

# Cruise Report for Knorr 199-4 (October 15- November 4, 2010)

The U.S. GEOTRACES Atlantic Shipboard Team<sup>1</sup>

January 18, 2011

## Prelude:

This cruise constitutes the first survey section as part of the U.S. participation in an international program named GEOTRACES. The first challenge in organizing the cruise was the fact that requests from participating groups were made for a total of 46 scientific berths on a ship that could house only 32. During the pre-cruise planning meeting at Old Dominion University (ODU) in March, 2010, discussion focused around how we would accomplish cruise objectives within this berthing limitation. A plan was developed that included a core group of “shared super-technicians” whose responsibilities included staging for and sampling of the trace-metal clean GO-FLO carousel, helping with the pumping casts, and deploying/retrieving and sampling the Niskin rosette. Sampling for properties such as stable isotopes, dissolved inorganic carbon, radiocarbon, etc. would be accomplished by designated cruise participants in addition to their own programmatic responsibilities. It was also agreed that standard hydrographic analyses (salinity, dissolved oxygen, and micromolar nutrients) would be carried out by the Ocean Data Facility (ODF) group, along with CTD data reduction and archiving, as well as primary data management operations. We felt that this latter function was extremely important for a GEOTRACES cruise from the viewpoint of metadata assembly and data submission requirements to BCO-DMO and ultimately to the GEOTRACES data assembly center at BODC. At the ODU planning meeting, sampling protocols and a skeleton cast plan were constructed, both of which were further refined in subsequent months as the scope and scale of sampling requirements became clearer.

Prior to the KNORR’s departure from Woods Hole in late August, the Dynacon winch and A-Frame for the GEOTRACES trace metal clean carousel were mounted on the ship. In addition, the chemical reagents required for the cruise were secured in the chemistry van on the 02 level. Some sampling equipment and supplies were also stored in the scientific hold. A leased freezer van was mounted on the 02 level, and a bulwark was fabricated and installed on the forward side of the van to protect the machinery from salt spray and waves. The base for the NASA optical tower was installed on the flying bridge. Finally, a large number of compressed gas cylinders (nearly 60) were mounted and secured on racks both on the 01 level and in the aft hangar. We are grateful to Eric Benway and the Port Office for their assistance in arranging these modifications.

## Cruise Narrative and Preliminary Observations<sup>2</sup>:

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<sup>2</sup> *Please note that the results presented here are both preliminary and proprietary to the individual investigators.*

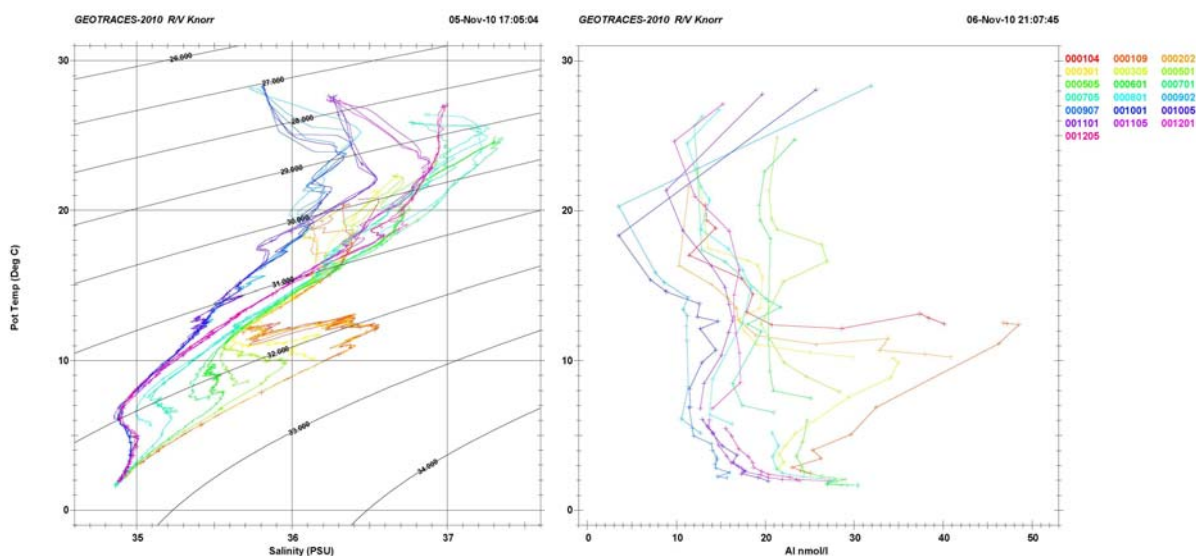
**Cruise mobilization** commenced on October 11 in the port of Lisbon. On the first day, six laboratory vans were loaded onto the ship, 4 on the main deck and 2 on the 01 level. Space on the ship was at a premium. A major challenge for managing deck space was the large number (48) of pallet boxes required for gear and sample storage. This challenge was met in part by compromising on the number of pallet boxes actually stored on board: 4 were shipped back to WHOI while the remainder was deployed on the 02 and 01 levels as well as the main deck. We are grateful to the ship's crew (and in particular the chief mate) for their patience, assistance, and advice during this trying process. Additional space was gained by having equipment crates and unused equipment and boxes shipped back to Woods Hole in shipping containers. In addition, 5 NEMO floats were placed on deck for deployment during the cruise.

Over the course of 4 days, a team of scientists consisting of the actual cruise participants along with 5 other scientists and Eric Benway worked hard loading gear on board, securing equipment, setting up the laboratory vans (including connecting electric, water, and compressed air supplies), and assembling the trace metal clean areas (bubbles) using plastic sheeting and HEPA filters. Liquid nitrogen tanks were topped up. Gas tank regulators were installed and tubing connected to equipment. The CTD rosettes were assembled and connected to the conducting wires, and various sampling and sample processing systems were set up. Because the very first station was just a few hours steaming from the dock, we held our first cruise science meeting on the dock the afternoon before departure.

There was a last-minute personnel change. Given the number of individuals involved in the cruise, there was finite probability that illness might prevent someone from sailing. As a backup plan, a member of the pumping group (Kuanbo Zhou) was "sailing standby" in that he had flown to Lisbon in case this happened. It was fortunate that he did because although the observer did show up, a member of the ODF group fell ill with influenza and could not sail with us (the captain was concerned about contagion). This meant that the pumping group benefited from having the additional participant, but the ODF group suffered from sailing short-handed. Despite this disadvantage, the ODF group performed admirably well, for which we are grateful.

**The first station** occurred within a few hours after departing Lisbon, and was a designated super-station, so that we had our hands full right off the bat. Prior to reaching station, the GEOTRACES carousel (GTC) was lowered to about 50 m depth in "blue water" for rinsing. When we reached the station additional test casts were deployed, alternating between the GTC and the ODF rosette (the 12 bottle 30 liter Niskin rosette) to insure mechanical integrity and to clean the bottles. A set of test samples were taken for the GTC which included both the main set of GO-FLO bottles and the backup ("B-Team") set. These samples were measured on board for Zn to diagnose for contamination. Some problems were identified and resolved. Additional "soak time" was used as a cleaning strategy for all the "A-team" GO-FLO bottles.

One of the key objectives for the first station was to sample the pronounced intermediate depth salinity maximum associated with the Mediterranean Outflow Waters (MOW) that are known to be flowing northward along the Iberian Peninsula at about the 1000 m isobath. The MOW at this station was manifested in a broad salinity maximum between 500 and 2000 m depths. This is exemplified in the left panel of Figure 1, which is a cumulative T-S plot for all of the Niskin CTD casts for the cruise. The multiple intermediate depth salinity maxima (at least 4 significant extrema) may be attributed to tidal fluctuations in mixing along the eastern boundary slope. The maximum salinity observed over this depth range exceeded 36.5, indicating a remarkably strong presence of MOW at this site. Indeed, the broad range of depths showing excess salinity suggested an opportunity to sample the trace-metal content of a particularly important end-member. Preliminary ship-board results obtained by the Measures-Hatta (U.H.) group show the expected high Al values (approaching 50 nmol l<sup>-1</sup>) associated with the core of the MOW (see right panel in Figure 1).



**Figure 1:** *Left:* a composite T-S plot of all Niskin CTD casts during the GEOTRACES cruise. Superimposed on the traces is the potential density anomaly in kg m<sup>-3</sup> referenced to 1000 dbars, and *right:* A composite T vs. Al plot of the Measures & Hatta preliminary shipboard data for all stations. Note the intermediate depth Al maximum for the first two stations associated with MOW.

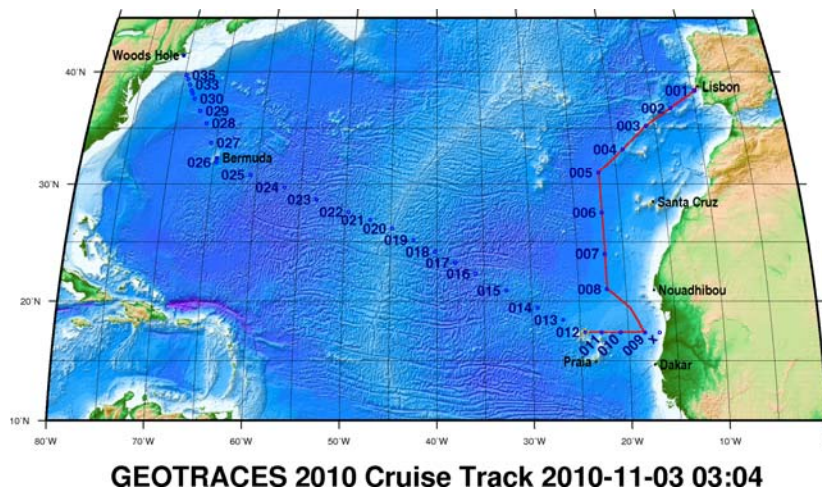
In addition to performing what we refer to as “full station” sampling, which consists of 2 GTC and 3 Niskin CTD casts, we did 3 extra Niskin casts for “super-station” sampling. This was aimed at obtaining extra water for properties not normally sampled on the full and demi-stations. For each full or super station, we also performed two pumping casts (one shallow and one deep) where McLane pumps were clamped on Vectran wire as a serial cast. On the deep pumping casts, 30 liter Niskin bottles were clamped above each pump and were tripped at the middle of the 4 hour pumping interval. As a standard protocol, we sampled each GO-FLO and each Niskin bottle (including the pump cast Niskins) for salinity and nutrients as a diagnostic of bottle integrity (whether the bottle leaked, or pre-/post-tripped). In addition, the Niskin bottles were sampled for dissolved oxygen, again as a bottle integrity check, and

also for calibration checks on the CTD oxygen sensor. In addition, the Niskin rosette was equipped with a nephelometer and an altimeter to enable close bottom approaches. This allowed us to sample full depth profiles to within 10-15 m of the bottom.

There was one alarming incident during station 1. An over-heated resistance coil in an apparatus burst into flame in the analytical lab. It was quickly extinguished, but not before the lab was filled with acrid smoke and a general fire alarm was triggered on the ship. This served as an object lesson in the dangers of fire at sea, while the ship's crew demonstrated efficiency and cool heads while dealing with the emergency. Although the fire itself caused little damage (aside from the need to clean up after the fire extinguisher), the subsequent power shut-down to the lab had a significant consequence: on-repowering the ODF data server computer died. We managed, thanks to hard work and creative programming by Mary Johnson, our ODF data manager, to set up the data server and web site on her laptop.

After spending more than two days testing and sampling at this first site, we continued our south-westward transect with alternating "demi" and full stations (see Figure 2). A demi-station typically involved single shallow GTC and Niskin cast (the one exception to this was station 4, where we only completed a Niskin cast so that the GTC sampling team could catch up). The T-S diagram in Figure 1 also shows the progressive attenuation of the MOW salinity maximum as we moved away from the European coast, as would be expected from our knowledge of the large scale distribution of salinity at mid-depths in the North Atlantic.

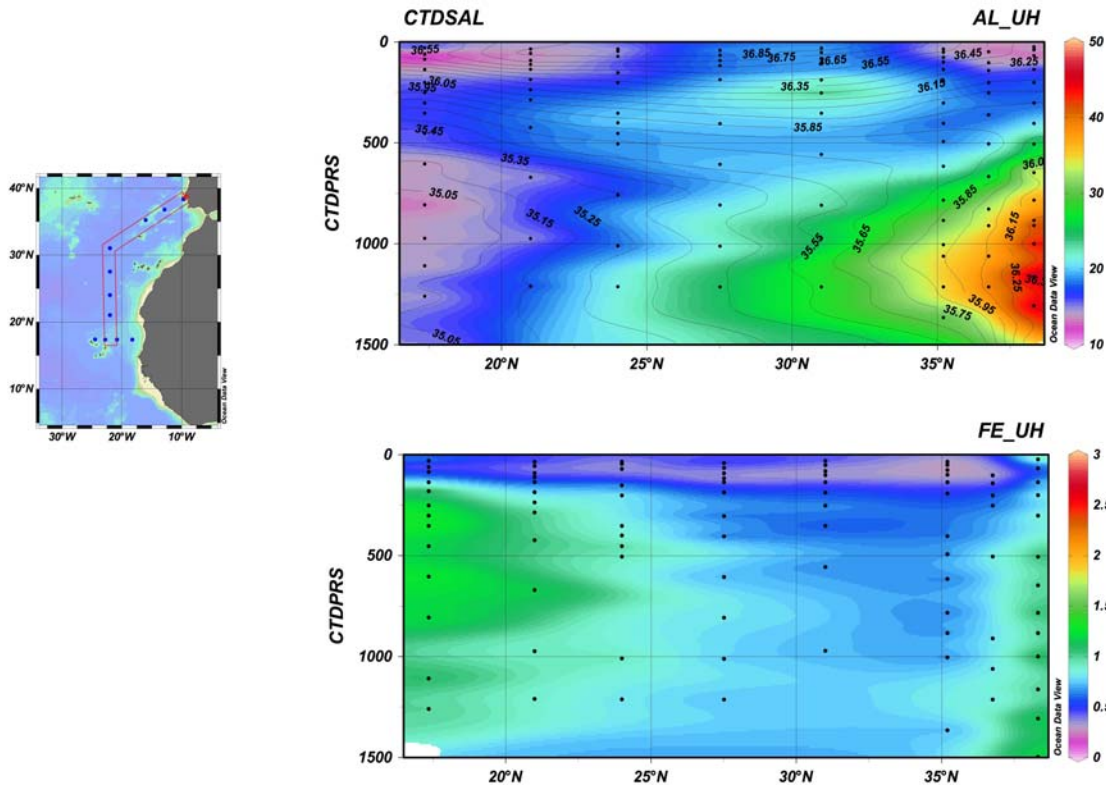
Station 5 found us at the beginning of our 22°W meridional section, where we turned due southward, alternating full- and demi-stations. Station 7, a full station, coincided with the recently sampled German GEOTRACES occupation (Meteor Cruise M81/1, GEOTRACES section A11 by Martin Frank and others). We attempted to replicate most of the depths sampled during the German cruise to allow maximum opportunity for inter-comparison. Unfortunately, stringent limitations in water availability (heavy subscription by participating U.S. analysts) prevented us taking any "library samples" for distribution to non-U.S. laboratories. Following this station we continued on to Station 8, a demi-station.



**Figure 2:** Our planned (numbered symbols) and actual (red line) cruise track.

Figure 3 shows a meridional section of shipboard measurements dissolved Al and Fe by the U. Hawaii group (Measures and Hatta). The Al section (upper panel) has salinity contours overlaid. The two

dominant features in the northern part (right hand) part of the section are the pronounced mid-depth MOW AI and salinity maxima and the shallow (~250 m) AI maximum. The latter is a signature of waters subducted in the northeast portion of the subtropical gyre just south of the Azores Current extension. Note also the vertical bifurcation of the MOW maximum in both AI and salinity. Although the MOW also appears to have elevated Fe concentrations, this signature doesn't propagate to any significant extent, a signature of Fe removal at depth.



**Figure 3:** Meridional sections along 22° W (see left-hand map) of AI (upper panel) and Fe (lower panel) measured by the U.H. group (Measures and Hatta) on board. Salinity contours overlay the AI section.

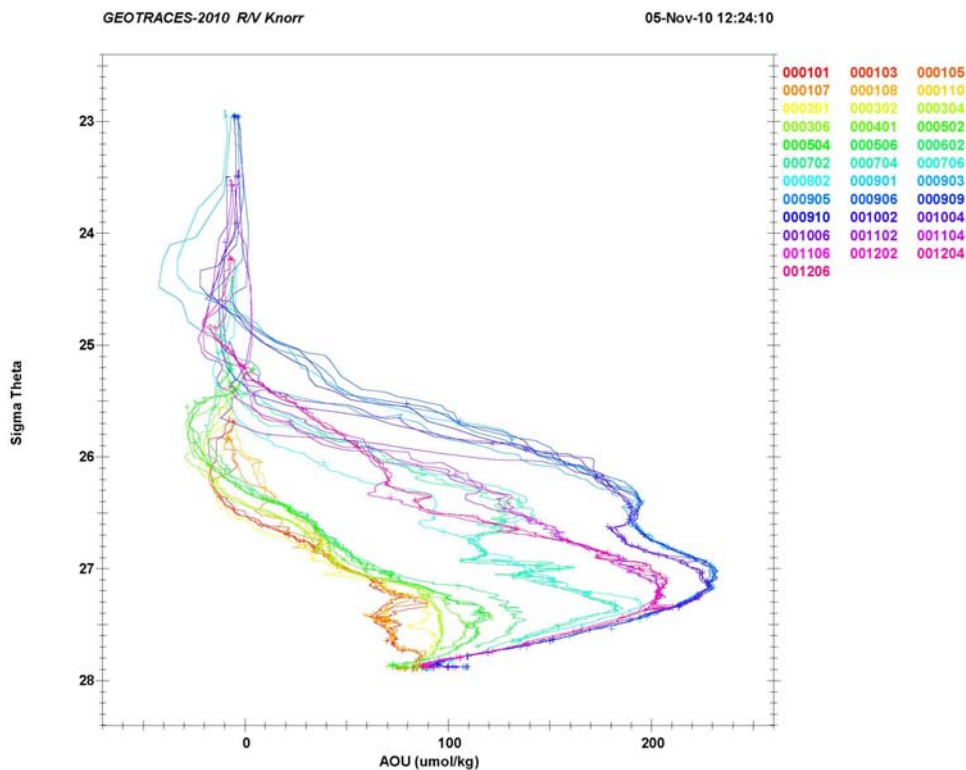
After Station 8, we had planned on a longer-than-normal steaming period that would allow our over-worked scientists a chance to catch up with their analytical work and maybe even get some sleep. However, this is when disaster struck.

The more aware of us detected an abrupt change in the ship's motion as we steamed toward station 9, our closest approach to the Mauritanian coast. Rather than making a steady 11-12 knots in the southeastward direction, the ship started to weave back and forth, averaging only about 7 knots. We learned that the port thruster had failed. At this point, the Captain informed us of the seriousness of the situation and of the likelihood that the cruise would have to be terminated "at any moment". The key problems present by the port thruster failure were reduced steaming speed, but more importantly

compromised station-keeping ability. How well the ship could maintain position and minimize wire angle in any significant seas was in question. At this point we were faced with a critical decision: with the distinct possibility of the cruise being aborted at any time, what steps could we take that would maximize the amount of science accomplished? After some discussion, we decided to abort the eastern-most station (situated in 500 m of water off Mauritania) to steam to the closer superstation. Although this would compromise the objectives of some groups (in particular the radium people), we felt that if we could just get the superstation done, we would have accomplished a major objective and provided samples for the broadest community of scientists. This, combined with the reduced steaming required going to the nearer station, seemed to be the best choice at the time.

It turned out that the weather gods were on our side, and the captain and crew became quite adept at managing the less-than-agile propulsion system. Consequently after a positive experience at the first station in the section, we were given the green light to try for another. Things worked so well that the captain agreed to a limited, but in our eyes very important objective of finishing the Mauritania-TENATSO section prior to pulling into port in the Cape Verde Islands. This raised our spirits immensely, and we are grateful to the captain and crew for going out on a limb for us.

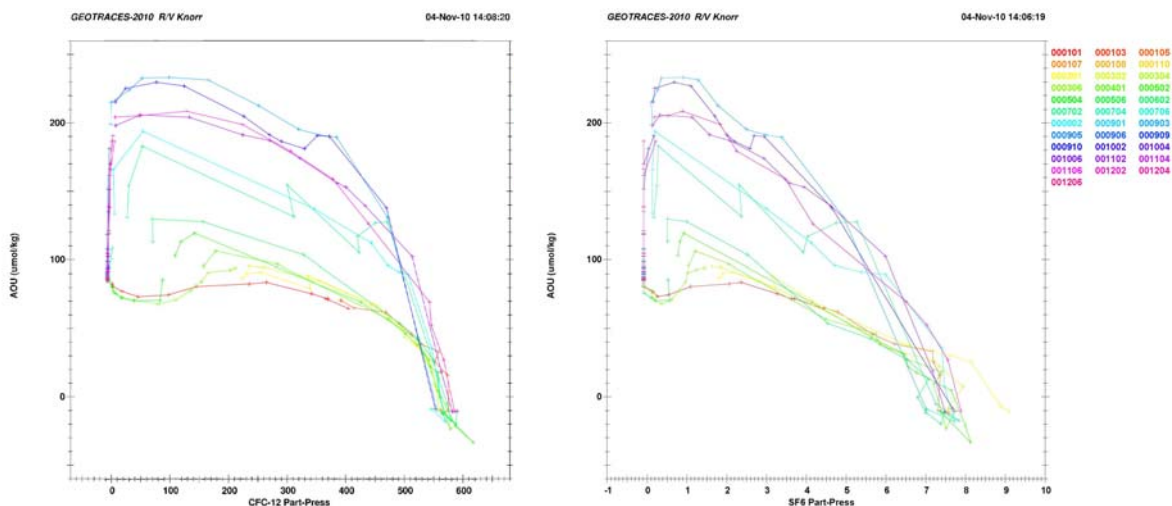
The Mauritania-TENATSO section proved extremely interesting. As shown in Figure 4, the oxygen minimum zone (OMZ) was most intense on the eastern-most station, and appeared as a double oxygen minimum. The shallow one near  $\sigma_0 = 26.4 \text{ kg m}^{-3}$  is a feature traceable to the north at stations 7 and 8,



**Figure 4:** AOU (in  $\mu\text{mol kg}^{-1}$ ) vs. potential density anomaly (in  $\text{kg m}^{-3}$ ). Note the double maximum that appears in stations 8, 9, and 10, but not for other stations.

but not directly to the west in stations 10-12 suggestive of a northward flowing eastern boundary current at these depths. The shipboard Al, Fe, and Mn analyses made by Measures and Hatta (see Figure 3 again) reveal an interesting feature: the oxygen minimum is characterized by high Fe, low Al at the southernmost station, but with no significant Mn signature (not shown). This is a signature of the high productivity waters associated with the upwelling zone: the Fe is remineralized (and hence associated with high AOU/low oxygen) while the low Al suggests dilution of its aeolian signature by high production. The low Mn indicates very little contribution to the oxygen minimum from sedimentary remobilization.

It is too soon to speculate on the “dynamics” of the trace metal signatures that we see in the oxygen minimum tongue, but the encouraging fact is that we are observing significant SF<sub>6</sub> and CFC-11/12 signatures in the oxygen minimum core (see Figure 5). These measurements were made by Eugene Gorman from Bill Smethie’s group at LDEO. The CFC and SF<sub>6</sub> vs. AOU curves differ in a manner that is entirely consistent with their respective atmospheric histories (remember that atmospheric CFC concentrations have been decreasing with time since the 1990s due to the Montreal protocol, whereas SF<sub>6</sub> continues to increase with time). The SF<sub>6</sub> partial pressures indicate an effective age for the oxygen minimum waters of approximately 2 to 3 decades. This observation is important, as it indicates that there is ample transient tracer “signal” in the oxygen minimum waters to characterize the advective-diffusive ventilation time scales. Combined with bomb radiocarbon and tritium-<sup>3</sup>He a very complete characterization of the transit time distribution should be possible, enabling a determination of the transformation rates and fluxes of the trace metal signatures and biogeochemical processes (e.g., oxygen utilization and nutrient remineralization rates) associated with the upwelling cell of the OMZ.



**Figure 5:** Plots of the partial pressures of CFC-12 (left panel) and SF<sub>6</sub> (right panel) vs. AOU. Note there are significant, non-zero CFC and SF<sub>6</sub> partial pressures within the oxygen minimum, and that the CFC values are higher over a broader range of AOU. Measurements were made by Eugene Gorman of Bill Smethie’s laboratory. Data are preliminary and may change by as much as 1-2%.

**Sampling and Analysis Accomplished:**

Not counting test casts for mechanical evaluation and rinsing of bottles, a total of 19 casts were made with the GEOTRACES carousel, and 34 ODF-Niskin rosette casts were completed. For the former system, 456 salinity and nutrient measurements were made for evaluation of bottle integrity, calibration check on the CTD, and generation of property profiles. For the latter casts, 408 oxygen, nutrient and salinity samples were drawn and analyzed for similar reasons. In addition, approximately 60 nutrient, salinity and oxygen samples were drawn from the deep pump cast Niskin bottles. Having this data nearly real-time after the analyses were completed was a real boon to the chief scientist, as it provided rapid assessment of sampling quality and strategies.

**Reports on sampling activities and individual groups participating in the cruise.**

**(1) GEOTRACES carousel sampling:** The Cutter (ODU) group provided the GEOTRACES sampling system, including the Dynacon winch with 7800m of Kevlar cable with conductors, A-frame, clean lab, and Seabird carousel/CTD with 24 12L GO-Flo bottles (and 14 spares). Peter Morton (FSU) and Jessica Fitzsimmons (MIT) were the “super technicians” in charge of the trace element sampling logistics, while Ed Boyle and Greg Cutter were in charge of the overall operation. In total, 19 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 µm). 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 Bill Landing (FSU). For the 12 stations occupied, this represented the acquisition of over 4600 trace element samples! Shipboard analyses of Al, Fe, and Zn indicated multiple sporadic (e.g., not confined to a single GO-Flo or element) contamination events in the first 2 stations, but with very few questionable results. A number of samples were taken from the GTC in support of shore-based analysis. These are summarized in the table below:

Number Samples	Size (ml)	Property	P.I.
192	50	Fe(II)	Sedwick
216	125	Fe, Al, Mn, some Zn	Measures
240	60	Total and reactive Co	Saito & Noble
218	2000	Hg & Hg speciation	Lamborg
144	125	Nanomolar nutrients	Cutter
384	425	Fe speciation (shipboard and shore)	Buck
115	850	Cu speciation	Moffett
456	500	Salinity	ODF
456	30	Nutrients	ODF
192	125	Fe & Fe Speciation	Sedwick
216	125	Multi-element trace metal	Landing
407	1000	Fe, Mn, Cu, Cd, Zn	Wu
43	500	Zr, Hf, Nb, Ta	Orians/McAlister
		Al, Sc, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, Cd, Pb	Smith/Bruland
29	500	Ti	Murray
24	1000	As	Cutter



23	60	Os	Sharma
36	150	N- and O- isotope analysis of NO <sub>3</sub>	Casciotti
120	100	Shipboard Zn analysis for contam.	Boyle
203	2000	Total Pb, Pb isotopes	Boyle
216	125	Mn, V, REE, Ga	Shiller
26	125	Ag	Gallon
29	500	Ti	Murray
299	1000	Fe isotopes	John
216	2000-8000	Particulate samples for trace elements	Twining

(2) *Sampling the ODF (30 liter Niskin) rosette* was performed for non-contamination prone elements and compounds, and included the following:

Number Samples	Size (ml)	Property	P.I.
184	500	Dissolved inorganic carbon & alkalinity	Millero & Bates
184	500	<sup>13</sup> C and <sup>14</sup> C	Quay and NOSAMS
240	50	<sup>3</sup> He/ <sup>4</sup> He, dissolved He, Ne	Jenkins
228	1000	<sup>3</sup> H	Jenkins
408	30	Nutrients	ODF
408	250	Dissolved oxygen	ODF
408	500	Salinity	ODF
240	500	CFCs and SF <sub>6</sub>	Smethie
192	30	<sup>18</sup> O in H <sub>2</sub> O	Voelker & Coleman
67	250	DOC/CDOM/POC	Hooker (NASA)
191	125	Hg Thiols	Lamborg
191	30	Ba concentration	Falkner
157	5000	<sup>232</sup> Th, <sup>230</sup> Th, <sup>231</sup> Pa, <sup>232</sup> Th colloids	Anderson, Edwards, Moran, Robinson, Pahnke, Scher, Goldstein
157	5000	Nd isotopes	Anderson, Edwards, Moran, Robinson, Pahnke, Scher, Goldstein
157	5000	Rare Earth Elements	Anderson, Edwards, Moran, Robinson, Pahnke, Scher, Goldstein
32	20000	210Pb, 210Po	Church
32	2000	Si isotopes	Brzezinski
20	20000	<sup>239</sup> Pu, <sup>240</sup> Pu, <sup>137</sup> Cs, <sup>237</sup> Np	Kenna
56		HPLC pigments	Hooker
174		<sup>234</sup> Th	Buesseler
99		<sup>238</sup> U	Buesseler
64		<sup>226</sup> Ra	Charette
56	1000	flow cytometry, metagenomic and qPCR	Chisholm
46	2000	NIF-H RNA analysis	LaRoche
741	60	<sup>15</sup> N-NO <sub>3</sub>	Casciotti/Sigman

Filtered samples for non-contamination prone elements were collected from the ODF Niskin rosette (12 x 30L Niskin bottles) using AcroPak 500 filter cartridges with a Supor 0.45/0.8µm membrane attached to Teflon-lined Tygon tubing. The number of depths from which samples for each parameter were taken is listed in Table 1. The samples for radioactive and radiogenic isotopes (Th, Pa, Nd, Pb, Po, Pu) were acidified with 6 N hydrochloric acid (optima grade: Pa, Th, Nd; trace-metal grade: Pb, Po, Pu) to a pH of ~2 within two hours of collection. The samples were parafilmmed, double-bagged, and stored in pallet boxes.

*All samples for nitrogen isotopes were frozen at -20°C.* Deviating from the original plan to collect samples for Th, Pa, and Nd analyses from 16 depths at each standard station, we maximized the number of samples for this group at stations 9-12. At these stations, we collected 3 x 5L samples from all 24 depths sampled by the Niskin rosette, and one sample that was provided from the towed fish (G. Smith, K. Bruland) upon arriving at those stations. At three stations (9, 11, 12), we separated 15mL from seventeen (station 9) and thirteen (stations 11, 12) of the Th-Pa samples into 50mL centrifuge tubes containing an Amicon Ultra centrifugal filter insert (UltraCel - 10K) and centrifuged the samples for 20 mins at 3,500 rpm. The filter inserts were then removed and the centrifuges capped and parafilmmed. These filtrates were acidified with 60 µl of 6 N optima grade hydrochloric acid on November 4 and will be analyzed for colloidal <sup>232</sup>Th.

**(3) Pumped Sampling:** Size-fractionated suspended (<51 micron) and sinking (>51 micron) particulate matter was collected via dual-flowpath in situ pumps at eight stations, up to 16 depths per station. The dual flowpath design allowed simultaneous collection of particles on quartz fiber filters for particulate organic carbon and other analyses and on Supor (polyethersulfone) filters for trace element, isotopic, and biogenic silica analyses. Typical volumes filtered were ~1100L through the quartz filter and ~500L through the Supor filter over a 4 hr pumping period. Filters were processed at sea using trace-metal clean techniques in a clean space. All filters were photographed, misted lightly to remove salts, subsampled for distribution to groups that required fresh samples, and the remainder dried for later subsampling and analysis on land. Particle subsamples will be distributed to eleven groups for analysis of major particulate phase composition, biochemical composition, and a broad suite of particulate trace elements and isotopes.

**(4) The coupled biogeochemistries of arsenic and phosphate.** Arsenic and phosphorus are chemically and biochemically very similar, so much so that arsenate (AsV) is toxic to phytoplankton due to its substitution in ATP, effectively decoupling energy metabolism. This toxicity is therefore a function of arsenic's chemical speciation, but also the arsenate:phosphate ratio; in oligotrophic waters where phosphate concentrations drop below 10 nmol/L, arsenate is > 10 nmol/L and toxicity is a problem. However, many phytoplankton are able to ameliorate As toxicity by reducing arsenate to arsenite (AsIII) and/or methylating it to mono (MMAs) and dimethyl As (DMAs); these compounds are non-toxic to phytoplankton. Interestingly, in these same conditions of low phosphate phytoplankton are already experiencing P stress or even limitation, so it is possible that reduced and methylated As can function as markers/tracers of P stress. On the transect to date the coupled biogeochemical cycling of As and P were examined by determining the concentrations of reactive phosphate and nitrate+nitrite

continuously (every 30 sec) along the cruise track from pumped and filtered “clean tow fish” using colorimetry and liquid core waveguides. Arsenic speciation (total inorganic, arsenite, MMAs, and DMAs) was also determined every 2 hours along the track, together with assays of alkaline phosphatase activity at 6 hour intervals, both from tow fish samples. By Station 12 when the main cruise was aborted, more than 150 As determinations, >25 AP assays, and >20,000 nutrient measurements had been made. Additional measurements were made underway during the transit to the shipyard.

**(5) Aerosol and Rain Sampling:** Aerosol and rainfall samples were collected on the GEOTRACES North Atlantic section cruise (cruise KN199-4) using three high-volume aerosol samplers and two automated rain samplers. Aerosols were collected on acid-cleaned Whatman-41 (cellulosic) filters (for inorganic trace elements and isotopes – TEIs) and pre-combusted quartz microfiber (QMA) filters (for organic species, Hg, and nitrogen compounds). One sampler was equipped with a 5-stage Sierra-style slotted cascade impactor to collect size fractionated aerosols (from >7 $\mu$ m to <0.49  $\mu$ m). With collaboration from researchers around the world, the 24-hour integrated aerosol samples, and event-based rain samples, will be analyzed for a large suite of TEIs. All aerosol samples will be analyzed for ultra-pure water soluble, seawater soluble, and total (residual) TEIs. The rain samples will be analyzed, both filtered and unfiltered, to quantify the soluble and particulate TEI concentrations. Air mass back-trajectories for all sampling days have been modeled using the NOAA HYSPLIT program. The seawater and ultra high purity (UHP) water aerosol solubility samples will be analyzed at Florida State University for Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb using a shore-based, off-line column extraction method prior to determination by high-resolution magnetic sector ICPMS using isotope dilution.

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

- 14 x 24 Whatman-41 filters (frozen for storage)
- 14 x 5 impactor filter stages + backing filters (frozen for storage)
- 14 x QMA filters (frozen for storage)
- 1 full set of aerosol sampler blanks (frozen for storage)

Seawater and UHP water leaches were conducted at sea using aerosol-laden Whatman-41 filters, resulting in:

- 41 x 100 mL seawater leaches; 85 mL acidified to 0.024 M HCl; 15 mL frozen
- 41 x 100 mL UHP water leaches; 85 mL acidified to 0.024 M HCl; 15 mL frozen

Two rain events were sampled, resulting in:

- 2 x 100 mL filtered (0.4  $\mu$ m), acidified
- 1 x 100 mL + 1 x 25 mL unfiltered, acidified
- 1 x 10 mL + 1 x 15 mL unfiltered, frozen

In an effort to constrain the empirical estimate of the solubility of aerosol-derived iron in seawater, a new approach was tested onboard. This protocol slowly leaches aerosols with larger volumes (15 L) of filtered surface seawater, and compares concentrations of iron from leached and unleached filters. Instantaneous leaches with filtered surface seawater (200 ml) and with Milli-Q water (200 ml) were also performed, and leachates were collected for the analysis of size fractionated iron (<0.02 $\mu$ m, and <0.4  $\mu$ m), redox speciation and organic speciation of iron. Organic speciation analysis was carried-out on board by Kristen Buck (BIOS) as part of a collaborative study.

In total six slow leaches (each in triplicate) were carried out on board with freshly collected aerosols (European, maritime and N. African origin) and freshly collected filtered surface seawater. Surface seawater was obtained from the University of California Santa Cruz surface sampler (GEOFish). In addition a slow leach (in triplicate) was performed on aerosols obtain from an Alaskan forest fire, and another on Arizona dust reference material. Filtered surface seawater freshly collected on board was also used to leach these last two aerosol types. Instantaneous leaches with seawater (in duplicate) and Milli-Q water were carried out on replicate filters of aerosols used in the slow leaches. The seawater used in the instantaneous leaches was the same as used in the slow leaches. Filters not leached onboard were frozen and will be taken back to the lab for subsequent leaching and/or analysis.

**(6) Fe speciation:** A total of ~125 samples (stations 1, 3, 5, 7, 9) were analyzed shipboard for dissolved Fe speciation (organic complexation) following the Competitive Ligand Exchange- Adsorptive Cathodic Stripping Voltammetry (CLE-ACSV) method of Buck et al. (2007). Replicates of all samples analyzed have been stored frozen for a comparison of stored (frozen, -20<sup>o</sup> C) versus fresh results. These frozen samples may also be analyzed for dissolved Cu speciation (CLE-ACSV method: Buck and Bruland 2005, Buck et al. 2010) in the laboratory at BIOS in the spring. An additional 75 samples (stations 10-12) were collected and stored frozen for analysis back in the lab. Preliminary results indicate that the Fe-binding ligands at station 1 were saturated with dissolved Fe at all depths (possibly due to Fe contamination), while stations 5 and 7 presented the largest excesses of Fe-binding ligands in the water column, particularly around the chlorophyll max and near the bottom boundary layer. Stations 3 and 9, on the other hand, appeared to have very small, if any, excesses in Fe-binding ligands.

In collaboration with Dr. Ana Aguilar-Islas (University of Alaska, Fairbanks), 6 sets of seawater leaches of collected aerosols, and their associated seawater blanks, were also analyzed shipboard for dissolved Fe speciation. There were distinct differences in the amount of Fe leached from these aerosols, likely reflecting Fe-binding ligand concentrations in the surface seawater used for the leach and aerosol source. Final Fe speciation data (ligand concentrations and conditional stability constants) from station profiles and aerosol leaches will be worked up when dissolved Fe totals are finalized.

**(7) Mercury:** The Lamborg and Hammerschmidt groups were funded to receive samples from the various sampling systems, conduct on board determinations of 4 dissolved Hg species and also preserve samples for analysis back on shore (dissolved and particulate thiols and particulate Hg species). The mercury group sent two participants on the US GEOTRACES North Atlantic cruise, including Katlin Bowman, a Master's Student at Wright State University and PI Lamborg from WHOI. This was fieldwork contributing to Ms. Bowman's thesis research, and analysis of the preserved thiol samples will comprise WHOI PhD student Tristan Kading's generals project. The mercury group occupied a UNOLS fleet 20' van outfitted with ceiling HEPA units. This space was shared with Bettina Sohst from Pete Sedwick's (ODU) lab. The space worked well and suited their needs. In the future, a clean van may not be necessary if they could include equipment to make the space adequately clean. Inside, Bowman and Lamborg operated two Hg species analysis systems, one for mono- and dimethylmercury and the other for total and elemental Hg. As the cruise was prematurely halted due to thruster failure, they were not able to

complete our primary goal of measuring Hg species across the entire North Atlantic basin. They did, however, measure Hg species in the stations we were able to occupy, and which amounted to greater than 200 determinations the four Hg species each. In addition, about 150 samples for thiols and particulate species were received from the regular rosette and in-situ pumps. This dataset, while less than hoped for, is still substantial in size and will be an important contribution to basin-scale studies of Hg. The particulate samples will be analyzed for total and monomethylmercury at Wright State, while the thiols will be determined at WHOI. Findings thus far include:

- Dissolved total Hg in most, if not all the profiles, showed “hybrid-type” profiles, including substantial surface depletions, a subsurface maximum in concentration co-incident with minima in dissolved oxygen and relatively uniform concentrations in deep water (>1000m depth).
- Dissolved elemental Hg showed a similar profile as total Hg, and comprised a large percentages of the total...approaching 100% in the mixed layer. This species is known to be photochemically generated from Hg(II), and therefore this finding was to be expected. It’s also the Hg species that participates in sea-to-air gas exchange, and along with particle scavenging contributes to the shallow water depletions of total Hg.
- Dimethylmercury, a somewhat exotic species generally only seen in measurable concentrations in the deep ocean, was notably absent from all profiles. This certainly is not true for other parts of the North Atlantic, including the Mid-Atlantic Bight (Hammerschmidt and colleagues, unpublished) and the Sargasso Sea (Lamborg and colleagues, unpublished). Where in the basin and at what rates dimethylmercury reappears in the water column would have been a major piece of new information had the rest of the zonal section been completed. However, the simple observation that the eastern and western “end members” of the basin look quite different is an important result and challenges what we thought we knew about Hg biogeochemistry in the ocean.
- Finally, monomethylmercury, the species that bioaccumulates in fish and people was prevalent in all profiles and easily observed using the method for determination developed by Ms. Bowman and PI Hammerschmidt. Intriguingly, many of the profiles showed evidence for more than one maxima in the subsurface, usually associated with oxygen anomalies arising from both vertical and horizontal transport of organic carbon and apparent oxygen utilization. These data, when eventually combined with the tracer (e.g., SF<sub>6</sub> and CFCs), ancillary data (e.g., chlorophyll, particles, oxygen) and other metals (e.g., Co) will help determine the source of this important species, and processes that give rise to it.

**(8) Particulate Analysis:** Samples for Synchrotron X-ray Fluorescence (SXRF) and ICP-MS analyses were collected at 11 stations during the GEOTRACES North Atlantic Section cruise. At each station, unfiltered water samples (250 mL) were taken for SXRF samples from the GEOTRACES GO-Flo rosette from the surface mixed layer and the deep chlorophyll maximum layer. Cells were preservation with 0.25% trace-metal clean buffered glutaraldehyde and centrifuged onto C/formvar-coated Au and Al TEM grids. 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. Eighty eight grids were prepared for analysis. Bulk particulate samples were collected at each depth sampled (24 depths per station) using the GEOTRACES GO-Flo rosette. The filtration was performed directly from pressured GO-Flo bottles onto membranes (25mm Supor 0.45µm polyethersulfone) which were

mounted in Swinnex polypropylene filter sandwiches. An average of 8.5L of water was filtered through each membrane. Two hundred and sixty three samples are being stored for analysis via ICP-MS. Before 5 of the stations, bulk particle samples were collected from surface waters with the towed fish. Water from the fish was collected in a 10-L acid-washed carboy and distributed among three, 4L carboys. These were pressurized with 0.2- $\mu\text{m}$  filtered air to force water through replicate 25-mm Supor 0.45 $\mu\text{m}$  membranes held in Swinnex polypropylene filter sandwiches. At each station, one of the three replicate filters was oxalate soaked then rinsed with chelexed NaCl, the other two filters remained untreated. These replicate filters will be used to compare methods for isolating trace elements in biogenic particulate matter at a later date.

**(9) Copper Speciation:** To measure Cu speciation, Jeremy Jacquot used an electrochemical method called competitive ligand exchange adsorptive cathodic stripping voltammetry (CLE-ACSV), which allows one to determine the concentration of organic ligands binding free Cu ( $\text{Cu}^{2+}$ ) and their binding strength. In order to calculate  $[\text{Cu}^{2+}]$ , Jacquot will need to find  $[\text{Cu}_T]$  by using isotope dilution with an inductively coupled plasma mass spectrometry (ICP-MS) system at USC. In total, he obtained 140 1 liter filtered samples from the GEOTRACES rosette (125 ml for the totals analysis with ICP-MS and 875 ml for the speciation work) and 56 1 liter samples for the Chisholm filtration work. Because he didn't have any time to analyze his speciation data, he can't draw any particular conclusions though it does seem as though  $[\text{Cu}^{2+}]$  was elevated in the mixed surface layer at stations 9, 10 and 11—those most affected by inputs from dust.

**(10) Al, Fe, and Mn onboard measurements:** Sampling for dissolved Al, Fe, and Mn was accomplished using 12 L GO-FLO bottles on the GEOTRACES 24 place rosette. The University of Hawaii group (Measures and Hatta) performed shipboard determinations on subsamples of water taken from these bottles collected using an Acropak filter by the subsampling team. Dissolved trace elements were determined on samples drawn at each of the 11 stations where the GEOTRACES rosette was deployed. Note that at one “Demi-station” the GEOTRACES rosette was not deployed. Additionally, surface samples were also collected arriving on or departing from station from the UCSC towed fish. In addition, a limited number of samples was collected between stations by this means. In total trace element determinations were made on 249 discrete samples. Data generated onboard were submitted to the shipboard data assembly system and each parameter on each subsample was assigned a quality flag. Dissolved Al, Fe and Mn were determined on these water samples using Flow Injection Analysis. Precisions of each method were established by replicate determination of the same sample at the beginning of a day's run the values were typically: approximately 2% for Al at 10nM; 2% for Fe at 1 nM, and ~ 4% for Mn at 1 nM. In addition to the shipboard determinations 1L samples were collected for shore-based ICPMS determinations of dissolved and dissolvable Fe, Mn, Zn and Cd, by isotope dilution by co PI J. Wu, (University of Miami). These samples were acidified on board, within a few hours of collection. Ultrafiltration of 25 samples was also performed at station 5 for subsequent shore-based determination of the colloidal fraction at the University of Miami.

**(11) Cobalt Analysis:** The Saito/Noble group collected samples from all GTC casts, and all arriving-on-station Towfish samples, totaling 239 samples. All of these were analyzed shipboard for total dissolved cobalt after a UV oxidation step using adsorptive cathodic stripping. In addition to total dissolved

cobalt, all samples were analyzed shipboard for labile cobalt after an equilibration period with the electroactive ligand, dimethylglyoxime, using adsorptive cathodic stripping voltammetry. A duplicate set of samples were taken for all depths at stations 9, 10, 11, and 12 and preserved in heat-sealed pouches with oxygen absorbers to test this as a preservation method for samples taken within oxygen minimum zones. These samples will be analyzed at a later date and will be compared to shipboard analyses.

**(12) Radium Isotopes:** To measure the quartet of radium isotopes ( $^{224}\text{Ra}$ ,  $^{223}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{226}\text{Ra}$ ) to quantify horizontal and vertical transport of dissolved trace elements and isotopes (TEIs), as well as shorter lived thorium isotopes:  $^{234}\text{Th}$  and  $^{228}\text{Th}$ , used to quantify particle scavenging, vertical fluxes and remineralization rates of bioactive and/or particle reactive TEIs. At each major station a 16 point in situ pump profile was carried out. Eight pumps were deployed for an upper water column shallow pump cast and then turned around to be deployed again for a deep pump cast. The pumps used were heavily modified McLane in situ pumps, which were outfitted to accommodate 2 \* 142 mm filter heads containing different filter types (see cruise report by Dan Ohnemus). After water had passed through the dual filter heads the streams were joined passed through a  $\text{MnO}_2$  impregnated cartridge filter for scavenging dissolved radium and thorium isotopes. The pumps were programmed to pump for 4 hours and typically pumped a total of 1500-1700 l of seawater. Three flow meters at various points along the pump plumbing allowed accurate determination of water filtered. The pumps were hung on a 3/8" plastic coated Vectran line. The dissolved radium and thorium isotopes were scavenged onto  $\text{MnO}_2$  impregnated Cuno cellulose cartridge filter. The cartridge was fitted to the exhaust flow of the modified McLane in situ large volume pump. Each pump typically passed 1500-1700 l of pre-filtered seawater through the  $\text{MnO}_2$  cartridge filter over a 4 h pump time. 16 depths were sampled over 2 pump casts: a shallow and a deep, at 8 stations. After recovering the cartridges from the pumps, they were rinsed with radium-free fresh water to remove salt and then dried to dampness before measurement of the short-lived radium isotopes on board the ship.  $^{224}\text{Ra}$  ( $t_{1/2} = 3.7$  d) and  $^{223}\text{Ra}$  ( $t_{1/2} = 11.4$  d) were measured on the Radium delayed coincidence counter (RaDeCC) system and were typically measured <24 h after sample collection. After 3 weeks ( $6 * t_{1/2}$  of  $^{224}\text{Ra}$ ) the background activity of  $^{224}\text{Ra}$  was measured again to determine the supported activity of  $^{224}\text{Ra}$  from its parent isotope  $^{228}\text{Th}$ , thus allowing the measurement of  $^{228}\text{Th}$ . This second round of counting is currently being carried out by Kuanbo Zhou as the Knorr transits back the US. Some previous work by Matt Charette and Kanchan Maiti on the GEOTRACES intercalibration cruise has shown that  $\text{MnO}_2$  cartridges do not scavenge radium at 100% efficiency. Therefore, to determine the extraction efficiency of the Cuno cartridge filter a discrete seawater sample was taken in parallel with every pump depth sampled for direct calibration determinations of  $^{226}\text{Ra}$  and  $^{234}\text{Th}$ . For shallow pump casts these samples were taken from the 30 l Niskin rosette on a separate niskin cast and for deep pump casts a 30 l Niskin bottle was hung next to each pump and triggered with a messenger. For  $^{226}\text{Ra}$ , 20-25 l of seawater was passed over a column of  $\text{MnO}_2$  impregnated acrylic fiber, which is known to remove radium at 100% efficiency. These samples were bagged and will be analyzed for  $^{226}\text{Ra}$  through its daughter,  $^{222}\text{Rn}$  back in the lab. For details of  $^{234}\text{Th}$  determination refer to the  $^{234}\text{Th}$  cruise report by Stephanie Owens. Stephanie was responsible for taking both the  $^{226}\text{Ra}$  and the  $^{234}\text{Th}$  samples, and she is processing the  $^{234}\text{Th}$  samples.  $^{226}\text{Ra}$  samples will be processed by Paul Morris. In total 122  $\text{MnO}_2$  cartridge samples were taken out of a planned 380.

A limited number of underway samples for surface radium measurements were collected from a high volume deck pump. 260 l of filtered seawater was rapidly collected into barrels and then subsequently passed through MnO<sub>2</sub> acrylic fiber for determination of all 4 radium isotopes. The underway sampling was particularly focused in collecting samples for short-lived radium isotopes (<sup>224</sup>Ra and <sup>223</sup>Ra) during the close pass to the Mauritanian coast. Unfortunately, while under way to the shallow water demi-station closest to shore the ship suffered failure of the port thruster and the ship was diverted to the deep water super-station further off shore. A smaller set of underway samples were collected while in transit to the super-station. These samples were processed in a similar manner to the MnO<sub>2</sub> cartridges for short-lived radium isotopes while on board ship.

**(13) <sup>234</sup>Th and <sup>228</sup>Th:** At each regular and super station, samples for total <sup>234</sup>Th were collected by Stephanie Owens and Kuanbo Zhou from a 30L shallow Niskin cast and Niskin bottles attached to the wire during deep pump casts. All sample processing and preliminary sample analysis by beta counting was completed on board, a requirement because of the short half-life of <sup>234</sup>Th (24.1 days). At regular and super stations, ~20 point profiles were collected with 16 of those depths matching the *in situ* pump depths while the additional depths were used to obtain higher resolution through the euphotic zone. In addition, a surface sample was collected using a pump located on the port side of the ship. At demi-stations, 13-point profiles were collected from the shallow Niskin cast and the surface pump. In all 209 samples were collected for total <sup>234</sup>Th. Initial data analysis suggests a decrease in POC export from coastal waters off of Lisbon to the open ocean followed by an increase in export during the Mauritanian leg of the trip that concluded at the TENATSO site. Samples for particulate <sup>234</sup>Th were collected from the shallow pump cast and counted on board the ship. Back on shore these samples will be analyzed for their organic carbon content in order to determine <sup>234</sup>Th/POC ratios. This ratio can be used to estimate the POC export flux based on the <sup>234</sup>Th flux determined by the total <sup>234</sup>Th measurements as described above. Samples for <sup>228</sup>Th were also collected from the pump casts. These particulate samples will be processed back onshore and be analyzed in conjunction with Mn cartridges also deployed during the pump casts. The combined measurement of <sup>234</sup>Th and <sup>228</sup>Th will be used to obtain insight into particle dynamics taking place in the water column.

**(14) Biogeochemical Sampling:** Jacquot also collected filters from each station for the Chisolm group that will be used to conduct flow cytometry, metagenomic and qPCR analyses. Boyle collected samples for LaRoche and performed reduced-pressure filtration. These samples were kept frozen at -70°C and transferred to the research station at Cape Verde Islands for shipment back to Kiel.

**(15) CFC and SF<sub>6</sub> Sampling:** was done on deep and shallow Niskin casts at each regular and super-station (for a total of 24 depths per station) and the Niskin cast at all demi-stations (12 depths per station). Samples were analyzed on board and the data reported to the ODF data manager and made available to cruise participants. A total of 240 samples were taken and analyzed.

**(16) Tritium and helium sampling:** Tritium and <sup>3</sup>He sampling were done on all regular, super-, and demi-stations. A total of 240 <sup>3</sup>He and 228 tritium samples were taken. The <sup>3</sup>He samples were taken in



crimped copper tubing and the tritium samples were stored in pre-cleaned, argon-filled 1 liter flint glass bottles.

**(17) Compilation of samples taken and associated metadata:** was accomplished during the cruise by assembling all CTD cast information, cast sheets, and event logs and entering them into a database. An ODF staff member was responsible for this task and for quality checking and merging the relevant information. As a consequence, we have a complete record of all samples taken on the cruise, and their relationship to critical metadata parameters (time, location, etc). Bottle data have been compared to the sensor records in order to check instrument calibration and to establish bottle integrity against pre/post tripping and leakage. The hydrographic data (temperature, salinity, oxygen, nutrients) have been quality controlled and merged into a relational database for use by cruise participants. This data was available in near-real time to cruise participants. For example, CTD data was usually available for plotting within an hour or two of the cast, and the discrete hydrographic measurements (oxygen, nutrients, and salinity) were available within a day or two of the station.

**(18) NASA Sampling:** During the 2010 Geotraces Atlantic cruise NASA's Calibration and Validation Office staff performed 31 bio-optical casts for the measurement of apparent optical properties (AOPs) in the upper ocean at 9 of the 12 stations occupied during the cruise. The AOP work was conducted to support calibration and validation activities for the current suite of NASA ocean color satellite missions (SeaWiFS and MODIS) with opportunistic application to international missions (e.g., MERIS and OCM-2). The AOP measurements included in-water instruments (Submersible Biospherical Optical Profiling System, SuBOPS; Biospherical Instruments, Inc.) to determine spectral water-leaving radiances that are essential to remote sensing applications. The AOP in-water system had a solar reference, which was mounted on a telescoping mast to ensure unobstructed viewing of the sky—when the mast was extended, the solar reference was the highest structure on the *Knorr*. In addition to the bio-optical data, at each of the stations where AOP measurements were conducted, near-surface water was collected for: the analyses of phytoplankton pigments using state-of-the-art HPLC techniques, light absorption by particulates ( $A_p$ ), particulate organic carbon (POC), gravimetric determination of suspended particulate matter (SPM), dissolved organic carbon (DOC), and absorption by colored dissolved organic matter (aCDOM). These parameters are valuable for development and further refinement of algorithms for the determination of phytoplankton pigments and other novel data products (e.g. DOC, POC) from remote sensing platforms. In collaboration with WHOI's Ra/Th group, samples for pigments analyses were collected at all 12 stations from a shallow Niskin cast at four depths (at surface and at, and above and below, the chl-a maximum). These data will enhance the interpretation of POC export estimations derived using the U/Th approach. In addition, samples for DOC/aCDOM were collected at 13 selected depths from shallow and deep Niskin casts at all 12 stations. These data will contribute to databases that support studies that employ CDOM as a tracer of global biogeochemical cycles and meridional overturning circulation. NASA's participation in the recent GEOTRACES campaign allowed the collection of valuable data for the support of ocean color remote sensing activities, while collaborating with other branches of the ocean science community. Given the difficulties associated with obtaining *in situ* measurements from remote areas of the ocean, the data currently used to develop and validate bio-optical algorithms are limited in their geographical range and their dynamic representation of bio-optical conditions. During the

GEOTRACES campaign we were able to collect bio-optical, pigment, and biogeochemical data during atmospheric conditions that, with current algorithms, prevent the extraction of remotely-sensed quantities. Dust blowing off the Saharan desert was evident on true-color images from the NASA MODIS-Aqua Satellite, and on surfaces on board the *R/V Knorr*, during the cruise. This valuable data set, for example, will allow the development of new atmospheric correction approaches for the retrieval of ocean color products.

**(19) Underway (towed fish) Sampling:** As part of the U. S. GEOTRACES North Atlantic project Dr. Ken Bruland's research group was funded to deploy our surface tow-fish (the GeoFish) for the collection of 0.5 liter samples to provide high resolution data along surface transects between and upon arrival at the vertical stations for assaying a suite of contamination prone trace metals (Al, Sc, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, Cd, and Pb) in the dissolved (<0.2 $\mu$ m filtered) and unfiltered, weak acid dissolvable (at pH 1.7), phases in surface sea water. We are also funded to obtain 0.5L samples from each depth of the GEOTRACES rosette vertical profiles as part of a library for future studies and to assay the superstation profile samples for this suite of trace metals to complement the vertical GEOTRACES profile data obtained by others. Geoffrey Smith is participating on the cruise and responsible for maintaining and operating the GeoFish for the collection of our surface samples during transit between stations and providing bottles for the vertical profile samples to the GEOTRACES sampling team and performing onboard acidification of these samples and those collected for Kristin Orians' group and Mukul Sharma for long term preservation. Geoffrey also has been periodically collecting a subset of filtered surface samples between stations for Bill Landing, Alan Shiller and Chris Measures and unfiltered samples for Benjamin Twinning, Julie La Roche and Penny Chisholm prior to arrival on station. In addition to these samples, Geoffrey has supplied large volumes of 0.2 $\mu$ m filtered surface water for Ana Aguilar-Islas and Bill Landing's, and Phoebe Lam's groups for aerosol and particulate leaching experiments respectively. During the U.S. GEOTRACES North Atlantic cruise from Lisbon, Portugal to the Cape Verde Islands, Oct. 15 to Nov. 3, Geoffrey has performed eighty-eight GeoFish sampling events and collected the following samples:

- 149 surface sea water samples designated with only GeoFish ID #'s which include 64 each 0.2  $\mu$ m filtered 0.5L trace metal samples and 50ml ODF nutrients, and twenty one 125ml unfiltered pH 1.7 dissolvable trace metals samples .
- 88 samples collected during transects between stations designated with GEOTRACES sample #'s for the samples described above and additional 125ml samples for each of W. Landing, A. Shiller, C. Measures, 50ml ODF nutrients, 125ml ODU nanomolar-nuts., and 250ml ODF salinities.
- Over 140 samples collected at three Demi-stations including arriving fish samples for those described as above with GEOTRACES designated sample numbers and additional samples for other researchers obtaining samples from the GEOTRACES rosette.
- Over 324 samples collected at three regular stations including arriving fish samples for those described as above with GEOTRACES designated sample numbers and additional samples for other researchers obtaining samples from the GEOTRACES rosette. Several departing fish samples for dissolved and dissolvable trace metals along with samples for W. Landing, A. Shiller and C. Measures were collected in addition at two of the regular stations

- Over 112 samples collected at the two super stations including arriving fish samples for those described as above with GEOTRACES designated sample numbers and additional samples for other researchers obtaining samples from the GEOTRACES rosette.

### **Data Dissemination and Communication**

All CTD, hydrographic, and metadata have been assembled and organized by the ODF data operator. These data will be posted on a publicly available website, but under password protection until it is finalized and submitted to BCO-DMO.

### **Lessons Learned**

This was the first U.S. GEOTRACES survey cruise, and as such, although it was terminated early due to engine problems, it represents an opportunity to learn from experience. The biggest challenge was the complexity and scale of the seagoing operations, and the limits on the number of science personnel that could participate. Certainly the berthing limitation was a major challenge as all groups were operating short-handed. While we all agree that there could be improvements, the fundamental conclusion is that we were close to an optimally working system. Having said this, we would point out that everyone aboard worked very hard, and cooperated fully in making this cruise the success that it was.

(1) Overall coordination: the four “overboard” groups, name the GTC/trace metal samplers, the ODF/Niskin samplers, the pumping group, and the bio-optical (NASA) sampling coordinated well together. Cast ordering was planned to minimize time on station when something wasn’t in the water, and little time was lost between individual casts. Prior to arriving on station, a cast plan was published via email as a spreadsheet with an assigned schedule so that the groups, along with the bridge and deck crew were aware of the timing and order of events. These plans were posted in the main lab as well. One thing that could be done better in the future is the use of the white board to notify science crew when a cast was due up, and to post wake-up schedules. This would supplement the “on-line” schedule for those without ready access to email. The ODF web-site proved useful during steaming periods as it provided an ETA for the next station. It would be helpful if it could be augmented to incorporate station/cast progress while on station as well.

(2) Having a critical station (station 1 was a super-station) so soon after leaving the dock was problematic. It would have been better to schedule an extra day to allow for rinsing and testing of the GTC GO-FLO bottles for contamination checking. Preloading of the GO-FLOs with uncontaminated seawater a day or two prior to departing from the dock might help.

(3) The “super-tech” idea was a good one, but it became clear that the two technicians assigned to staging the GO-FLO casts were severely overtaxed. Having two extra technicians to handle these operations would permit watch-standing and avoid overloading when stations become back-to-back, and with the work associated with the extra sampling associated with the super-stations. In addition, having a larger, dedicated area for staging of sample bottles would be helpful.

(4) Like the GTC sampling team, the pumping team was also stressed and could have benefited from 2 additional members. For example, the deep pumping cast involved several hours of intensive deck work during deployment and retrieval, and having an additional team member would have reduced the risk of fatigue-related errors and enabled some “shift-work”.

**Final Note:** Despite the early termination of the cruise, we can safely regard this effort as a success. There were a lot of moving parts in the GEOTRACES machinery, and things worked remarkably well. All this was down to a group of motivated, hard working, and cooperative scientists that worked together well. It should also be said that the ship's crew were extraordinarily helpful and went out of their way to make this a safe and productive cruise. We are grateful to Captain Adam Seamans for his efforts and hospitality.