quality as for the at-sea temperature and salinity data from cruises for the US Global Ocean Carbon and Repeat Hydrography program, and provide usable CTD dissolved oxygen profiles (and CTD fluorometer and transmissometer profiles). ODF carried out analyses of inorganic nutrients (nitrate, nitrite, phosphate, and silicate) from every rosette bottle closed at every rosette level sampled (and from ice stations, samples from small boat casts, and niskins paired with McLane pumps), dissolved oxygen at every ODF rosette level sampled, and conductivity (salinity) check samples from every CTD/rosette cast (and from ice stations, samples from small boat casts, and niskins paired with McLane pumps).

Bottle data are indexed by cruise, station, cast, and sample/bottle, and Geotraces identifiers are used as per Geotraces policy. Each/every sample drawn is logged, and scans of the log sheets will be archived at STS/ODF. Experience during WOCE, CLIVAR, SBI, previous Geotraces cruises and many other programs has amply demonstrated that these procedures make it straightforward to merge disparate bottle parameter data from different laboratories.

The core ODF CTD/hydrographic data (CTD pressure, temperature, salinity, oxygen; bottle salinity, oxygen, and nutrients) from all ODF rosette casts from this expedition (both 12x30 and 36x10, from both Geotraces and repeat hydrography stations) are by NSF, US Geotraces, and US repeat hydrography (now US GO-SHIP) policies officially "public" data. The CFC/SF6 and ocean carbon data in the hydrographic data files are also included in this data availability policy for all ODF rosette casts.

The data citation information for the water column CTD/hydrographic/CFC/carbon data is as follows:

# Data Provided by:

#

| # Program | Affiliation | PI | email |
|-----------|-------------|----|-------|
|-----------|-------------|----|-------|

#

|                   |     |             |                |
|-------------------|-----|-------------|----------------|
| # Chief Scientist | FIU | David Kadko | dkadko@fiu.edu |
|-------------------|-----|-------------|----------------|

|        |          |             |                 |
|--------|----------|-------------|-----------------|
| # CTDO | UCSD/SIO | James Swift | jswift@ucsd.edu |
|--------|----------|-------------|-----------------|

# (and Salinity, Oxygen, Nutrients)

|            |      |                 |                          |
|------------|------|-----------------|--------------------------|
| # CFCs/SF6 | LDEO | William Smethie | bsmeth@ldeo.columbia.edu |
|------------|------|-----------------|--------------------------|

|                |                |               |                          |
|----------------|----------------|---------------|--------------------------|
| # Ocean Carbon | UofMiami/RSMAS | Frank Millero | fmillero@rsmas.miami.edu |
|----------------|----------------|---------------|--------------------------|

|   |  |                |                          |
|---|--|----------------|--------------------------|
| # |  | Dennis Hansell | dhansell@rsmas.miami.edu |
|---|--|----------------|--------------------------|

# (Total Alkalinity, pH, DIC, DOC)

#

# The data included in these files are preliminary, and are  
# subject to final calibration and processing. They have been made  
# available for public access as soon as possible following  
# their collection. Users should maintain caution in their  
# interpretation and use. Following American Geophysical Union  
# recommendations, the data should be cited as: "data  
# provider(s), cruise name or cruise ID, data file name(s),  
# CLIVAR and Carbon Hydrographic Data Office, La Jolla, CA,  
# USA, and data file date." For further information, please  
# contact one of the parties listed above or cchdo@ucsd.edu.  
# Users are also requested to acknowledge the NSF/NOAA-funded  
# U.S. Repeat Hydrography Program and the NSF-funded Geotraces  
# program in publications and presentations resulting from their use.

**Nutrients:**

PI: James H Swift

Institute: SIO

Analyst/Sampler:

Susan Becker

Melissa Miller

**Summary of Analysis:**

4,049 samples were analyzed from 66 stations.

The cruise started with new pump tubes and they were changed 4 times, before stations 021, 034, 046, and 056.

6 sets of Primary/Secondary standards were made up over the course of the cruise.

The cadmium column efficiency was checked periodically and ranged between 93%-100%. The column was replaced if/when the efficiency dropped below 97%.

**Equipment and Techniques:**

Nutrient analyses (phosphate, silicate, nitrate+nitrite, and nitrite) were performed on a Seal Analytical continuous-flow AutoAnalyzer 3 (AA3). The methods used are described by Gordon et al (1992) Hager et al. (1968) and Atlas et al. (1971). Details of modifications of analytical methods used in this cruise are also compatible with the methods described in the nutrient section of the GO-SHIP repeat hydrography manual (Hydes et al., 2010).

**Nitrate/Nitrite Analysis:**

A modification of the Armstrong et al. (1967) procedure was used for the analysis of nitrate and nitrite. For nitrate analysis, a seawater sample was passed through a cadmium column where the nitrate was reduced to nitrite. This nitrite was then diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine to form a red dye. The sample was then passed through a 10mm flowcell and absorbance measured at 520nm. The procedure was the same for the nitrite analysis but without the cadmium column.

**REAGENTS****Sulfanilamide**

Dissolve 10g sulfanilamide in 1.2N HCl and bring to 1 liter volume. Add 2 drops of 40% surfynol 465/485 surfactant.

Store at room temperature in a dark poly bottle.

Note: 40% Surfynol 465/485 is 20% 465 plus 20% 485 in DIW.

**N-(1-Naphthyl)-ethylenediamine dihydrochloride (N-1-N)**

Dissolve 1g N-1-N in DIW, bring to 1 liter volume. Add 2 drops 40% surfynol 465/485 surfactant.

Store at room temperature in a dark poly bottle. Discard if the solution turns dark reddish brown.

#### Imidazole Buffer

Dissolve 13.6g imidazole in ~3.8 liters DIW. Stir for at least 30 minutes to completely dissolve. Add 60 ml of CuSO<sub>4</sub> + NH<sub>4</sub>Cl mix (see below). Add 4 drops 40% Surfynol 465/485 surfactant. Let sit overnight before proceeding

Using a calibrated pH meter, adjust to pH of 7.83-7.85 with 10% (1.2N) HCl (about 20-30 ml of acid, depending on exact strength). Bring final solution to 4L with DIW.

Store at room temperature.

#### NH<sub>4</sub>Cl + CuSO<sub>4</sub> mix:

Dissolve 2g cupric sulfate in DIW, bring to 100 ml volume (2%)

Dissolve 250g ammonium chloride in DIW, bring to 1 liter volume.

Add 5ml of 2% CuSO<sub>4</sub> solution to this NH<sub>4</sub>Cl stock. This should last many months.

#### **Phosphate Analysis:**

Ortho-Phosphate was analyzed using a modification of the Bernhardt and Wilhelms (1967) method. Acidified ammonium molybdate was added to a seawater sample to produce phosphomolybdic acid, which was then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The sample was passed through a 10mm flowcell and absorbance measured at 880nm.

#### REAGENTS

##### Ammonium Molybdate

##### H<sub>2</sub>SO<sub>4</sub> sol'n:

Pour 420 ml of DIW into a 2 liter Erlenmeyer flask or beaker, place this flask or beaker into an ice bath. SLOWLY add 330 ml of conc H<sub>2</sub>SO<sub>4</sub>.

This solution gets VERY HOT!! Cool in the ice bath. Make up as much as necessary in the above proportions.

Dissolve 27g ammonium molybdate in 250ml of DIW. Bring to 1 liter volume with the cooled sulfuric acid sol'n. Add 3 drops of 15% DDS surfactant. Store in a dark poly bottle.

##### Dihydrazine Sulfate

Dissolve 6.4g dihydrazine sulfate in DIW, bring to 1 liter volume and refrigerate.

#### **Silicate Analysis:**

Silicate was analyzed using the basic method of Armstrong et al. (1967). Acidified ammonium molybdate was added to a seawater sample to produce silicomolybdic acid which was then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. The sample was passed through a 10mm flowcell and measured at 660nm.

## REAGENTS

### Tartaric Acid

Dissolve 200g tartaric acid in DW and bring to 1 liter volume. Store at room temperature in a poly bottle.

### Ammonium Molybdate

Dissolve 10.8g Ammonium Molybdate Tetrahydrate in 1000ml dilute H<sub>2</sub>SO<sub>4</sub>\*.

\*(Dilute H<sub>2</sub>SO<sub>4</sub> = 2.8ml conc H<sub>2</sub>SO<sub>4</sub> or 6.4ml of H<sub>2</sub>SO<sub>4</sub> diluted for PO<sub>4</sub> moly per liter DW) (dissolve powder, then add H<sub>2</sub>SO<sub>4</sub>)

Add 3-5 drops 15% SDS surfactant per liter of solution.

### Stannous Chloride

stock: (as needed)

Dissolve 40g of stannous chloride in 100 ml 5N HCl. Refrigerate in a poly bottle.

### NOTE:

Minimize oxygen introduction by swirling rather than shaking the solution. Discard if a white solution (oxychloride) forms.

working: (every 24 hours)

Bring 5 ml of stannous chloride stock to 200 ml final volume with 1.2N HCl. Make up daily - refrigerate when not in use in a dark poly bottle.

### **Sampling:**

Nutrient samples were drawn into 40 ml polypropylene screw-capped centrifuge tubes. The tubes and caps were cleaned with 10% HCl and rinsed 2-3 times with sample before filling. Samples were analyzed within 1-3 hours after sample collection, allowing sufficient time for all samples to reach room temperature. The centrifuge tubes fit directly onto the sampler.

### **Data collection and processing:**

Data collection and processing was done with the software (ACCE ver 6.10) provided with the instrument from Seal Analytical. After each run, the charts were reviewed for any problems during the run, any blank was subtracted, and final concentrations (micro moles/liter) were calculated, based on a linear curve fit. Once the run was reviewed and concentrations calculated a text file was created. That text file was reviewed for possible problems and then converted to another text file with only sample identifiers and nutrient concentrations that was merged with other bottle data.

### **Standards and Glassware calibration:**

Primary standards for silicate ( $\text{Na}_2\text{SiF}_6$ ), nitrate ( $\text{KNO}_3$ ), nitrite ( $\text{NaNO}_2$ ), and phosphate ( $\text{KH}_2\text{PO}_4$ ) were obtained from Johnson Matthey Chemical Co. and/or Fisher Scientific. The supplier reports purities of >98%, 99.999%, 97%, and 99.999 respectively.

All glass volumetric flasks and pipettes were gravimetrically calibrated prior to the cruise. The primary standards were dried and weighed out to 0.1mg prior to the cruise. The exact weight was noted for future reference. When primary standards were made, the flask volume at 20C, the weight of the powder, and the temperature of the solution were used to buoyancy-correct the weight, calculate the exact concentration of the solution, and determine how much of the primary was needed for the desired concentrations of secondary standard. Primary and secondary standards were made up every 7-10 days. The new standards were compared to the old before use.

All the reagent solutions, primary and secondary standards were made with fresh distilled deionized water (DIW).

Standardizations were performed at the beginning of each group of analyses with working standards prepared prior to each run from a secondary. Working standards were made up in low nutrient seawater (LNSW). Two different batches of LNSW were used on the cruise. LNSW was collected off shore of coastal California and treated in the lab. The water was first filtered through a 0.45 micron filter then re-circulated for ~8 hours through a 0.2 micron filter, passed a UV lamp and through a second 0.2 micron filter. The actual concentration of nutrients in this water was empirically determined during the standardization calculations.

The concentrations in micro-moles per liter of the working standards used were:

|    | uM    | uM  | uM   | uM   |
|----|-------|-----|------|------|
|    | N+N   | PO4 | SiO3 | NO2  |
| 0) | 0.0   | 0.0 | 0.0  | 0.0  |
| 3) | 15.50 | 1.2 | 30   | 0.50 |
| 5) | 31.00 | 2.4 | 60   | 1.00 |
| 7) | 46.50 | 3.6 | 90   | 1.50 |

### **Quality Control:**

All data was reported in micro-moles/Liter.  $\text{NO}_3$ ,  $\text{PO}_4$ , and  $\text{NO}_2$  were reported to two decimal places and SIL to one. Accuracy is based on the quality of the standards the levels are:

$\text{NO}_3$  0.05 uM (micro moles/Liter)  
 $\text{PO}_4$  0.004 uM  
SIL 2-4 uM  
 $\text{NO}_2$  0.05 uM

As is standard ODF practice, a deep calibration “check” sample was run with each set of samples and the data are tabulated below.

| Parameter       | Concentration ( $\mu\text{M}$ ) |
|-----------------|---------------------------------|
| NO <sub>3</sub> | 13.66 +/- 0.11                  |
| PO <sub>4</sub> | 1.18 +/- 0.01                   |
| SIL             | 22.5 +/- 0.1                    |
| NO <sub>2</sub> | 0.477 +/- 0.016                 |

Reference materials for nutrients in seawater (RMNS) were also used as a check sample run with each set of seawater samples. The RMNS preparation, verification, and suggested protocol for use of the material are described by (Aoyama et al., 2006, 2007, 2008) and Sato (2010). RMNS batch CA was used on this cruise, with each bottle being used once or twice before being discarded and a new one opened. Data are tabulated below.

| Parameter       | Concentration ( $\mu\text{M}$ ) | Assigned ( $\mu\text{M}$ ) |
|-----------------|---------------------------------|----------------------------|
| NO <sub>3</sub> | 19.94 +/- 0.11                  | 20.02                      |
| PO <sub>4</sub> | 1.45 +/- 0.01                   | 1.45                       |
| SIL             | 37.3 +/- 0.2                    | 36.9                       |
| NO <sub>2</sub> | 0.07 +/- 0.008                  | 0.06                       |

**Analytical problems:**

No major analytical problems.

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## **Oxygen Analysis**

PI: James H. Swift

Institute: SIO

Analyst/Sample:

Andrew Barna

Joseph Gum

## **Equipment and Techniques**

Dissolved oxygen analyses were performed with an SIO/ODF-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by PC LabView software. Thiosulfate was dispensed by a Dosimat 665 buret driver fitted with a 1.0 ml burette. ODF used a whole-bottle modified-Winkler titration following the technique of Carpenter (Carpenter 1965) with modifications by Culberson (Culberson 1991) but with higher concentrations of potassium iodate standard approximately 0.012N, and thiosulfate solution of 55 gm/l or greater (see narrative). Pre-made liquid potassium iodate standards were run every day (approximately every 1-2 stations), unless changes were made to the system or reagents. Reagent/distilled water blanks were determined every day or more often if a change in reagents required it to account for presence of oxidizing or reducing agents.

## **Sampling and Data Processing**

1724 oxygen measurements were made.

Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon and silicone drawing tube, nominal 125ml volume-calibrated iodine flasks were rinsed 3 times with minimal agitation, then filled and allowed to overflow for at least 3 flask volumes. The sample drawing temperatures were measured with a digital thermometer embedded in the drawing tube. These temperatures were used to calculate  $\mu\text{mol/kg}$  concentrations, and as a diagnostic check of bottle integrity. Reagents ( $\text{MnCl}_2$  then  $\text{NaI/NaOH}$ ) were added to fix the oxygen before stoppering. The flasks were shaken twice (10-12 inversions) to assure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 30-40 minutes.

The samples were analyzed within 2-14 hours of collection, and the data incorporated into the cruise database.

Thiosulfate normalities were calculated for each standardization and corrected to 20 deg C. The 20 deg C normalities and the blanks were plotted versus time and were reviewed for possible problems. The blanks and thiosulfate normalities for each batch of thiosulfate were smoothed (linear fits) in three groups during the cruise and the oxygen values recalculated.

## **Volumetric Calibration**

Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at ODF's chemistry laboratory.

This is done once before using flasks for the first time and periodically thereafter when a suspect volume is detected. The volumetric flasks used in preparing standards were volume-calibrated by the same method, as was the 10 ml Dosimat 765 buret used to dispense standard iodate solution.

## **Standards**

Liquid potassium iodate standards were prepared in 6 liter batches and bottled in sterile glass bottles at ODF's chemistry laboratory prior to the expedition. The normality of the liquid standard was determined by calculation from weight. The standard was supplied by Alfa Aesar and has a reported purity of 99.4-100.4%. All other reagents were "reagent grade" and were tested for levels of oxidizing and reducing impurities prior to use.

## **Narrative**

Setup in Dutch Harbor occurred on 2015-08-05, initial reagents were made. Reagents were allowed to settle for 24 hours before the first standardization runs were conducted. Reagents were stable throughout frequent initial standardization runs. Standards were run once a day regardless of station spacing.

A very wide range of oxygen concentrations were encountered at the early stations, from approximately 19  $\mu\text{mol/kg}$  to 480  $\mu\text{mol/kg}$ . The low concentrations required using the slower "LOW O<sub>2</sub>" titration option. The higher concentrations often needed over 1ml of thiosulfate for the titration, required a burette refill. The automatic titration would not always resume after a burette refill. If the burette refill occurred while the program was attempting to find the end point, the software would sometimes force an over titration. The thiosulfate concentration was increased after station/cast 026/03 by adding a few extra grains to the stock. Only two samples after the increased thiosulfate concentration required a burette refill. A new stronger batch of thiosulfate was utilized starting with station 47. No sample required over 1ml of thiosulfate since using the stronger batch.

The stir plate failed while running station/cast 044/01, resulting in the loss of a sample. The stir plate was immediately replaced with a spare. Upon rig reassembly, the UV pen lamp would not turn back on. Both the lamp and the power supply were evaluated for stability, it was found that the only stable combination was using a spare power supply with a spare lamp. The lamp was stable since replacement.

The day to day thiosulfate stability was excellent, averaging less than  $\pm 0.00015\text{N}$  per day with a small trend toward increasing concentration with age. The entire min/max range for any single batch of thiosulfate was approximately 0.00065 over a 20 day period. One standard run exceeded the day to day concentration change specification, this was likely the result of using an almost depleted KIO<sub>3</sub> standard. The out of spec standardization was removed during thiosulfate smoothing.

## **Salinity Analysis**

PI: Jim H. Swift

Analyst/Sample:

John Cumiskey

Brett Hembrough

## **Equipment and Techniques**

A Guildline Autosal 8400B salinometer (S/N 65-715), located in the wet lab, was used for salinity measurements. The salinometer was configured by SIO/STS to provide an interface for computer-aided measurement.

The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 12-24 hours after collection.

The salinometer was standardized for each group of analyses (usually 2-4 casts, up to approximately 75 samples using at least two fresh vials of standard seawater per group. Once it was determined that the salinometer was providing stable readings, standardization was performed every 24 hours and additionally if a bath temperature change occurred. Salinometer measurements were made by computer, the analyst prompted by the software to change samples and flush.

## **Sampling and Data Processing**

A total of 2,726 salinity measurements were made and approximately 120 vials of standard seawater (IAPSO SSW batch P158) were used.

Salinity samples were drawn into 200 ml Kimax high-alumina borosilicate bottles, which were rinsed three times with sample prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. The draw time and equilibration time were logged for all casts. Laboratory temperatures were logged at the beginning and end of each run.

PSS-78 salinity (UNESCO 1981) was calculated for each sample from the measured conductivity ratios. The difference (if any) between the initial vial of standard water and the next one run as an unknown was applied as a linear function of elapsed run time to the data. The corrected salinity data were then incorporated into the cruise database.

## **Laboratory Temperature**

The water bath temperature was set to 24 degrees Celsius during setup. With lab temperatures around 22 degrees Celsius, the water bath temperature was lowered to 21 degrees Celsius before running samples from station 6, cast 2. The lab temperature then averaged higher, closer to 23-24 degrees Celsius, so the salinometer water bath temperature was changed back to 24 degrees Celsius before running samples from station 17, cast 7.

**Cruise report for HLY-1502.**

PI: William Smethie

Institute: LDEO

Analyst/Sampler:

Eugene Gorman

Ben Hickman

Angelica Pasqualini

The Lamont CFC group measured F12, F11, F113, and SF6 on Geotraces 2015. A total of 1140 samples were collected on a 12 bottle and a 36 bottle rosette. A total of 66 stations were sampled. The samples were collected in 500 ml bottles and analyzed on a purge-and-trap system in tandem with a gas chromatograph.

## **Discrete pH Analyses**

PI: Frank Millero/ Ryan Woosley

Institute: UM/RSMAS

Analyst/Sampler:

Ryan Woosley

Fen Huang

Andrew Margolin

## **Sampling**

Samples were collected in 50ml borosilicate glass syringes rinsing a minimum of 2 times and thermostated to 25 or 20°C before analysis. Two duplicates were collected from each repeat hydrography station. Due to water budget limitations, no duplicates could be collected on GEOTRACES station. Samples were collected on the same bottles as total alkalinity or dissolved inorganic carbon (DIC) in order to completely characterize the carbon system. One sample per station was collected and analyzed with double the amount of indicator in order to correct for pH changes as a result of adding the indicator, this correction has not been applied to the preliminary data. All data should be considered preliminary.

## **Analysis**

pH ( $\mu\text{mol/kg}$  seawater) on the seawater scale was measured using an Agilent 8453 spectrophotometer according to the methods outlined by Clayton and Byrne (1993). An RTE10 water bath maintained spectrophotometric cell temperature at 25 or 20°C. A 10cm micro-flow through cell (Sterna, Inc) was filled automatically using a Kloehn 6v syringe pump. The sulfonephthalein indicator m-cresol purple (mCP) was also injected automatically by the Kloehn 6v syringe pump into the spectrophotometric cells, and the absorbance of light was measured at four different wavelengths (434 nm, 578 nm, 730 nm, and 488 nm). The ratios of absorbances at the different wavelengths were input and used to calculate pH on the total and seawater scales using the equations of Liu et al (2011). The equations of Dickson and Millero (1987), Dickson and Riley (1979), and Dickson (1990) were used to convert pH from the total to seawater scale. The isobestic point (488nm) will be used for the indicator correction. Salinity data were obtained from the conductivity sensor on the CTD. These data were later corroborated by shipboard measurements. Temperature of the samples was measured immediately after spectrophotometric measurements using a Fluke Hart 1523 digital platinum resistance thermometer.

## **Reagents**

The mCP indicator dye was a concentrated solution of  $\sim 2.0$  mM. Purified indicator batch 7 provided by Dr. Robert Byrne, University of South Florida was used.

## **Standardization**

The precision of the data can be accessed from measurements of duplicate samples, certified reference material (CRM) Batch 146 (Dr. Andrew Dickson, UCSD) and TRIS buffers (Ramette et al. 1977). The measurement of CRM and TRIS was alternated at each station. The mean and standard deviation for the CRMs was  $7.8927 \pm 0.0044$  (n=32). For TRIS buffer there was a sudden jump in the value at station 32, before station 32 and after station 32 the mean and standard deviation was  $8.0947 \pm 0.0040$  (n=15) and  $8.1694 \pm 0.0047$  (n=22) respectively. The

cause of the jump is currently unknown, but it was constant over the 3 bottles run after station 32.

### **Data Processing**

Addition of the indicator affects the pH of the sample, and the degree to which pH is affected is a function of the pH difference between the seawater and indicator. Therefore, a correction is applied for each batch of dye. One sample from each station was measured twice, once normally and a second time with double the amount of indicator. The change in the ratio is then plotted versus the change in the isobestic point to develop an empirical relationship for the effect of the indicator on the pH. This correction has not yet been applied to the preliminary data.

Table 1. Preliminary Quality Control

|                                |             |
|--------------------------------|-------------|
| <b>Number of Samples</b>       | <b>1274</b> |
| <b>Good (flag=2)</b>           | <b>1141</b> |
| <b>Dup (flag=6)</b>            | <b>58</b>   |
| <b>questionable (flag = 3)</b> | <b>12</b>   |
| <b>bad (flag=4)</b>            | <b>42</b>   |
| <b>lost (flag = 5)</b>         | <b>21</b>   |

### **Problems**

One major problem occurred on the first station when the four water baths running the lab van caused the temperature to rise rapidly to  $90 \pm F$  (and still rising), causing bubbles to form in the cell and instruments to over heat. Due to the location of the van on the ship, the seawater air conditioning unit could not be connected. In order to maintain the temperature at a reasonable level the door to the van was left open whenever the instruments were run. Temperatures throughout the cruise were maintained between 50-75°F.

On station 32 the water bath would not longer heat to 25°C, starting at this station through the remainder of the cruise samples were measured at 20°C and corrected to 25°C using the equation of Millero (2007).

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## **Total Alkalinity**

PI: Frank Millero/Ryan Woosley

Institute: UM/RSMAS

Analyst/Sampler:

Ryan Woosley

Fen Huang

Andrew Margolin

## **Sampling**

At each station total alkalinity (TA) samples are drawn from Niskin bottles into 500 ml borosilicate flasks using silicone tubing that fit over the petcock. Bottles are rinsed with a small volume, then filled from the bottom and allowed to overflowing half of the bottle volume. The sampler is careful not to entrain any bubbles during the filling procedure. Approximately 15 ml of water is withdrawn from the flask by halting the sample flow and removing the sampling tube, thus creating a reproducible headspace for thermal expansion during thermal equilibration. The sample bottles are sealed at a ground glass joint with a glass stopper. The samples are then thermostated at 25°C before analysis. Three duplicates are collected at each repeat hydrography station. Due to water budget issues, no duplicates could be taken on GEOTRACES stations. Samples are collected on the same bottles as pH or dissolved inorganic carbon (DIC) in order to completely characterize the carbon system.

## **Analyzer Description**

The sample TA is then evaluated from the proton balance at the alkalinity equivalence point, 4.5 at 25°C and zero ionic strength. This method utilizes a multi-point hydrochloric acid titration of seawater (Dickson 1981). The instrument program uses a Levenberg-Marquardt nonlinear least-squares algorithm to calculate the TA and DIC from the potentiometric titration data. The program is patterned after those developed by Dickson (1981), Johansson and Wedborg (1982), and U.S. Department of Energy (DOE) (1994). The least-squares algorithm of the potentiometric titrations not only give values of TA but also those of DIC, initial pH as calculated from the initial emf, the standard potential of the electrode system (E<sub>0</sub>), and the first dissociation constant of CO<sub>2</sub> at the given temperature and ionic strength (pK<sub>1</sub>). Two titration systems, A and B are used for TA analysis. Each of them consists of a Metrohm 765 Dosimat titrator, an Orion 720A, or 720A+, pH meter and a custom designed plexiglass water-jacketed titration cell (Millero et al, 1993). The titration cell allows for the titration to be conducted in a closed system by incorporating a 5mL ground glass syringe to allow for volume expansion during the acid addition. Both the seawater sample and acid titrant are temperature equilibrated to a constant temperature of 25 ± 0.1°C with a water bath (Neslab, RTE-10). The electrodes used to measure the EMF of the sample during a titration are a ROSS glass pH electrode (Orion, model 810100) and a double junction Ag, AgCl reference electrode (Orion, model 900200). The water-jacketed cell is similar to the cells used by Bradshaw and Brewer (1988) except a larger volume (~200 ml) is employed to increase the precision. Each cell has a solenoid fill and drain valve which increases the reproducibility of the volume of sample contained in the cell. A typical titration records the stable solution EMF (deviation less than 0.09 mV) and adds enough acid to change the voltage a pre-assigned increment (~13 mV). A full titration (~25 points) takes about 20 minutes. A 6 port valve (VICI, Valco EMTCA-CE) allows 6 samples to be loaded into the instrument and successively measured.

## **Reagents**

A single 50-l batch of ~0.25 m HCl acid was prepared in 0.45 m NaCl by dilution of concentrated HCl, AR Select, Mallinckrodt, to yield a total ionic strength similar to seawater of salinity 35.0 (I = 0.7 M). The acid is standardized with alkalinity titrations on seawater of known alkalinity (certified reference material, CRM, provided by Dr. Andrew Dickson, Marine Physical Laboratory, La Jolla, California).

The calibrated molarity of the acid used was  $0.24361 \pm 0.0001$  N *HCl*. The acid is stored in 500-ml glass bottles sealed with Apiezon® M grease for use at sea.

### Standardization

The reproducibility and precision of measurements are checked using low nutrient surface seawater collected from the ship's underway seawater system, used as a substandard, and Certified Reference Material (Dr. Andrew Dickson, Marine Physical Laboratory, La Jolla, California). The CRM is utilized to account for instrument drift over the duration of the cruise and to maintain measurement precision. A CRM was measured on each system on all odd numbered station and a low nutrient surface water sample was measured on each. Duplicate analyses provide additional quality assurance, and three duplicates, 2 samples taken from the same Niskin bottle, at each repeat hydrography station. The duplicates are then analyzed on system A, system B, or split between systems A and B. This provides a measure of the precision on the same system and between systems. Laboratory calibrations of the Dosimat burette system with water indicate the systems deliver 3.000 ml of acid (the approximate value for a titration of 200 ml of seawater) to a precision of  $\pm 0.0004$  ml, resulting in an error of  $\pm 0.3$   $\mu\text{mol/kg}$  in TA. All samples were analyzed less than 12 hours after collection.

### Data Processing:

Measurements were made on CRM bath 146. The difference between the measured and certified values on system A is  $-2.60 \pm 2.43$  (N=30) and on B is  $0.65 \pm 2.28$  (N=39). System A tended to run low, no correction to the CRM has been made on the preliminary data. Nine different batches of low nutrient surface water were used. They generally had standard deviations of  $\sim 3$   $\mu\text{mol/kg}$  or less except for batch 1 which was slightly higher. The mean and standard deviations of the duplicates were  $0.40 \pm 1.80$  (N=33),  $-0.46 \pm 2.13$  (N=36), and  $-2.04 \pm 3.18$  (N=21) on system A, system B, and one on each system respectively (A-B). The preliminary quality control results are shown in table 1.

**Table 1:** Preliminary quality control

|                       |      |
|-----------------------|------|
| Total Samples         | 126  |
|                       | 6    |
| Good (flag=2)         | 1149 |
| Duplicate (flag=6)    | 90   |
| questionable (flag=3) | 7    |
| Bad (flag=4)          | 12   |
| lost (flag=5)         | 8    |

### Problems:

The only major problem occurred on the first station when the four water baths running the lab van caused the temperature to rise rapidly to  $90 \pm$  F (and still rising), causing bubbles to form in the acid and instruments to over heat. Due to the location of the van on the ship, the seawater air conditioning unit could not be connected. In order to maintain the temperature at a reasonable level the door to the van was left open whenever the instruments were run. Temperatures through out the cruise were maintained between 50-75°F.

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## **Dissolved Inorganic Carbon (DIC)**

PI: Frank Millero/Ryan Woosley

Institute: UM/RSMAS

Analyst/Sampler:

Ryan Woosley

Fen Huang

Andrew Margolin

### **Analysis**

The DIC analytical equipment (DICE) was designed based upon the original SOMMA systems (Johnson, 1985, '87, '92, '93). These new systems have improved on the original design by use of more modern National Instruments electronics and other available technology. In the coulometric analysis of DIC, all carbonate species are converted to CO<sub>2</sub> (gas) by addition of excess hydrogen to the seawater sample using 8.5% H<sub>3</sub>PO<sub>4</sub>. The evolved CO<sub>2</sub> gas is carried into the titration cell of the coulometer, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH<sup>-</sup>. CO<sub>2</sub> is thus measured by integrating the total charge required to achieve this. (Dickson, et al 2007).

### **Standardization**

The coulometer was calibrated by injecting aliquots of pure CO<sub>2</sub> (99.995%) by means of an 8-port valve outfitted with two calibrated sample loops of different sizes (~1ml and ~2ml) (Wilke et al., 1993). The instrument was calibrated at the beginning of each cell with a minimum of two sets of the gas loop injections. 256 loop calibrations were run during this cruise.

Secondary standards were run throughout the cruise. These standards are Certified Reference Materials (CRMs), consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO). Their accuracy is determined manometrically on land in San Diego. DIC data reported to the database have been corrected to the batch 146 CRM value. The reported CRM value for this batch is 2002.93 μmol/kg. The average and standard deviation measured values was 2000.72 ± 2.45 (N=61) μmol/kg. Tubing was replaced on valves 4 and 5, which may have altered the volume of the pipette. There was an increase in the CRM value after changing the tubing, and the volume will be recalibrated upon return to the lab.

### **Sample Collection**

The DIC water samples were drawn from Niskin-type bottles into cleaned, pre-combusted 500mL borosilicate glass bottles using silicon tubing. Bottles were rinsed twice and filled from the bottom, overflowing by at least one-half volume. Care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5mL headspace, and 0.400mL of 100% saturated HgCl<sub>2</sub> solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored in a 20°C water bath for a minimum of 20 minutes to bring them to temperature prior to analysis.

### **Data processing**

About 1,000 samples were analyzed for discrete DIC. Only about 8% of these samples were

taken as replicates as a check of our precision. These replicate samples were typically taken from the surface, oxygen minimum, and bottom bottles. Due to water budget limits duplicates could not be taken on GEOTRACES stations, and were thus only collected on repeat hydrography stations. The replicate samples were interspersed throughout the station analysis for quality assurance and integrity of the coulometer cell solutions and no systematic differences between the replicates were observed. The mean and standard deviation between duplicates was  $-0.21 \pm 2.77$  (N=73)

The DIC data reported at sea is to be considered preliminary until further shore side analysis is undertaken.

### **Problems**

One major problem occurred on the first station when the four water baths running the lab van caused the temperature to rise rapidly to  $90 \pm$  F (and still rising), causing bubbles to form in the cell and instruments to over heat. Due to the location of the van on the ship, the seawater air conditioning unit could not be connected. In order to maintain the temperature at a reasonable level the door to the van was left open whenever the instruments were run. Temperatures throughout the cruise were maintained between 50-75°F.

On station 46 the pipette was not fully draining into the stripper. Tubing was replaced on valves 4 and 5. This could potentially change the volume of the pipette and it will be recalibrated once the instrument is returned to shore. After replacing the tubing CRMs averaged higher than before, but still within the uncertainty.

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**Density**

PI: Frank Millero/Ryan Woosley

Institute: UM/RSMAS

Analyst/Sampler:

Ryan Woosley

Fen Huang

Andrew Margolin

**Sampling**

Over the course of ARC01, 5 stations were sampled for a total of 179 density samples. Each Niskin was sampled using a 125 mL HDPE bottle. The bottles were rinsed 3 times, allowed to fill until overflowing, capped, and sealed with Parafilm. This procedure leaves as little head space as possible to minimize evaporation until analysis.

**Analyzer Description**

The sealed samples will be shipped to our lab in Miami where the salinity will be re-measured on a salinometer (Guildline Portosal), and the density will be measured using an Anton-Paar DMA 5000 densitometer and compared to the calculated density to determine  $\Delta\rho$  and absolute salinity.

## Oxygen isotopes

PI: Peter Schlosser

Institution: LDEO

Sampler:

Angelica Pasqualini

During the U.S. Geotraces 2015/Hydro-ARC01 icebreaker expedition, a total of 1100\* water samples were collected for measurement of  $^{18}\text{O}/^{16}\text{O}$  ratios in the top 500m of the water column. (1100 is an estimate; 895 bottles sampled after station 56).

Water samples for the measurement of oxygen isotope ratios were collected in 50 ml glass bottles. The bottles were rinsed in water from the Niskin bottle to be sampled, filled, and sealed using polypropylene caps and electrical tape. Oxygen isotope ratios will be measured at Lamont Doherty Earth Observatory using a Picarro L2130-i Analyzer.

In combination with salinity and nutrients, oxygen isotope ratios are useful to distinguish between freshwater components in the upper Arctic Ocean. Oxygen isotope ratios provide a useful tracer to separate the sea-ice melt-water from meteoric water (river runoff plus local precipitation/ evaporation [e.g. Newton *et al.*, 2013; Newton *et al.*, 2008; Schlosser *et al.*, 2002; Schlosser *et al.*, 1994;].

## References:

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**For PI list:**

| Analysis | Email  | Institution | Principal Investigator |
|----------|--|-------------|------------------------|
| DOC/TDN  | <a href="mailto:dhansell@rsmas.miami.edu">dhansell@rsmas.miami.edu</a> | RSMAS/UM    | Dennis Hansell         |

**For participant list:**

| Duties  | Name            | Affiliation | Email  |
|---------|-----------------|-------------|--|
| DOC/TDN | Andrew Margolin | RSMAS/UM    | <a href="mailto:amargolin@rsmas.miami.edu">amargolin@rsmas.miami.edu</a> |

**Dissolved organic carbon (DOC)**

*Principal Investigator: Dennis Hansell*

*Sampler: Andrew Margolin*

*Institution: Rosenstiel School of Marine and Atmospheric Science, University of Miami*

DOC and total dissolved nitrogen (TDN) samples were collected from nearly all stations (excluding stations 2-6 and 34), including four ice stations (31, 33, 39 and 42). In total, 1350 samples (1692 including duplicates) were taken from 60 stations. Samples from depths of 250 m and shallower were filtered through GF/F filters (0.7 µm nominal pore size) using in-line filter holders, while samples from greater depths were not filtered. Filters were combusted at 450°C prior to the cruise, and polycarbonate (PC) filter holders and silicone tubing were cleaned with 10% HCl and rinsed with Milli-Q water before sampling. All primary samples were collected in 60 mL PC bottles, pre-cleaned with 10% HCl and rinsed with Milli-Q water. Duplicate samples were collected in 40 mL glass vials, combusted at 450°C prior to the cruise. All sampled bottles and vials were rinsed three times with the seawater before filling with 40-60 mL of seawater. Nitrile gloves were worn while sampling. Samples collected in PC bottles were frozen standing upright inside the ship's freezer, while duplicates collected in glass vials were stored in the dark at room temperature, stowed in the ship's science cargo hold. Frozen and room temperature samples will be shipped from Seattle to Miami for laboratory analysis.

## STARC Support for GeoTraces/ODF/ HLY1502

STARC technicians in cooperation with ODF personnel assisted with installation and adjustment of CTD sensors and niskin bottles throughout the cruise. We had 2 instances of damage to the .322 wire, one caused by a snag on an ice floe, the other resulting from the wire getting pinched on deck (under the CTD cart rail) while moving the rosette in and out of the staging bay. Both incidents required re-termination. Initially the cruise plan called for using the 12 place 30L rosette for GeoTraces casts and the 36 place 10L rosette for the Repeat Hydrography casts. Throughout the first few stations the 30L rosette experienced frequent leaking from multiple niskin bottom caps. To stop the leaks required tapping the top/bottom caps closed with a rubber mallet as soon as the CTD was brought on deck. These issues were recorded on the cast data sheet and details for individual casts can be accessed there. Eventually (after station 26) it was decided that the 36 place rosette would replace the 12 place for both sampling programs and could provide the same water quantity from the more reliable 10L niskins. The altimeter and PAR sensor were switched from the 12 place to the 36 place. Once we switched over to the 36 place 10L rosette we experienced relatively few bottle closure problems. Bottle 35 failed to close at station 30 (cast 12). Between stations 47 and 52 bottle position #29 began having intermittent closure problems. The carousel would trigger, but the latch did not release immediately. This was addressed by changing the vertical position of the bottle and by replacing the latch with a spare. Other small adjustments were made when necessary, such as o-ring seating/replacement (bottles #3 #14, #23, #31), spigot repairs, and clearing obstructions from the lanyard path (#29). These instances are also detailed on the cast log data sheets.

The installed O<sub>2</sub> sensors were susceptible to damage when exposed to sub-freezing temperatures, to counter this, a large, rolling heater fan was positioned near the rosette while it was staged on deck, pre deployment and upon recovery. The warm air from the fan helped to prevent freezing of the sensitive membrane inside the O<sub>2</sub> sensor by keeping the surrounding air temps 1-2 degrees C above zero. Despite these efforts two oxygen sensors appear to have been damaged or at the least the data was suspect, resulting in a swap out for a spare sensor.

The UVP unit was recharged in between casts according to instructions provided by the technician (Andrew McDonald) who installed it. We did encounter rare instances when the unit would not accept a charge from the deck box. This required rigging up a small electric fan that would drain the battery to a lower threshold, then reconnecting the deck box to begin charging. On Station 43 Cast 2 the power shunt was accidentally not installed, this resulted in an electrical current arcing between 2 exposed pins and caused one pin to corrode away. The damaged cable was replaced with a spare. Throughout the cruise we had no indication that the unit was not working as intended. We kept in close contact with Andrew and provided him data on battery voltages and casts depths.

The 36 place rosette had two upward looking mini-chipods and two downward facing thermistors installed. These were installed in Seattle prior to sailing, plugged in at the first science station (only unplugged once to save battery during a multi-day break from using the 36 place rosette) and left powered and installed the remainder of the cruise. One of the the thermistors was damaged when the CTD was recovered at station 30. A piece of ice had fallen onto the pallet, (either brought aboard stuck inside the rosette or fell from the a-frame) and the thermistor happened to come down on top of this piece of ice when the rosette was placed on the pallet. This damaged thermistor was removed and a spare sensor tip swapped in.

At the request of a science party member, close inspection and cleaning of the transmissometer was initiated at each station and between casts. This included a thorough cleaning of the lenses with Kim wipes and Milli-Q water, after cleaning the lenses were kept capped until immediately prior to a cast. After cleaning the

CTD was powered up and deck tested to observe the voltage readings for the transmissometer were at or above 4.6 volts.

## **Haardt fluorometer**

Rainer Amon

Professor, Department of Marine Sciences and Oceanography

Texas A&M University at Galveston

Ocean and Coastal Studies Building

Building 3029 room #351

200 Seawolf Parkway, P.O. Box 1675

Galveston, Texas 77553, USA

Phone: 409-740-4719; fax 409-740-4429

Email: amonr@tamug.edu<<mailto:amonr@tamug.edu>>

The Haardt fluorometer is a backscatter fluorescence sensor that excites at 350-460nm and measures the emission at 550nm HW 40nm. It was designed to measure the chromophoric dissolved organic matter (CDOM) that originates in the terrigenous environment, but also responds to CDOM produced in the ocean. The same sensor was used during AOS 2005 and will allow us to see changes in the distribution of the transpolar drift, riverine dissolved organic matter, as well as the CDOM maximum associated with the halocline. Sensor data will be complemented with measurements of optical properties and terrigenous and marine biomarkers on discrete water samples. The Haardt sensor is both an important water sampling guide as well as a water mass tracer for the upper Arctic Ocean. During the 2015 Healy cruise the Haardt sensor data and biomarker data will be paired with trace element (TE) measurements to understand the role of riverine DOM for the transport of TE in Arctic Ocean surface waters. We duplicated the same science plan on the 2015 Polarstern cruise covering the Eurasian Arctic to gain a pan-Arctic view comparable to 2005.

## **WetLabs C-STAR transmissometer**

Wilf Gardner and Mary Jo Richardson  
Texas A&M University  
wgardner@ocean.tamu.ed  
mrichardson@ocean.tamu.edu

The WetLabs C-STAR transmissometer on the ODF rosette (and the one on the GEOTRACES rosette) measures the attenuation of light at 650 nm (red). The amount of attenuation is a proxy for particle concentration at each depth in the water column. Generally one sees high concentrations in surface waters due to phytoplankton with a rapid decrease in concentration in the upper 100 m. Much of the water column will show very low values. If sediment is resuspended near the bottom or advected laterally from shallower topography, attenuation increases. These resuspended sediments could affect benthic biogeochemical cycles and trace element scavenging. Our goal is to quantify the distribution of particulate matter in both surface and bottom Arctic waters to add to the 9000 plus profiles we have collected in all other oceans of the world. In addition to our past syntheses of particle regimes in surface waters, we are constructing the first global map of nepheloid layers - resuspended sediment . We will also compare the attenuation signal with the UVP data of Andrew McDonnell, who is measuring the abundance and size distribution of particles in the 64  $\mu\text{m}$  to 2.5 cm range throughout the water column.

## **Chi-Pod microscale temperature gradient measurements**

Jonathan Nash  
104 CEOAS Admin Bldg.,  
Oregon State University,  
Corvallis OR 97331  
(541) 737-4573  
nash@coas.oregonstate.edu  
mixing.coas.oregonstate.edu

Systematic Direct Mixing Measurements within the Global Repeat Hydrography Program (SYSDMM) is an NSF-funded project (Nash, Moum, and MacKinnon) to obtain repeated sequences of turbulent mixing, distributed broadly throughout the global oceans and over full-ocean depths. To this end, we have developed chi-pods, self-contained instruments that measure microscale temperature gradients using fast-response FP07 thermistors, along the sensor motion/trajectory using precision accelerometers. From these measurements, we are able to compute the dissipation rate of temperature variance ( $\chi$ ) and the eddy diffusivity of heat and other tracers. Unlike traditional microstructure/turbulence measurements based on shear probes,  $\chi$  is not highly sensitive to vibration of the sensor itself, so it is possible to make these measurements from a standard CTD rosette, provided that the sensor tips can be placed in a part of the flow that is uncontaminated by the wake of the CTD rosette itself. For sensor calibration, we require the raw 24 Hz CTD data; computations also require knowledge of the background stratification and vertical temperature gradient. Chi-pods have now been used on several repeat hydrography cruises, including A16S, P16N and P16S, with an ultimate goal of obtaining a global dataset of microstructure observations.

## **Underwater Vision Profiler**

Dr. Andrew M. P. McDonnell  
Assistant Professor of Oceanography  
School of Fisheries and Ocean Sciences  
University of Alaska Fairbanks  
Phone: 907-474-7529  
amcdonnell@alaska.edu

The Underwater Vision Profiler 5 (UVP5), serial number 009, was mounted onto the ODF CTD-Rosette in order to obtain in situ images of marine particles and plankton throughout the water column. It was positioned in the center of the rosette with the camera looking downward and the lighting units illuminating a volume of water several inches above the bottom of the rosette. The instrument was powered with an internal rechargeable battery and stores image and pressure data internally on hard drive, and data will be offloaded and analyzed after the cruise ends. The UVP5 was programmed in depth acquisition mode, taking advantage of the CTD's initial descent (@20 m/min) and pre-cast soak at 20 m below the surface as the signal to initiate image acquisition. Image acquisition was stopped (to conserve battery power and data storage space) after the UVP5 detected a 50 dbar upturn from the bottom of the cast. While the rosette was on deck, the UVP5 was connected to deck leads coming from the UVP deck box, providing battery charging. The image volume of UVP5 serial number 009 was calibrated in a tank and determined to be 0.930 L. Particle concentration was determined by counting the number of detected particles and normalizing with respect to the image volume. Particles detected by the UVP5 range in size between 0.064 mm and several cm (equivalent spherical diameter). The UVP5 was operated in mixed processing mode, meaning that particle characteristics were quantified in real time onboard the UVP5 and the images of the largest particles (greater than about 2 mm in ESD) were segmented out of the image files and saved as individual images with their corresponding metadata. The instrument and data processing are described in Picheral et al., 2010. Due to berthing restrictions, the UVP had no dedicated technician onboard to actively monitor the performance of the instrument and data. Deployments and basic maintenance were kindly carried out by Johna Winters, Croy Carlin, and Brett Hembrough.