

US GEOTRACES Pacific Meridional Transect – GP15 Cruise Report

18 September – 24 November 2018

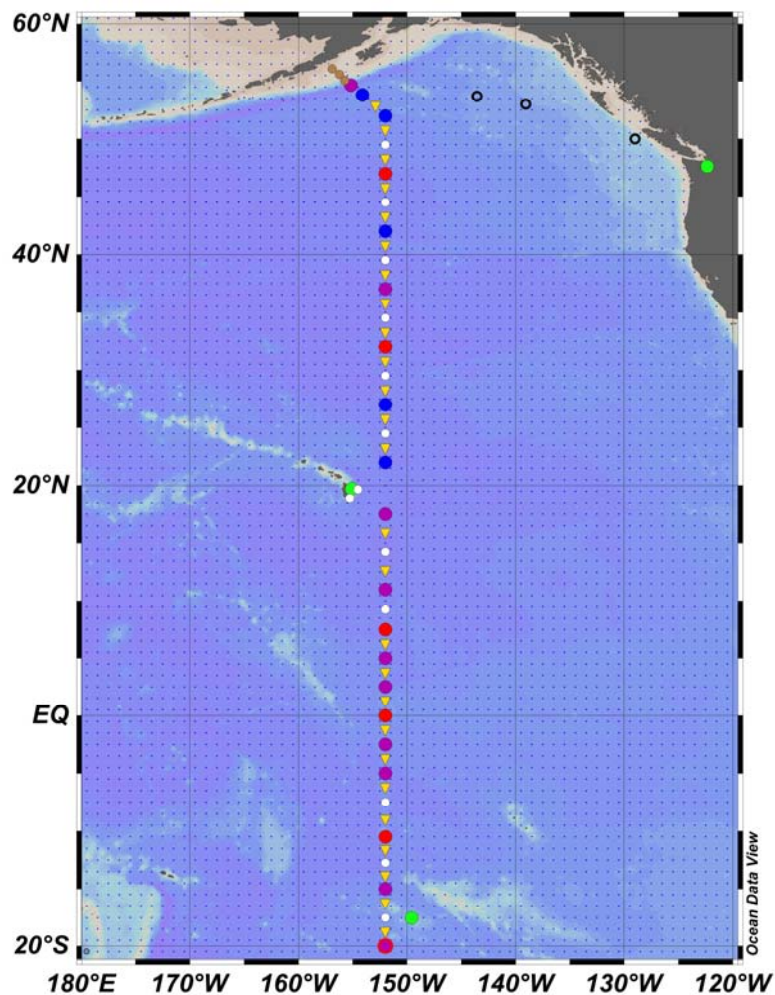
Seattle, Washington – Papeete, Tahiti (port stop in Hilo, Hawaii, 21-25 October 2018)

R/V Roger Revelle

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GP15 Cruise Track: Green circles: ports; open black circles: rinse stations; brown circles: shelf and slope stations; Purple circles: Full-36 stations; Blue circles: Full-24 stations; white circles: demi stations; yellow triangles: intermediate fish.

1. Introduction

The fact that many trace elements are bioactive and essential (e.g., Fe, Zn), or toxic (e.g., As, Hg), underlies interest in studying them, but their effects on primary production and oceanic carbon dioxide uptake are the primary drivers. In parallel, many radioactive and stable isotopic tracers allow trace element sources to be identified (e.g., ^3He , ^{56}Fe) and rates of transformation or fluxes determined (e.g., ^{230}Th , ^{228}Ra , ^{15}N and $\delta^{13}\text{C}$). The use of multi-element, high-resolution sampling on GEOTRACES, coupled with various modeling approaches, allows the inputs/sources and internal cycling of TEIs to be revealed and quantified in an unprecedented fashion. The Pacific Meridional Transect in the central Pacific basin along 152°W from 56°N to 20°S (GEOTRACES GP15) allowed us to sample: strong margin fluxes, sub-Arctic HNLC waters, the oldest deep water in the world's oceans, the distal ends of hydrothermal plumes from the Juan de Fuca Ridge and East Pacific Rise, as well as the relatively recent inputs from Loihi Seamount. We also sampled the far-field oxygen minimum zones originating well to the east, equatorial upwelling, and some of the most oligotrophic waters in the world's oceans in the South Pacific gyre at 20°S . In total, we sampled 36 vertical profile stations over a 67 day period.

To address our overall goals of examining fluxes at ocean interfaces and studying the internal cycling of trace elements and isotopes (TEIs), we sampled at 36 vertical profile stations using 3 primary sampling systems: GTC (GEOTRACES Trace element Carousel) for contamination-prone, dissolved TEIs; ODF (Ocean Data Facility) conventional rosette for the rest of dissolved TEIs, and McLane in-situ pumps for particulate TEIs. Stations were divided into 3 major types: Full where samples were taken at 24 ("Full-24"; 2 GTC and 3 ODF casts, 2 pump casts) to 36 ("Full-36"; 3 GTC and 4 ODF casts, 2 pump casts) depths from surface to bottom; Demi where samples were taken at 12 depths in the upper 1000 m (1 GTC and 1 ODF casts), and Super where 36 depths were also sampled but additional hydrocasts were undertaken to acquire larger volumes and particle sampling resolution was increased (4 GTC and 4 ODF casts, 3 pump casts). In addition to these vertical profile stations, we also sampled surface waters while underway using a towed fish ("Geo-fish" from a 40' aluminum boom extending off the starboard side, forward of the squirt boom) and the ship's flow-through seawater system. These samples were taken within one hour of arriving at a vertical profile station ("arriving fish"), and at locations midway between the vertical profile station ("intermediate fish"). Finally, atmospheric aerosols and event-based rain sampling occurred throughout the entire cruise. More complete descriptions of the stations and sampling systems are found below. Specialized sampling for parameters such as ^7Be and Ra isotopes are discussed in their individual science reports. Appendix 1 is a list of the stations occupied with exact locations, dates, and observed bottom depths, while Appendix 2 is a list of science participants on the cruise. Appendix 3 contains the list of all parameters sampled and to be measured at sea or at land-based laboratories as part of the GP15 cruise.

2. Station Descriptions

Mobilization. R/V Revelle was loaded and all science systems set up in Seattle, Washington at Pier 91 from September 14-18, 2018. Four science lab "vans" (built within 20' cargo container) were loaded and secured: US GEOTRACES (ODU) Clean lab (main deck fantail, starboard), WHOI Café Thorium (main deck fantail, port), University of Hawaii Sampling and Analytical Lab (main deck, port quarter), and UNOLS General Purpose lab van (01 deck, aft, port). The

GEOTRACES winch and A-frame were installed on the main deck just aft of the hangar and overboarded on the starboard side. This required removal of one bulwark. On the spare winch (DESH5) the existing drum of .322" metal hydrowire was replaced with one containing 6200 m of 0.322" Vectran cable for the McLane pumps and lead through a composite sheave on the starboard hydroboom. For pump deployments to facilitate safety from boarding seas, one starboard bulwark under the hydroboom was moved 2' inboard and 2' forward (by one set of deck threaded openings in and forward); ratchet straps acted as lifelines between this inboard bulwark and existing ones fore and aft.

To move the ODF 36-place rosette from its storage in the hangar, a track and cart system driven by an air tugger was installed on the starboard quarter deck and the rosette deployed using the ship's automated CTD Launch and Recovery System (LARS) deployment/recovery device and Markey CAST-6 Winch. The tow-fish pedestal and boom were mounted on the main quarter deck, immediately aft of the 01 rescue boat storage location. The boom was swung from vertical storage to a horizontal deployed position using 3/8" Amsteel 12 strand line from the tip of the boom through a block on the 02 deck and down to an air tugger on the quarter deck. It was also guyed forward with a 1/4" stainless cable and turnbuckle led to the 02 deck and a 5/8" line led to an aft cleat. Eight McLane pumps were kept in the hangar and secured to the deck using deck bolts through aluminum bars. The four spare McLane pumps were kept aft of the CafeTh van and accessed as needed for spare parts. Finally, a winch for the ⁷Be pump system and 7 polyethylene tanks were installed under and near the ship's aft A-frame. Five high volume aerosol samplers, an automated rain sampler, and wind sensors were placed against the forward rail of the 03 deck (just forward of the Chief Scientist and Captain's staterooms).

Test Stations. After leaving Seattle for Leg 1 on 18 September 2018, three test stations were occupied (Appendix 1) to test the sampling systems and operations. At Test 1 only the GTC system was deployed to rinse and fill the GO-FLO sample bottles with clean seawater; this required two hydrocasts. Test 2 also filled the GTC bottles, and the water from these casts was analyzed on board for Al, Fe, Mn, and Zn to evaluate potential contamination. Test 2 also included a shallow cast of the ODF and McLane pump systems. Test 3 included two GTC casts and the waters again analyzed for contamination-prone trace metals. The ODF rosette was also deployed with the monocoar at test station 3 to test the altimeter cloaking device.

Leg 1 stations. Although the transit ran from Stations 1-18 (Fig. 1, Appendix 1), we first occupied Station 5 (24-25 September) on our way north because it was a deep, offshore station that allowed us to practice our sampling routines without the exact timing required of a shallow shelf station (i.e., fast surface currents). Stations 1-3 on the Alaskan shelf and slope were occupied from 26 to 28 September in stormy conditions with large, 6 m seas and swell. Likely due to these conditions, the electrical termination on the GTC cable failed, necessitating us hoving to in the lee of Chirikof Island to allow repairs. The shelf-deep transit was completed at Station 6 on 1 October and thereafter the transit was directly south along 152° W. It should be noted that our GEOTRACES Intercalibration Crossover station with the 2017 Japanese GP2 cruise was at Station 8 on 4-5 October. In terms of sampling problems on Leg 1, the tow-fish had considerable problems with breaching in the high seas in the northern portion and required numerous adjustments of its fin angles to allow it to reliably stay underwater. Also, at Demi Station 11 the electric motor on the GTC A-frame seized and we could not perform a cast with

this system; the ODF cast was successfully conducted. The ship's electrician Harry Smith rebuilt the motor and it worked excellently for the rest of the cruise. More significantly, at Station 16 a winch operator error resulted in significant damage to the first 2247 m of the Hytrel plastic coating of the 0.322" Vectran pump cable such that it was questionable whether the cable could hold the pumps without failure. Temporary repairs (Scotch coat and electrical tape) were made to allow continued pump operations for the next 2 stations, but the cable would have to be properly repaired during the Hilo port stop. See further details in the McLane pump section.

Puna Ridge bonus station. By Station 16 we were 14 hours ahead of schedule and we decided to conduct a bonus station sampling of the Puna Ridge where the highest concentrations of ^{226}Ra have ever been measured in the ocean (Moore et al., 2008) and likely could be a unique source of TEIs to this region. We added Station 18.3 to our transit from Station 18 to our port stop in Hilo, HI. At this station (Appendix 1) we did one cast each to 2130 m (bottom depth was 2160 m) of the GTC, ODF, and McLane pump systems.

Port stop in Hilo, Hawaii. The Hilo port stop was from 21-24 October where we refueled the ship, added provisions, received some scientific gear, offloaded 9 pallet boxes of samples, 15-20 ice chests of frozen samples, plus two dry shippers, and samples for Po/Pb, $\Delta^{17}\text{O}$, and Ra groups. 13 scientists (including the two resident technicians) and more than half the crew were also exchanged in Hilo. As an important outreach event coordinated by Mariko Hatta, over 50 undergraduate and graduate students from the University of Hawaii, Hilo, toured the ship and learned about the GEOTRACES science we were conducting. Finally, and most importantly, the Vectran pump cable was repaired. The latter involved air shipping a spool of used Vectran cable from UC Santa Cruz, cutting out the damaged original Vectran, and splicing a 3849 m piece of Vectran onto the remaining 3245 m of cable on the winch drum. To do this, a technician from Cortland Cable, the manufacturer, flew in to perform the splicing. All of this forced a 12 hour later departure than planned.

Leg 2 stations. We left Hilo at 9 pm on 24 October and very soon thereafter occupied another bonus Station, 18.6, above the Loihi Seamount crater (1320 m depth) to serve as a bench mark/end-member for hydrothermal emissions from this source to the North Pacific. The station itself was only sampled with the GTC and ODF systems, in effect a demi station, but with the sampling focus on the deep, near-bottom waters. This only added 4 hours to our Leg 2 times. Thereafter, we sampled Station 19 on the original transect at 152°W (Appendix 1) that was originally placed to sample the Loihi plume for which we now had an end member for comparison. However, we still had to make up for the 12 hour "Vectran deficit" so we chose to eliminate Demi Stations 24, 26, 28, 30 and 32 near the equator, replacing them with a surface-only fish sampling. A benefit to this elimination, besides saving some time, was that closely-spaced stations around the equator were causing worker stress from lack of sleep and we all benefitted from the added rest times. Otherwise, the stations and sampling during Leg 2 occurred without interruptions.

In terms of any sampling problems during Leg 2, the major one was that the Vectran repair made the cable substantially wider for ca. 1 m and caused very poor level winding and cable crossings that slowed deployment and recoveries by ca. 2 hours. The problem turned out to be the poorly fitted shrink wrap coating the cable splice. After we removed it and replaced it with Scotch coat

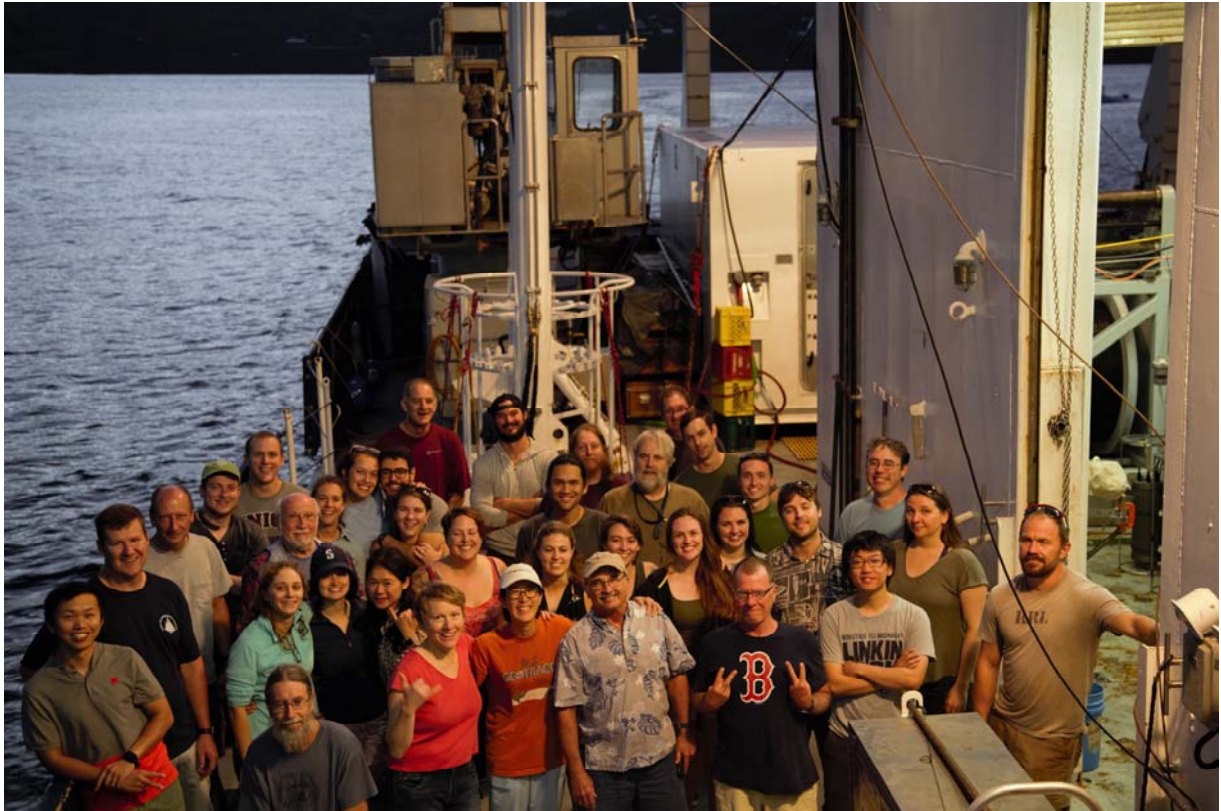
and electrical tape, the level winding went perfectly and without delay. The second sampling issue was due to the tow-fish breaching. The cause this time was a missing steering fin and the ship engineers fabricated a replacement until this too broke off at Station 35. Thereafter, we deployed and recovered the fish between uses (arriving and intermediate fish) while only steaming at 8 knots during use.

Due to increased efficiency, we were able to conduct sampling at full-36 resolution at station 37, rather than the reduced full-24 resolution. Our final station, 39, at 20° S, was sampled on 21-23 October and was modified slightly from the original plan of being a Full-36 station. In view of its location in the ultra-oligotrophic South Pacific gyre and the probable location for the first station of the next (2021?) US GEOTRACES transect (GP17), we added an additional pump cast so that 24 rather than 16 depths were sampled for particles. This added 12 hours to our station time, but we completed it on time to get to Tahiti as scheduled and with a much more complete sampling for this future Crossover Station.

Demobilization in Papeete, Tahiti. We arrived in Papeete at 0710 on 24 November and immediately started demobilization. This was completed on 26 November with virtually of the scientific gear and samples removed from the ship and on their way for the United States by container and air.

Reference

Moore, W.S., Ussler III, W., Paull, C.K., 2008. Marine Chemistry. Short-lived radium isotopes in the Hawaiian margin: Evidence for large fluid fluxes through the Puna Ridge, 109: 421-430.



GP15 Leg 1 (RR1814) group photo.



GP15 Leg 2 (RR1815) group photo

3. Sampling systems

3.1 GTC

The Cutter (ODU) group provided the GEOTRACES Trace Element 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 11 spares). Laramie Jensen (TAMU) and Brent Summers (USF) were the “super technicians” in charge of the trace element sampling itself as well as deploying and recovering the GTC. Lisa Oswald (ODU) oversaw the logistics including maintaining the cruise Event Log for the entire cruise. Kyle McQuiggan and Greg Cutter ran the GTC sampling operations (data acquisition, winch operations) with assistance from ODU graduate student Sveinn Einarsson.

In total, 72 GTC hydrocasts were conducted and 2 GO-FLOs per depth were triggered (3 per depth for super stations to accommodate water requests), with subsequent filtration using Acropak capsules (0.2 μ m). An average of 10 sample bottles were filled from each Acropak-filtered GO-FLO, but this number varied based on station type and depth. For the 35 stations occupied on Leg 1 and Leg 2, which includes shelf, slope, demi, full, super, and “bonus” stations between 56°N and 20°S, this represented the acquisition of upwards of 15,500 trace element samples. Shipboard analyses of Al, Mn, and Fe (UH), and Zn (ODU) indicated intermittent contamination for some GO-FLOs, and these were replaced with a backup bottle upon discovery of a consistent contamination pattern. Additionally, intermittent leakage or mistrips occurred in some GO-FLO bottles, and a “GO-FLO Leaker List” on an Excel Spreadsheet has been created and distributed.

Besides samples for ship-based analyses, most samples were taken from the GTC in support of shore-based analyses. Including these, the following groups received samples: Anderson (LDEO; colloidal Th); Boyle/Rember (MIT/UAF; Cr and Pb isotopes); Conway/John (USF/USC; TEI isotopes); Cutter (ODU; shipboard H₂S, Zn and nanonutrients); Fitzsimmons (TAMU; colloidal TEIs); Fitzsimmons/Till (Humboldt; dissolved metals); Hatta/Measures (UH; shipboard Al, Fe, Mn); Horner (WHOI; Ba); Mason (UConn; Hg); Moffett (USC; inert Cu); Repeta (WHOI; ligands); Saito (WHOI; Co); Shiller (USM; REEs). In addition to these parameters, samples of opportunity were taken at select stations for Lamborg (UCSC; total Hg); Dulaquais (UBO; DOM); Fitzsimmons/Buck/Bundy/Hurst (TAMU/USF/UW/Humboldt; Fe ligands) when water budgets allowed. It should also be noted that a malfunction with the A-frame motor did not allow us to use the GTC at Demi Station 11.

3.2 ODF Rosette

The 36-place Scripps Ocean Data Facility (ODF) rosette was used to sample water for less contamination-prone elements (Table 1). Casciotti (Stanford, co-cruise leader), along with Marty Fleisher (LDEO) and Colette Kelly (Stanford) were responsible for managing the water budget and overall sampling of the ODF rosette. The ODF group was responsible for maintenance and calibration of the rosette bottles and instrumentation. Costs associated with management of the rosette and sample collection on this cruise was covered by Casciotti’s portion of the GP15 management grant (OCE-1657944), with subcontracts to Swift (SIO) and Anderson (LDEO).

Sampling order for unfiltered samples was: CFCs, He, ODF O₂, $\Delta^{17}\text{O}-\text{O}_2$ (where collected; see ODF sample log appendix), N₂O (where collected), CH₄, $\delta^{13}\text{C}-\text{DIC}$, salts and nuts, and $\delta^{18}\text{O}-\text{H}_2\text{O}$. DOC and genomics samples were collected after the gas sampling was completed. When DOC and genomics samples were collected from ‘gas’ bottles, they were collected after Si and NO₂⁻/NO₃⁻ isotope samples. For filtered samples, the order of collection was Si (where collected), NO₂⁻/NO₃⁻, DOS (where collected). Nutrients were sampled from every bottle. O₂ and salts were collected from one (usually the first) bottle at every depth.

Gas samples, Si, and NO₂⁻/NO₃⁻ samples were also collected from the first bottle at every depth. Large volume samples were collected from additional bottles tripped at a given depth: Th/Pa, Nd/REE, Po/Pb (where collected), artificial radionuclides (where collected), U series isotopes (where collected), and Th/Pa archive samples (where collected). Po/Pb, Th/Pa, Nd/REE and artificial radionuclides were generally sampled in that order. Cubitainers for Po/Pb samples were not acid washed, while those for Th/Pa and Nd/REE were. To save water, sample rinses went from acid washed into non-acid washed containers. Po/Pb cubitainers were processed by Mark Stephens immediately after collection. Th/Pa, Nd/REE, and artificial radionuclide samples were acidified with 6N HCl (20 mL in 5 L samples, 40 mL in 10 L samples, and 60 mL in 20 L samples). Cubitainers were sealed with parafilm and double bagged before transfer to pallet boxes on deck. Please see individual science reports for more details of onboard sample processing.

Table 3.2-1: PI, parameters, and samplers of ODF rosette.

Role (PI-param)	Sampler (Leg 1)	Sampler (Leg 2)
Lead/Bottle cop	Karen Casciotti	Karen Casciotti
Super tech	Marty Fleisher	Marty Fleisher
Super tech	Collette Kelly	Collette Kelly
ODF O ₂	Erin Hunt	Susan Becker
	Melissa Miller	Andrew Barna
ODF salts and nuts	John Calderwood	Erin Hunt
	John Collins	Kelsey Vogel
Fine-CFCs	David Cooper	Jim Happell
German/Jenkins- ³ He	Kevin Cahill	Zoe Sandwith
Casciotti—N ₂ O	Colette Kelly	Colette Kelly
Shiller-CH ₄	Laura Whitmore	Virginie Sanial
Quay- $\delta^{13}\text{C}-\text{DIC}$, $\Delta^{17}\text{O}-\text{O}_2$	Chuck Stump	Chuck Stump
Sikes-- $\delta^{18}\text{O}-\text{H}_2\text{O}$	Kevin Cahill	Zoe Sandwith
Casciotti— $\delta^{15}\text{N}-\text{NO}_2^-/\text{NO}_3^-$	Casciotti/Kelly/Fleisher	Casciotti/Kelly/Fleisher
Repeta-Ligands, DOC	Lydia Babcock-Adams	Jingxuan Li
Buesseler- ²³⁴ Th, ¹²⁹ I	Jennifer Kenyon	Jennifer Kenyon
Charette/Moore-Ra	Paul Henderson	Emilie LeRoy
Biogeotraces	Sveinn Einarsson	Sveinn Einarsson
Pigments	Alex Fox	Alex Fox
Brzezinski--Si isotopes	ODF super techs	ODF super techs
Anderson—Th/Pa	ODF super techs	ODF super techs

Kadko/Cochran-Po/Pb	ODF super techs	ODF super techs
Goldstein--Nd/REE	ODF super techs	ODF super techs
Kenna—Art. radionuclides	ODF super techs	ODF super techs
Cutter—DOS	ODF super techs	ODF super techs

Cast types included ‘Demi’ station casts to 1000 m, shallow casts to 400-1000m, intermediate casts from 400-2000 m, and deep casts to within 40 m of the bottom. At each full and super station, an additional cast of the ODF rosette was conducted to sample large volumes for pigments, Radium, and Thorium isotopes (PigRaTh). On the PigRaTh casts, eight depths were selected to match the shallowest eight pump depths. Another four depths were chosen for resolution of Th-234, and a surface bottle was tripped for a 13th sample depth. The surface bottle was used primarily to sample dissolved gases at the sea surface, rather than drawing from the towfish or the ship’s underway system. Surface bottle sampling also occurred at demi stations (13 depths sampled instead of 12).

Pigments were sampled from the shallowest 6 depths on every PigRaTh cast (including the surface bottle). Pigments were collected into 2L amber bottles, triple rinsed with sample prior to filling. They were immediately filtered under vacuum through 47 mm GF/F filters. They were folded and placed inside cryovials, labeled with appropriate GEOTRACES numbers, and frozen at -80 °C.

Samples for $\Delta^{17}\text{O}-\text{O}_2$ were collected at the shallowest 7-8 depths on PigRaTh. On Leg 2, CH_4 was also sampled from the shallowest 8-10 depths on PigRaTh. At super stations, N_2O was sampled from PigRaTh instead of the shallow ODF cast. Cesium isotope samples were collected from the ODF rosette at Stations 7, 9, 11, 13, 15, 17, 20, and 22 (Table 2).

Additionally, 47 samples were collected for shipboard Al, Fe, and Mn from Station 18.3 (Puna Ridge), Station 18.6 (Loihi Seamount) and one superstation (station 35) for comparison to analyses from the GEOTRACES rosette. These samples were collected by M. Hatta and G. Weiss, filtered through the 0.8/0.45 μm Acropak 500 capsule filter prior to collection of the $\text{NO}_2^-/\text{NO}_3^-$ isotope samples.

Filtered samples were collected through Acropak filters (nested 0.8, 0.45 μm filter capsules). These filters were reused on similar casts (shallow, intermediate, or deep), drained, and kept refrigerated between uses. Tubing for filters was reused for every cast, rinsed with milliQ between casts. There were 36 filters in use at any one time, with 12 in use for shallow and demi cast depths, 12 in use for intermediate cast depths, and 12 in use for deep cast depths. All 36 filters were changed out between Leg 1 and Leg 2. One filter was used exclusively for all depths on the shelf stations, and then discarded.

For details on CTD instrumentation, data processing, nutrient, salts, and oxygen measurements at sea, please see ODF facility report.

Reported sampling issues:

Water budgets were prepared based on requested water amounts from each group. In some instances, the ‘gas’ bottle contained less than the expected amount of water. In such cases, water was sometimes borrowed from Th/Pa and Nd/REE bottles.

On occasion, when a 30-L niskin bottle deployed with the McLane pumps did not close properly, water was collected from the ODF niskin rosette at the appropriate depths.

$\delta^{18}\text{O}$ -H₂O samples were filled as prescribed, though it was difficult to avoid bubbles with the shoulder on the scintillation vials. Tightly capped bottles were wrapped twice with electrical tape (mostly clockwise).

Teflon liners on the caps of Si isotope sample bottles were difficult to contend with, as they were not secured to the caps. Some were lost in rough seas.

3.3 McLane Pumps

The McLane pumping operations were part of Phoebe Lam’s (UCSC) management proposal with subcontract to Steve Pike (WHOI). The McLane pumps were used to collect size-fractionated small (~1µm-51µm) and large (>51µm) particles using “mini-MULVFS” filter holders and short-lived radionuclides (Ra quartet, Th-228, Ac-227) using 1-2 Mn-coated cartridge(s) attached downstream of the filter holders.

3.3.1 Equipment:

In-situ pumps, wire, 30 L Niskins

WHOI provided 12 dual-flow battery-operated McLane pumps with two cartridge holders (modified WTS-LV-upright) from the WHOI UNOLS pump pool, and 6200 m of 0.322” OD Hytrel-coated non-conducting Vectran wire, MBS=5700 lbs (property of Ken Buesseler at WHOI). Two titanium pressure cases rated to 6000 m depth were purchased on the management grant for the two deepest McLane pumps (normal upright McLane pump pressure cases are rated to 5000 m), and will become part of the WHOI UNOLS pump pool.

The Vectran was spooled onto a refurbished and newly powder coated SIO drum at MarFac prior to the cruise (summer 2018) and deployed from the DESH-5 winch and squirt boom on Revelle. Up to eight McLane pumps were deployed at a time on a cast. The remaining four pumps were used for parts and as spares. WHOI also supplied eight 30L Niskin bottles (plus two spares) that were mounted on the pump wire on intermediate and deep casts.

SBE 19-plus Seacat CTD with optical sensors

Lam provided a SBE 19-plus Seacat self-recording CTD that was shackled to the end of the non-conducting Vectran wire for each pump cast. The Seacat CTD was outfitted with the following optical sensors:

- Seapoint Turbidity Meter (S/N 15785 at stns 5,3; S/N 10595 at Stns 4-16; S/N 12809 at Stns 18-39) (V0)
- WetLab ECO-AFL/FL Fluorometer (S/N FLNTURTD-870) (V1)

- prototype WetLabs/UC Berkeley Particulate Inorganic Carbon Sensor (S/N PIC 011) from Dr. Bishop (V2)
- WetLabs C-Star Transmissometer (S/N CST 1450) on loan from Dr. Jim Bishop (UC Berkeley) (V3)

Three Seapoint Turbidity Meters were used:

- S/N 15785 (Lam—UCSC) was deployed at the first station 5, but sustained damage when the CTD hit bottom on Station 5d (see “Problems encountered” section). It was deployed again at Station 3 before damage was noticed.
- S/N 10595 (Bishop—UCB) was deployed from Station 4-16, but it had 10x lower sensitivity and so was changed out.
- S/N 12809 (Bishop—UCB) was deployed from Station 18-39.

Pingers

Four pingers were used on the cruise to determine proximity of the Seacat CTD to the bottom. The pingers were attached by hose clamps and shackles onto the Seacat CTD frame. The first pinger was supplied by WHOI (Oceanographic Instrument Systems, Hi-Power Pinger, Model 6000), and the other three belonged to SIO STS (Benthos).

WHOI Pinger:

- This was deployed on the test cast (Rinse Station 2).
- The signal was too faint and was lost as the package was lowered, and was not used again.

SIO STS Pinger 1 (#1291):

- This was deployed on all subsequent pump casts during leg 1. The signal strength was variable. The direct pinger signal was usually (but not always) visible for the whole cast, and the bottom reflection was visible on about half of the casts. The pinger stayed on the CTD for all casts, but was turned on only for deep casts to save batteries.
- At the port stop at the end of leg 1, mineral oil was purchased to fill the transducer head in an attempt to boost the signal strength, but the bolt broke when it was tightened to (apparent) specifications

SIO STS Pinger 2 (#1214):

- This was tested when the newly spliced Vectran wire was unspooled and respooled onto the drum (see “Problems encountered”) at the beginning of leg 2 and had a strong signal.
- It was subsequently deployed at stations 19 and 21. The bottom reflection was only visible 100 m from the bottom (visible at 5040m) at station 19D; pinger reflection was never visible on station 21D. There was an oily film on the outside of the transducer end after the 21D recovery, indicating an oil leak from the transducer. The pinger stayed on the CTD for shallow and deep casts of these two stations, but was turned on only for deep casts to save batteries.

SIO STS Pinger 3 (#1074)

- This was deployed on Station 23D and a pinger reflection appeared at payout=3275m (bottom depth = 5210m).
- Deployed on Station 25D—pinger fainter, and reflection not visible. Oily film on outside after 25D recovery, indicating an oil leak.

No more pingers were deployed after station 25D. Vectran level-wind on the drum was good by this point, so wire payout was within 5 m of depth as sensed by the CTD.

3.3.2 McLane pump team:

The pump team consisted of the two McLane pump “supertechs”, Steve Pike (WHOI) and Yang Xiang (UCSC), Vinicius Amaral (UCSC), Jennifer Kenyon (WHOI-short-lived thorium), Paul Henderson (WHOI-radium isotopes, leg 1), Emilie LeRoy (LEGOS-radium isotopes, leg 2), and Phoebe Lam (UCSC). Pike was responsible for pump programming and maintenance; Xiang led the particle processing and subsampling with help from Amaral; Lam oversaw pump operations and particle processing; Henderson/LeRoy were responsible for Ra sampling from Mn-coated cartridges attached to the pumps; Kenyon was responsible for sampling for Ra and Th from the 30L Niskin bottles. She also sampled all Niskins for nutrients and salts, which were analyzed by the ODF group. All helped with pump deployments and recoveries.

3.3.3. McLane pump operations:

McLane pumps were programmed with a trigger delay time that was determined based on our best estimate of the deployment time from start to finish (reaching of final target depth), plus a small (usually ~10 minute) cushion. The CTD was deployed first and was allowed to debubble for 1 minute just below the surface. Starting at Station 6S, a snap shackle was attached to the bottom frame of the CTD to lift the CTD to a horizontal position to let bubbles escape from the vertically-mounted PIC sensor. This was found to improve PIC sensor data quality. Just after the CTD was deployed, the pumps were triggered using a screwdriver to short the connection, setting the pumps to countdown to start pumping (see “Problems encountered” section for more).

A 30 L Niskin was mounted above each pump on all intermediate and deep casts to collect water for the radium and short-lived thorium groups. Niskins were not mounted above pumps on the shallow casts because water for these groups was collected on the ODF PigRaTh cast that followed each shallow McLane pump cast.

On shallow casts, the McLane pumps were mounted at wire out readings determined from target sampling depths. On intermediate and deep casts, the 30L Niskin was mounted first, then a pump was mounted 1-2m below the Niskin. A long lanyard with Teflon-coated messenger was attached to the Niskin and the messenger was clipped below the pump, thereby bypassing the Niskin and pump pair. On these deeper casts, a messenger was dropped halfway (2 hours) through pumping to trigger the Niskin bottles to close.

3.3.4. McLane pump cast statistics:

See Table 3.3-1 and bullet points below for a summary of how many and where McLane pumps were deployed.

- McLane pumps were deployed at a total of 23 stations: 12 stations on leg 1 and 11 stations on leg 2
- The number of McLane casts on each station was one at shelf and slope stations, two at full-24 and full-36 stations, and three at super and full-36-PLUS stations.
 - A total of 49 McLane casts were completed (not including the test cast at Rinse station 2): 23 casts on leg 1 and 26 casts on leg 2.
- The number of pumps deployed was 388: 180 on leg 1, and 208 on leg 2.

- Including dipped blank filters, we collected 437 of each of QMA pairs, Supor pairs, QP prefilters, and SP prefilters.
- The total volume filtered in-situ by pumps was about 491,891 L over the whole cruise.

Table 3.3-1: McLane pump cast statistics

Leg	Station #	station type	# pump casts	# pumps/cast	#pumps/station	#QMA pairs/station	#Supor pairs/station	#51um over QMA/station	#51um over Supor/station
1	5	full	2	8	16	18	18	18	18
1	1	shelf	1	4	4	5	5	5	5
1	3	slope	1	8	8	9	9	9	9
1	4	full-36	2	8	16	18	18	18	18
1	6	full-24	2	8	16	18	18	18	18
1	8	Super	3	8	24	27	27	27	27
1	10	full-24	2	8	16	18	18	18	18
1	12	full-36	2	8	16	18	18	18	18
1	14	Super	3	8	24	27	27	27	27
1	16	full-24	2	8	16	18	18	18	18
1	18	full-24	2	8	16	18	18	18	18
1	18.3	shelf	1	8	8	9	9	9	9
2	19	full-36	2	8	16	18	18	18	18
2	21	full-36	2	8	16	18	18	18	18
2	23	Super	3	8	24	27	27	27	27
2	25	full-36	2	8	16	18	18	18	18
2	27	full-36	2	8	16	18	18	18	18
2	29	Super	3	8	24	27	27	27	27
2	31	full-36	2	8	16	18	18	18	18
2	33	full-36	2	8	16	18	18	18	18
2	35	Super	3	8	24	27	27	27	27
2	37	full-36	2	8	16	18	18	18	18
2	39	full-36-PLUS	3	8	24	27	27	27	27
Whole cruise total	23		49		388	437	437	437	437
Leg 1 total	12		23		180	203	203	203	203
Leg 2 total	11		26		208	234	234	234	234
Total volume filtered (L)					491,819				

leg 1 total					234,979				
leg 2 total					256,841				

3.3.5 Particle Sample collection:

Each pump contained two “mini-MULVFS” style filter holders (Bishop et al. 2012) plumbed into the pump head. One holder was loaded with a 51um polyester mesh prefilter (underlain by a 150um polyester mesh support filter) above paired 0.8um polyethersulfone Supor membrane filters on a separate stage (0.8-51um size fraction) for contamination prone TEIs; the second holder was loaded with a 51um polyester mesh prefilter (underlain by a 150um polyester mesh support filter) above paired Whatman QMA quartz fiber filters underlain by a 150um polyester mesh support filter on a separate stage (1-51um size fraction) for particulate organic carbon and TEIs requiring higher volumes (e.g. short-lived radionuclides). The 51um prefilters over the Supor and QMA filters are referred to with the suffixes “Sp” and “Qp”, respectively. Typically the volumes filtered through the Supor and QMA sides were ~400 L and 1100 L, respectively. One of the pumps (“Pump 3”) had a larger top plate that allowed the attachment of two additional filter holders loaded with a Supor set and a QMA set of filters, each filter set overlain by a 0.2 um Supor to act as a particle prefilter. These holders were not plumbed into the pump head, but were exposed to seawater for the duration of the cast and functioned as seawater/process blanks (“dipped blanks”) for each filter type (i.e., Sp, Qp, Supor, QMA).

Please refer to the narrative from the Radium group for details and statistics about the Mn-coated cartridge sample collection.

3.3.6 Particle sample handling and subsampling:

Excess seawater in the headspace of filters holders was sucked down on deck using an aspirator pump before removing filter holders from the pump. Filter holders were brought into the main lab bubble and sample processing began within an hour (usually within half an hour) of recovery of all pumps.

In the bubble, filter holders were again connected to a vacuum pump to remove excess seawater before disassembling. Digital photographs were taken under constant lighting conditions of each of the four filters to come off a pump (Qp, Sp, Q, S for QMA prefilter, Supor prefilter, QMA, and Supor, respectively). Dipped blank samples were processed first, then filters were processed from shallow to deep.

Table 3.3-2 summarizes the recipients of particle subsamples, the TEIs measured, and processing requirements. A total of 16 groups will receive particle subsamples to analyze over 23 TEIs. Filter subsamples that needed to be frozen or rinsed were subsampled immediately. Remaining QMA filters were dried in a 55°C oven in a 150 mm petri dish. Qp and Supor samples that could be stored dry were first dried in a laminar flow hood on eggcrate grids for >12 hrs, and then subsampled and bagged for distribution.

Table 3.3-2: Particle subsamples

PI	parameter	Which filter; processing notes	container	representative at sea
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Anderson/ Edwards	$^{230}\text{Th}/^{231}\text{Pa}$	Qp, Supor: laminar flow dry	6x8" cleanroom bag	Marty Fleisher
Basak/ Goldstein	eNd	Qp: proteins; supor: w/ Th/Pa	see proteins; Th/Pa	Marty Fleisher
Brzezinski	Si isotopes	Supor: laminar flow dry	6x8" cleanroom bag	none
Buesseler (CafeTh)	^{234}Th , ^{228}Th	Sp: CafeTh rinse then oven dry; QMA: oven dry	150mm petri (from CafeTh)	Jennifer Kenyon, Steve Pike
Casciotti	$\delta^{15}\text{N}$	QMA, Sp: post ^{234}Th	see ^{234}Th	Karen Casciotti
Charette/ Moore	^{226}Ra	QMA: oven dry	150mm petri (from CafeTh)	Paul Henderson, Emilie Le Roy
Cochran/ Kadko	^{210}Po - ^{210}Pb	Qp,Sp,Supor: laminar flow dry	6x8" cleanroom bag	Mark Stephens
Cutter	AVS&CrRS	Supor, QMA: -80C	cryovials	Nicole Buckley, Greg Cutter
Horner	Ba isotopes	Qp,Sp,Supor: laminar flow dry	6x8" cleanroom bag	none
John	TM isotopes	Supor: laminar flow dry	3x5" cleanroom bag	none
Kadko	^7Be	QMA: oven dry	150mm petri (from CafeTh)	Mark Stephens
Kenna	Artificial R. (Pu/Np)	QMA: oven dry	150mm petri (from CafeTh)	none
Lam/Lee	pTM	Qp: rinse then laminar flow dry; Supor: laminar flow dry	Qp: leached petrislide; Supor: 3x5"	Phoebe Lam, Yang Xiang, Vinicius Amaral
	PIC	Qp: laminar flow dry; QMA: oven dry	Qp: 3x5" (w/bSi); QMA: 3x5"	Phoebe Lam, Yang Xiang, Vinicius Amaral
	bSi	Qp, Supor: laminar flow dry	Qp: 3x5" (w/PIC); Supor: 3x5"	Phoebe Lam, Yang Xiang, Vinicius Amaral
	C/N+isotopes	Sp,QMA: post ^{234}Th	see ^{234}Th	Phoebe Lam, Yang Xiang, Vinicius Amaral
Hammer- schmidt	pHg	QMA: laminar flow dry in vials	Hg vials	Yipeng He, Rob Mason

Repeta	ligands	QMA: frozen	teflon-lined ziplocs	Lydia Babcock-Adams, Jingxuan Li
Saito	proteins	Qp, QMA: RNALater, then -80 freezer	Cryovials; Ziploc bags to foil to -80C for "QMA rest of filter"	Rebecca Chmiel

3.3.7 Transmissometer Maintenance:

Transmissometer windows were cleaned before and after each deployment with a kimwipe wetted with dilute Dawn detergent, a liberal MQ water rinse, and wiped dry with a kimwipe. On-CTD readings of Vair (unblocked beam) and Vdark (blocked beam) were taken every few stations. Windows were cleaned until Vair was maximized.

Transmissometers from the three main systems (GTC, ODF, McLane pumps) were intercalibrated by taking readings of Vair and Vdark powered by a 12V power supply and read by a multimeter. Two of these intercalibrations were conducted on leg 1 (start of cruise, after station 8D), and one on leg 2 (before station 38).

3.3.8 Problems encountered:

Initial spooling onto the drum:

Poor initial level-winding onto the drum at MarFac prior to the cruise led to skipping on the metering wheel and therefore significant underestimate of the actual wire out by the metering wheel payout reading. On the first deep cast, we hit bottom with the self-recording CTD at the end of the wire even though the wire payout reading at the final depth was 4575m and the multibeam bottom depth was 4610m. Luckily, the sensitive optical sensors on the CTD were not permanently damaged and were restored to working condition after a thorough cleaning. On subsequent casts, we paid much closer attention to the pinger and were much more conservative in our approach to the seafloor. Careful respooling and level winding of the wire back onto the drum after a few deep casts fixed the problem of the inaccurate wire payout.

Wire damage incident (10/16/18)

Winch operator error during the deep McLane pump deployment at station 16 (27°N, 152°W) on 10/16/18 during leg 1 led to damage of the first 2247m of the Vectran wire: the wire had gotten caught in a hook of a stanchion between the winch and the block, and abraded against this hook at high tension, severely damaging the Hytrel jacket. The Vectran strength core did not appear damaged, but the core was exposed at many places along the first 2247m of wire. For the rest of this cast (recovery) and the remaining three casts of this leg (station 18s, 18d and station 18.3), deployments and recoveries were significantly delayed as we attempted to patch the jacket wherever the core was exposed using a combination of ScotchKote and electrical tape. This became unsustainable, and a decision was made to rush freight a spare spool of Vectran wire from UC Santa Cruz belonging to Lam to Hilo, HI. The original line was chopped at 2955m, which included the damaged 2247m as well as damage on the wire from a previous cruise at 2955m. A travelling rigger from Cortland Cable company, the manufacturers of the Vectran wire, was engaged to fly to Hilo to splice the old line to the spare line. A length of 3855m of spare line was spliced to and spooled on top of 3245m of the remaining old line, for a total of 7094 m of spliced line on the DESH-5 drum for leg 2. During the transit to the first station of

leg 2 (Station 19), a small pigweight and SIO Pinger #2 were shackled to the end of the Vectran wire and 4200 m of wire (to pass the 3855 m splice) was unspooled (~150 lbs tension) and respooled (~300 lb tension).

The jacket that was placed around the splice at 3855m by the Cortland rigger increased the OD of the wire in the spliced section by a factor of 2, causing major level wind issues. On the first deep McLane cast of leg 2 (Station 19D), the Cortland jacket (two layers of heat shrink tubing) was cut off, and the exposed Vectran splice was Scotchkoted and electrical taped to approximately match the OD of the rest of the Hytrel-jacketed Vectran wire. This fixed the level winding issues.

Pumping issues:

a) The sum of the QMA and Supor flowmeters should be within 5% or so of the reading of the final flowmeter. If the final flowmeter is significantly greater than the sum of the QMA and Supor flowmeters, this indicates a leak in the plumbing, often associated with a Mn cartridge holder that is not sealed. In these cases, the QMA and Supor volumes are generally lower than usual, but should be ok. However, the appropriate volume to be used for the Mn cartridges may not be easily recoverable.

b) the ratio of volume filtered through the Supor/QMA sides is typically 0.38. If the ratio deviates significantly from this, this may indicate a leak in the Supor or QMA flowmeters.

c) The triggers for Pumps 1, 2 (with updated CF-2 firmware) stopped functioning starting station 33D; the trigger for pump 8 (old TT8 firmware) stopped functioning starting station 35S; the trigger for pump 3 (old TT8 firmware) stopped functioning starting station 37D (failed pump); the trigger for pump 4 (old TT8 firmware) stopped functioning starting station 39S. Pumps with failed triggers were programmed on a schedule just after the CTD was deployed. The remaining pumps were programmed with a trigger delay as usual.

d) We had 12 failed pumps out of a total of 388 deployed (3% failure rate). Failed pumps were generally due to one of the following problems:

i) corrosion in the pins connecting the pressure case to the motor cable: the solution was to carefully clean the pins and make sure the plug was properly seated and sealed. The McLane pump error for this was either “sudden flow obstruction”, or “sudden pressure release”.

ii) corrosion in the communication pins on the pressure case: the McLane pump error message for this was “stopped by user”. The solution was to carefully clean the pins and make sure the plug was properly seated and sealed.

iii) failed trigger: despite carefully cleaning the trigger pins and using a variety of screwdrivers to short the connection, we could not get these to work. Our solution was to switch to “Schedule” mode when programming pumps with failed triggers.

30L Niskin issues:

Several bottles failed to trip, especially on leg 1, due to the messenger lanyard getting caught on various Niskin hardware parts. When this happened, water for the Ra and short-lived thorium groups was often obtained from the ODF rosette cast at the expense of water for unfunded parameters.

3.4 Tow-fish

The clean sampling system using for obtaining clean trace element surface samples during transits and arriving on stations has been called the “Geo-fish” due to its designer and builder, Geoffrey Smith at UC Santa Cruise; for GP15 we simply called it the Tow-fish. This system was provided by Cutter (ODU) as a portion of this management grant. It consisted of a weighted torpedo with adjustable fins to control its depth and horizontal position relative to the ship’s hull, and a vane that directed the ½” Teflon sample tubing into fresh water while travelling up to 12 kts. These were held away from the ship with a 40’ aluminum boom mounted to a pedestal on the starboard, main quarter deck (see Mobilization section above). The Teflon tubing is lead to a compressed air-powered, Teflon bellows pump and another length of tubing leads to a filtration manifold kept in the main lab clean bubble. The manifold has Teflon valves that allow the water to be directly sampled unfiltered, or passed sequentially through a 0.45 µm, 10” filtration cartridge then a 0.2 µm, 10” cartridge. From these the water is directed into in a 60L, polyethylene tank for sampling non-contamination prone trace elements and isotopes (TEIs; in this case the ones sampled using the ODF system) or directly sampled for contamination-prone TEIs such as those sampled with the GTC sampling system. The flow rate through the systems averaged 4L per minute, and the filter cartridges were installed on 21 September 2018 before Station 1 and changed on 11 October and 11 November 2018.

Deployment, recovery and general system maintenance was done by Sveinn Einarsson and Kyle McQuiggan (both from ODU), with help from Greg Cutter (ODU). For Leg 1 Cliff Buck (SkIO) led the clean sampling efforts, while Chris Marsay (SkIO) did contamination-prone sampling on Leg 2. The non-contamination prone and BioGEOTRACES samplings were done by Karen Casciotti, Marty Fleisher, and Sveinn Einarsson. Tow-fish sampling occurred just before arrival at every station (“arriving fish”, also called Cast 1, 0 m, on the master data sheet) to obtain surface water for all TEIs, and at stations located half-way between vertical profile Demi, Full and Super stations (“intermediate fish” with a #.5 station number). The primary tow-fish problem during GP15 was fish breaching where the vane and torpedo would leave the water, largely due to ship’s roll in heavy, breaking seas, but also when fins came out of adjustment or were damaged/torn away. These problems led to no Tow-fish samples at Intermediate stations 6.5, 7.5, 9.5, 14.5, and 36.5, and Demi station 7. Otherwise, over the course of the GP15 transect, 1180 samples were collected from 54 stations. Table 3.4-1 lists the samples and labs to which they were distributed.

Table 3.4-1: PI and parameters of distributed fish samples

Parameter	PI	Filtered?	Station Type
Contamination-prone			
Cells	Twining	No	Stns.4,6,8,14
H2S	Cutter	Yes	Full & Super
pH	Cutter	Yes	Full & Super

Zn	Cutter	Yes	Full & Super
Nano nuts	Cutter	Yes	Full & Super
Pb/Cr	Boyle/Rember	Yes	Super
Fe	Fitzsimmons	Yes	All stations & intermediate fish
TMs	Fitzsimmons/Till	Yes	All stations & intermediate fish
Fe/Al/Zn	Hatta	Yes	All stations & intermediate fish
Ba	Horner	Yes	All stations & intermediate fish
TM isotopes	John	Yes	All stations & intermediate fish
TM isotopes	Conway	Yes	All stations & intermediate fish
Hg	Mason	Yes	All stations & intermediate fish
Siderophores	Repeta	Yes	All stations
Co	Saito	Yes	All stations
REE	Shiller	Yes	All stations & intermediate fish
Fe ligands	Jensen	Yes	Full & Super
TBD	Dulaquais	Yes	Demi & Super
Cu	Moffett	Yes	All stations & intermediate fish

Non-contamination prone

Salt	ODF	No	All stations & intermediate fish
Nuts	ODF	No	All stations & intermediate fish
d18O-H2O	Sikes	No	All stations
DIC	Stump	No	All stations
I-129	Buesseler	No	Stns. 3,6,10,16
Th-234	Buesseler	No	Demi & int. fish
Po/Pb	Cochran	No	Stns. 1,3,8,14,18
Biogeochemicals	Sven	No	All stations & intermediate fish
d15N-NO3	Casciotti	Yes	All stations & intermediate fish
d15N-NO2	Casciotti	Yes	All stations
DOS	Cutter	Yes	Stns. 4,6,8,10,12,14
Th/Pa/Nd/REE	Anderson	Yes	All stations & intermediate fish
Art. nukes	Kenna	Yes	Stns. 4,6,10,16

3.5 Aerosols and rain

Aerosol samples were collected over periods of two to three days using sector-controlled high-volume aerosol samplers (Tisch Environmental, model 5170V-BL). Four samplers were each loaded with twelve 47 mm filters, and a fifth was loaded with a five-stage Sierra-style slotted cascade impactor to collect size-fractionated aerosols (from $>7 \mu\text{m}$ to $<0.49 \mu\text{m}$) over periods of four to six days. A breakdown of replicate filter distribution to collaborating PIs is given in Table 3.5-1.

In total, 23 aerosol filter deployments/collections were made, resulting in:

- 23 \times 36 47mm Whatman-41 filters
- 23 \times 12 47mm GFF filters
- 12 \times size fractionated samples (six filters each)

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

Table 3.5-1 – allocation of aerosol samples collected on W41 and GFF filters during GP15.

PI	Treatment/ analyte	Odd deployment allocation	Even deployment allocation
W41 filters			
Buck/Landing	Archive	3	3
Buck/Landing	Total digest	3	3
Buck/Landing	UPW leach	3	3
Buck/Landing	0.2 μ m seawater leach	3	3
Buck/Landing	0.02 μ m seawater leach	3	3
Buck/Landing	Berger leach	3	3
Buck/Landing	Sequential leach	3	3
Anderson/Edwards/Hayes	$^{232}\text{Th}/^{230}\text{Th}/^{231}\text{Pa}$	3	--
Boyle/Zurbrick/Rember	Pb isotopes	2	--
Fitzsimmons	Colloidal TEIs	--	3
Goldstein/Basak/Wu	Nd/REE	--	3
Ingall	Solid state speciation	--	3
John/Conway	TM isotopes	2	
Cochran/Kadko	^7Be , ^{210}Po - ^{210}Pb	3	3
Till	Sc, Y, La	--	3
Horner	Ba isotopes	2	--
intercalibration reserve	---	3	--
	TOTAL	36	36
GFF filters			
Hastings	N isotopes	3	3
Mason	Hg speciation	3	3
spare/reserve		6	6
	TOTAL	12	12

Extractions of aerosol-laden W41 filters were carried out while at sea, using ultrapure water (UPW), filtered (0.2 μ m) seawater from the towfish, and ultra-filtered seawater (filtered seawater from the towfish, with a 0.02 μ m Anodisc filter loaded beneath the aerosol filter). Each extraction was carried out on three replicate filters from each deployment. These leaches included:

- UPW – 63 \times 100ml sample leaches and 17 \times 100ml blanks; subsamples also taken from one UPW leach per deployment for major anion analysis.
- 0.2 μ m filtered seawater – 63 \times 100ml sample leaches and 20 \times 100ml blanks.
- 0.02 μ m filtered seawater – 63 \times 100ml sample leaches and 20 \times 100ml blanks.

Additional extractions were carried out while at sea for collaborators Anderson, Conway, and Till.

In addition, an aethalometer and a condensation nuclei counter were installed to make autonomous measurements throughout the cruise.

Two automated rain samplers were used to collect rain (one dedicated to samples for analyses of multiple TEIs and the second designated for samples for Hg analysis). In practice, an electrical problem with one of samplers resulted in all samples coming from the remaining sampler. A total of 17 rain samples were collected. Priorities for rain samples were 0.2 μ m filtered samples for major ions and trace element analyses, followed by unfiltered samples for total mercury. Where sufficient volume was collected, unfiltered or 0.02 μ m filtered subsamples were also taken for trace element analyses.

4. Individual labs/PI Reports

4.1 ODF

Please see accompanying file “odf_report_gp15_2018.pdf” for full report on activities from the Ocean Data Facility group.

4.2 Mercury

PI: Robert Mason (at sea leg 2)

At sea leg 1: Yipeng He

Mason’s research group was responsible for monitoring the concentrations of various forms of mercury (Hg) in surface waters and in the atmosphere (i.e. elemental Hg (Hg^0), monomethylmercury (MeHg) and dimethylmercury (DMeHg)) using both continuous measurement devices and batch collection approaches. They also obtained water column samples from the GEOTRACES (GTC) rosette for the measurement of total methylated Hg ($\text{MeHg}_T = \text{MeHg} + \text{DMeHg}$), at all stations, as well as total dissolved Hg (Hg_T), and particulate Hg and MeHg samples (Hg_P and MeHg_P) from the *in situ* pumps at most stations besides the Demi stations. The continuous measurement of dissolved gaseous mercury ($\text{DGHg} = \text{Hg}^0 + \text{DMeHg}$) concentrations in surface seawater was achieved using a gas equilibrator system that sampled water from the ship’s underway sampling system that also provides measurements of underway parameters (temperature, salinity, fluorescence) and was also used by other groups measuring dissolved gases (methane, O_2/Ar , and pCO_2). The analysis of DMeHg was done using batch collections of 1-2 days, allowing for the determination of the dissolved Hg^0 concentration (DHg^0) concentration by difference. For comparison of data across sampling systems, and for validation, DGHg and MeHg_T surface water samples were collected at each station and at the intermediate stations from the underway “fish” sampler. Mostly, DMeHg was low (<2 fM) and was mostly $<5\%$ of the DGHg. Concentrations of DGHg were low in the North Pacific, and started increasing in the more tropical waters, with the highest levels in the Intertropical Convergence Zone and around the equator. Lower concentrations were found in the South Pacific. Overall, there was good agreement between measurements made using the underway system and samples collected from the over-the-side “fish” sampler.

For the atmospheric sampling, bulk aerosol samples will be obtained from the Buck/Marsay group for total Hg and MeHg analysis (Hg_{HV} and MeHg_{HV}) as well as splits from the rain samples they collected for measurement of Hg and MeHg in wet deposition (Hg_{TWD} and MeHg_{TWD}). For these measurements, the volume in the table below reflects the expected air

amount sampled by the filters to be analyzed and not the total air volume sampled. The Tekran air speciation unit continuously measures the Hg speciation in the air as three fractions: Hg^0 , reactive (oxidized) gaseous Hg (RGHg) and particulate Hg (Hg_{LV}). For comparison with this system, RGHg is also being collected using ion exchange filters (RGHg_{LV}). Finally, DMeHg was measured in the air (DMeHg_{LV}).

A summary of the samples collected and the typical sample resolution, volume collected and some details about where the analysis was/will be done is given in Table 4.2.1, as well as an estimate of the expected total number of samples collected for later analysis or analyzed on board during the cruise.

Table 4.2-1: Mercury Sampling and Analysis

*Notes: 1) Acronyms are defined in the text; 2) Sample Type: a) Underway: the ship's underway surface water sampling system that was sampled in the Hydrolab. While surface water sampling was continuous, it was not always sampled while on station, and there were times when it was stopped for maintenance and cleaning, and for system calibration; b) Fish: the surface water "fish" sampler deployed off the side of the ship while steaming between stations; c) GTC: GEOTRACES trace metal clean rosette system; d) Tekran: the Tekran mercury air speciation sampler; e) High vol: the high volume air samplers of the Buck/Marsay group 4) Resolution: a) The automated Tekran speciation units were set to sample gaseous Hg at 5 minute resolution; b) Batch analysis time depended on expected concentrations and for air sampling, the wind direction and fraction of time sampling (systems were sector-controlled to prevent contamination); and c) Station indicates water samples that were collected using the GTC rosette, or the fish sampler; and 5) Analysis: a) From the results of on board analysis, DHg^0 is calculated by difference; and b) samples still to be analyzed are indicated as UConn if they will be analyzed by Mason's group or UCSC if to be analyzed by Lamborg and Hammerschmidt's groups; 6) Note that the * indicates this is a volume of air rather than water and represents the air collected from the equilibrator system. Volumes are in L unless indicated otherwise.*

Parameter	Mode	Resolution	Sample Type	Volume (L)	Analysis	# Samples, analyses [#]
Water DGHg	Cont. Batch	5 min Station	Underway Fish	5* 1-6	On board On board	Many 100
DMeHg	Batch Batch	1-3 days Station	Underway Fish	1-3 m ³ * 1-6	On board On board	30 100
DHg^0	Cont. Batch	5 min Station	Underway Fish	5* 1-6	Calculated Calculated	Many 100
MeHg_T	Batch	Station	Fish and GTC	0.125	UConn	1000
Hg_T	Batch	Station	GTC	0.25	UCSC	600
Hg_{SPT}	Batch	Station	<i>In situ</i> pumps	Various	UCSC	670
MeHg_{SPT}	Batch	Station	<i>In situ</i> pumps	Various	UCSC	210
Air Hg^0	Cont.	5 min	Tekran	5	On board	Many
RGHg	Cont.	2 hr	Tekran	600	On board	800
Hg_{LV}	Cont.	2 hr	Tekran	600	On board	800

Hg _{HV}	Batch	1-2 days	High vol	1-5 m ³	UConn	25
MeHg _{HV}	Batch	1-2 days	High vol	1-5 m ³	UConn	25
DMeHg _{LV}	Batch	1-2 days	Air sample	1-3 m ³	On board	25
RGHg _{LV}	Batch	1-2 days	Air sample	1-3 m ³	UConn	25
Hg _{TWD}	Batch	Intermittent	Rain sample	0.05-0.2	UConn	12
MeHg _{TWD}	Batch	Intermittent	Rain sample	0.05-0.2	UConn	12

4.3 Nitrogen Isotopes

Onboard:

Karen Casciotti (PI, Stanford University; seawater nitrate, nitrite, and nitrous oxide isotopes)

Colette Kelly (Graduate Student, Stanford University, seawater nitrate, nitrite, and nitrous oxide isotopes)

Co-PIs:

Daniel Sigman (co-PI, Princeton University; seawater nitrate, particulate $\square^{15}\text{N}$),

Meredith Hastings (co-I, Brown University; subcontract to Stanford, aerosol nitrate)

4.3.1 Major overall goals

The objectives of our project are to collect and analyze samples for the stable isotope ratios of nitrate, nitrite, and nitrous oxide from the US GEOTRACES GP15 Pacific Meridional Transect to better understand the processes controlling the inventory of bioavailable N and its supply to surface waters across the Pacific. On this cruise, we sampled high nutrient waters in the Subarctic North Pacific and in the Equatorial upwelling, as well as some of the most oligotrophic ocean provinces in the north and south Pacific subtropical gyres. In addition, aerosol and rain samples were collected to constrain atmospheric inputs. Finally, suspended particle and sediment samples were collected to assess the N isotopic composition of sinking and suspended particles along the transect. Onboard, we also determined nitrite concentrations on all casts that sampled shallow waters (“ODF shallow” and ‘ODF Demi’ casts)¹, as well as underway surface samples, to determine which samples should be preserved for nitrite isotope analyses.

Samples for nitrous oxide isotope analyses were collected in duplicate from the ODF Niskin rosette at nearly every full and super station (we sampled Station 37 at lower resolution, and with single samples below 450 m, due to sample limitation). At all stations, a surface nitrous oxide isotope sample was collected from the surface bottle on the so-called PigRaTh¹ cast. At stations

¹ ODF rosette casts were one of five possible types: “shallow”, “intermediate”, and “deep ODF” casts, which included most of the ODF samplers/parameters, and a special “PigRaTh” cast to accommodate the large volume needs of pigments, radium, and thorium-234. Single ODF casts

4, 6, 8, 14, 16, 23, 29, and 35, shallow (upper 500 meters) nitrous oxide samples were collected from the PigRaTh cast; at all other stations, shallow nitrous oxide samples were collected from the shallow ODF cast. At some depths, these shallow nitrous oxide samples from the PigRaTh may not have associated nitrate and nitrite isotope samples, which were always collected from the shallow ODF cast. Nitrous oxide samples were collected only from niskin bottle casts, not from the fish or ship's underway system. Samples were filled through Tygon tubing into 160 mL glass serum bottles. The bottles were overflowed twice with water before withdrawing the tubing. A small (~ 1mL) headspace was introduced, and the bottles were capped with grey butyl septa immediately after sampling. After sampling the last bottle from each cast, N₂O samples were returned to the lab, then individually uncapped, poisoned with 100 uL of saturated mercuric chloride solution via pipette, and recapped and crimped with aluminum crimp seals. The bottles were then wrapped with bubble wrap and stored indoors at room temperature in the analytical lab, or inside the aft hold.

Samples for nitrate isotope analyses were collected in triplicate from every station and depth, including surface samples, either from the arriving fish (super and full stations) or the surface bottle (demi stations). On rare occasions, nitrate and nitrite isotope samples were also collected from the ODF PigRaTh cast to augment the resolution of the shallow ODF cast, if unique depths were being sampled on PigRaTh. Samples for nitrate and nitrite isotope analyses were collected through Acropak filters (nested 0.8, 0.45 um filter capsules). These filters were reused on similar casts, drained, and kept refrigerated between uses. There were 36 filters in use at any one time, with 12 in use for shallow and demi cast depths, 12 in use for intermediate cast depths, and 12 in use for deep cast depths. All 36 filters were changed out between Leg 1 and Leg 2. One filter was used exclusively for all depths on the shelf stations, and then discarded. The filters were rinsed prior to collection of NO₃⁻ and NO₂⁻ isotope samples by either sampling Si isotopes first (~2.5 L), or by allowing ~ 0.5 L to pass through the filters prior to rinsing and filling the NO₃⁻ and NO₂⁻ isotope bottles. No evidence of cross-contamination could be detected for nitrite concentration determination on samples tested with and without filtration. Nitrate isotope samples were collected in triplicate and frozen immediately.

Nitrite samples were collected into 50 mL square wide mouth HDPE bottles, numbered 1-13 (including the "13th" surface depth), which were reused throughout the cruise. Bottles were rinsed three times and filled with Acropak-filtered water, as for nitrate isotope samples. After sampling, nitrite concentrations were determined by spectrophotometry with SAN and NED, against a standard curve of 0-0.625 μ M NO₂⁻. Five (5) mL of each sample or standard was pipetted into 15 mL falcon tubes, and 0.2 mL of each SAN and NED were added. The samples were capped and shaken, then pipetted (2 mL each) into 1 cm path length plastic cuvettes. Absorbance at 543 nm was determined 5x for each sample and standard, and the readings were averaged. Samples with absorbance >0.004 (~ 0.1 μ M NO₂⁻) were subsampled for nitrite isotope analyses. 10 mL volumes were pipetted into 20 mL headspace vials. In parallel, 3 mL NO₂⁻-free seawater was pipetted into vials for 1 blank and 1-3 sets of six standards. A set of six standards

to 1000 m at Demi stations included a subset of these parameters. See ODF section of the cruise report for further information.

included 1 of each standard at 50 uL (10 nanomole) and 25 uL (5 nanomole) amounts. Batches with 1 sample (2 vials) generally had 1 set of standards, batches with 2-4 samples had 2 sets of standards, and batches with 5-6 samples (10-12 vials) had 3 sets of standards.

After samples and NO_2^- free seawater were pipetted into the vials, the standards were added by pipette. Then all vials were sealed, crimped and purged with N_2 gas for 15 minutes. After sparging, azide solution was added: 0.1 mL to 3 mL blanks and standards, 0.2 mL to 5-6 mL samples, and 0.3 mL to 10 mL samples. The samples were mixed and reacted for 30 minutes, then 6 N NaOH was added to match the azide reagent (0.1 mL for 3 mL blank and standards, 0.3 mL for 10 mL samples). After NaOH addition, samples were stored at room temperature. Vials were numbered on their caps, with 1-7 always being the blank and the first set of standards, followed by the samples, and then the second set of standards. For larger runs, samples were numbered consecutively from one set of standards, half of the samples, another set of standards, and so forth.

NO_2^- isotope standards N-23, N-7373, and N-10219 in 200 μM concentrations were aliquoted in 1.5 mL volumes in cryovials at the beginning of the cruise. Five sets of standards were used, each for 1-2 weeks. Standards were stored frozen between uses. A set of standards was retired with 300-400 uL remaining and will be tested in parallel upon return to the lab.

Samples collected include approximately 916 unique samples (2,748 sample bottles) for nitrate isotope analyses, 150 unique samples (~600 vials) for nitrite isotope analyses, and 738 unique samples (1,440 serum bottles) for N_2O isotope analyses.

Education and Outreach

To further outreach goals for our project, styrofoam cups decorated (prior to the cruise) by elementary school (K-4) students from 8 classrooms were deployed on the deep casts at 7 stations (4, 12, 18, 23, 29, 37, and 39). The cups were extensively photographed before and after deployment. Representative photos were emailed to teachers and in some cases, posted to Twitter. Communication with the classrooms resulted in students submitting additional questions during the cruise, which were answered in a timely fashion.

4.3.2 Preliminary findings

In the Subarctic North Pacific, we encountered high nitrate ($>10 \mu\text{M}$) surface waters (Figure 4.3-1), with the highest fluorescence seen on the entirety of the cruise (Figure 4.3-2). These stations also showed a relatively shallow mixed layer, with low but detectable levels of nitrite present throughout the mixed layer (Figure 4.3-3). The chlorophyll fluorescence showed a subsurface maximum between 50-52 °N. We sampled these HNLC waters for nitrate, nitrite, and nitrous oxide isotopes and will be looking for isotopic signals associated with nitrate utilization, and nitrite and nitrous oxide production.

In the subtropical North Pacific, nitrate and nitrite were below detection in the surface waters. A primary nitrite maximum (PNM) was detectable in the nitracline below the deep chlorophyll

maximum. In past work, nitrate isotopes have been used at Station ALOHA to estimate the contributions of N_2 fixation in the North Pacific Subtropical Gyre. Our data from this cruise will allow us to evaluate the extent of this signal over a larger region of the subtropical north Pacific.

In the Equatorial region, nitrite concentrations reached 1-2 μM in the PNM. This large amount of NO_2^- occurred despite lower NO_3^- concentrations ($\sim 4 \mu M$) than those found in the Subarctic North Pacific (Figure 4.3-1). We will use the isotopic composition of nitrate and nitrite together to better understand the effects of upwelling and iron limitation on nitrogen cycling in these HNLC waters.

The primary NO_2^- maximum was found just below the fluorescence maximum (Figure 4.3-2) at every station. In the subarctic Pacific and equatorial upwelling, where NO_3^- was present in surface waters, NO_2^- also extended into surface. There was generally enough nitrite to preserve at least one sample per station for nitrite isotopic analysis at the PNM.

In the subtropical South Pacific, nitrate and nitrite were below detection in the surface waters. For example, at station 38 the nutricline started at 135 meters (Figure 4.3-1), with a deep chlorophyll maximum at 120-150 m (Figure 4.3-2). At these south Pacific gyre stations, there was barely enough NO_2^- for isotopic measurements at the PNM, but we did preserve the samples with the highest NO_2^- concentrations ($\sim 0.1 \mu M$).

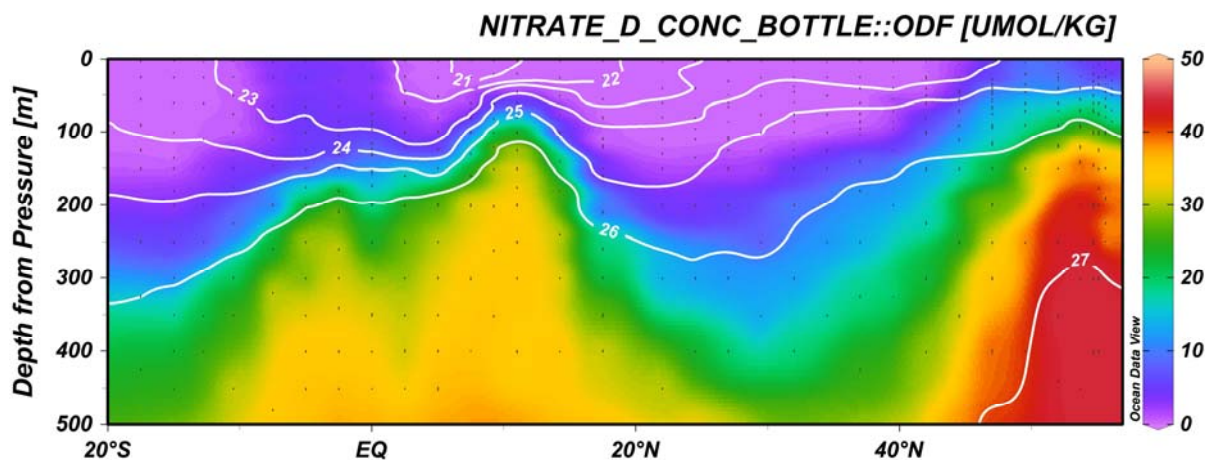


Figure 4.3-1. Preliminary nitrate concentrations from GP15 in the upper 500 m with contours of potential density (sigma-theta), courtesy of Scripps Ocean Data Facility (ODF).

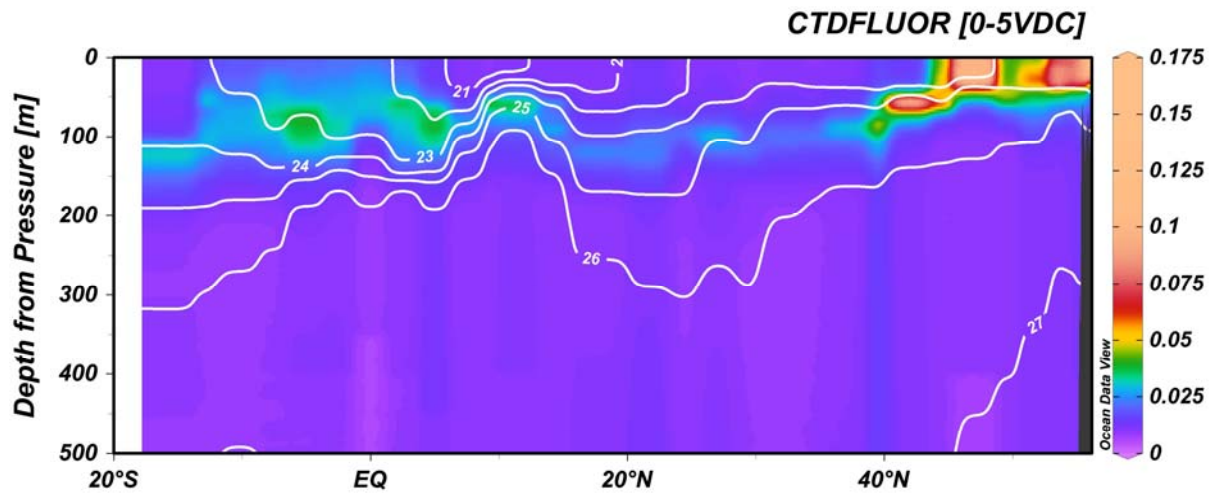


Figure 4.3-2. CTD fluorescence in the upper water column of GP15, with contours of potential density (sigma-theta), courtesy of Scripps Ocean Data Facility (ODF).

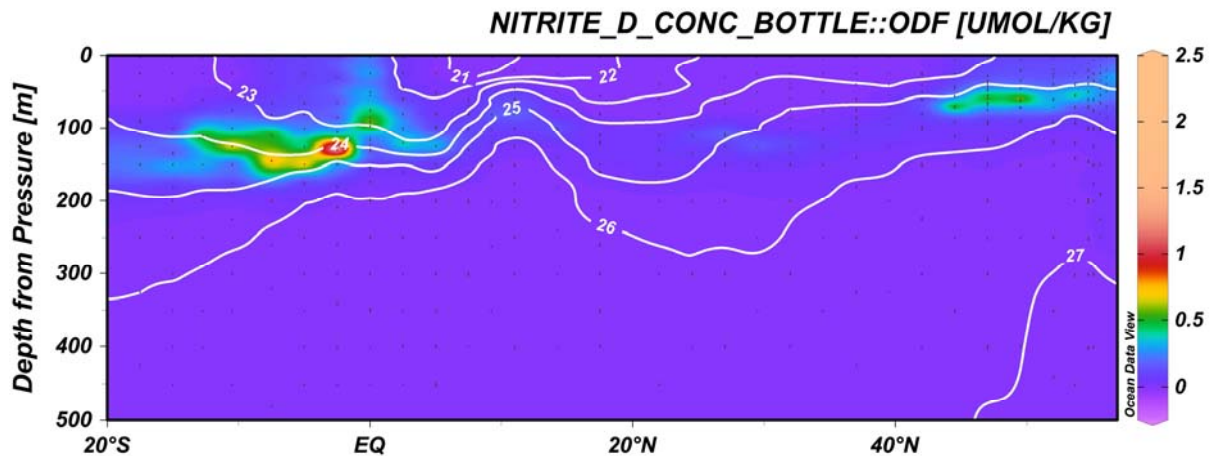


Figure 4.3-3. Preliminary nitrite concentrations from GP15 in the upper 500 m with contours of potential density (sigma-theta), courtesy of Scripps Ocean Data Facility (ODF).

Preliminary Equatorial ADCP readings

A strong eastward flowing equatorial undercurrent (EUC) was found centered on the equator around 150 m depth. This water is believed to be an important source of nitrate to equatorial surface waters (Rafter and Sigman, 2016) and helps ventilate the eastern tropical Pacific. A strong westward flowing south equatorial current (SEC) was sampled at 2.5 °N in the surface waters, and a weaker westward SEC was sampled at 5 °S. A strong eastward north equatorial counter current (NECC) was also sampled between at 9.25 and 7.5 °N, increasing in depth to the south. Finally, a weak westward north equatorial current (NEC) was sampled between 10-15 °N (Figure 4.3.4). These observations closely match those of earlier studies of equatorial circulation

between 150-160 °W (Wyrski and Kilonsky, 1984). We will use these samples to analyze nutrient and isotope transport by these strong equatorial currents.

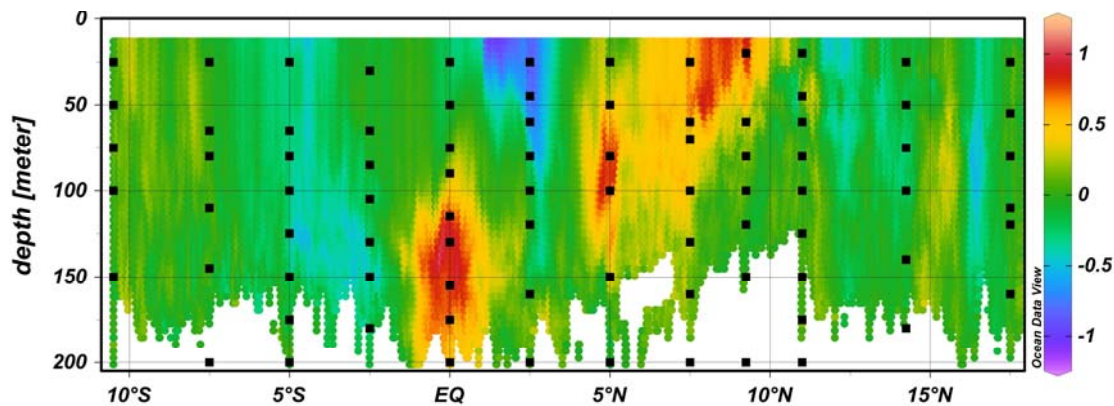


Figure 4.3-4. Eastward velocity on GP15 between 17.5 °N and 10 °S, with water sample depths marked with black squares.

4.4 CFC-11, CFC-12, and SF₆

PI: Rana Fine

At sea: Jim Happell (leg 2) and David Cooper (leg 1)

4.4.1 Sample Collection

All water samples were collected from the 10.4 liter Niskin bottles on the ODF rosette

A water sample was collected from the Niskin bottle petcock using silicone tubing to fill a 300 ml BOD bottle. The tubing was flushed of air bubbles. The BOD bottle was placed into a plastic overflow container. Water was allowed to fill BOD bottle from the bottom into the overflow container. The stopper was held in the overflow container to be rinsed. Once water started to flow out of the overflow container the overflow container/BOD bottle was moved down so the tubing came out and the bottle was stoppered under water while still in the overflow container. Additional surface water samples were also collected from the ships underway system. Air samples, pumped into the system using an Air Cadet pump from a Dekoron air intake hose mounted high on the foremast were also run. Air measurements are used as a check on accuracy.

4.4.2 Equipment and technique

Chlorofluorocarbons CFC-11, CFC-12, and SF₆ were measured on 39 stations for a total of ~900 samples. Analyses were performed on a custom built purge and trap gas chromatograph (GC) equipped with an electron capture detector (ECD). The samples were stored at room temperature and analyzed within 12 hours of collection. Every 12 samples were followed by a

instrument blank and a standard. The surface sample was held after measurement and was sent through the process in order to “restrip” it to determine the efficiency of the purging process.

4.4.3 Calibration

Two gas phase standards, 33780 and 426505, were used for calibration. The concentrations of the compounds in this standard are reported on the SIO 1998 absolute calibration scale. 6 calibration curves were run over the course of the cruise. Estimated accuracy is +/- 2%. Precision for CFC-12, CFC-11, and SF₆ was less than 1%. Estimated limit of detection is 1 fmol/kg for CFC-11, 3 fmol/kg for CFC-12 and 0.05 fmol/kg for SF₆

4.5 ²³²Th, ²³⁰Th, ²³¹Pa , and Nd isotopes/Rare Earth Elements and moncore sediment samples

PIs: Robert Anderson, Lawrence Edwards, Steve Goldstein, Chandranath Basak, Brian Haley

At sea: Martin Fleisher

Thanks to ODF personnel (Leg1-Melissa Miller, Joseph Gum, Erin Hunt, John Calderwood, John Collins. Leg 2-Susan Becker, Erin Hunt, Kelsey Vogel, Kenneth Jackson, Andrew Barna) and the ResTechs (Leg 1-Brendon Mendenhall, Keith Shadle. Leg 2-Josh Manger, Drew Cole) for their help with maintaining and deploying the ODF rosette.

4.5.1 ODF Rosette Filtered water

Sampling was carried by Karen Casciotti, Colette Kelly (both from Stanford University) and Marty Fleisher (Lamont Doherty Earth Observatory). Water from the ODF 36 place rosette, equipped with modified Bullister Bottles (10.3 liters), was passed through

Teflon-lined Tygon™ tubing connected to Pall Acropak500™ capsule filters (0.8µm/0.45µm filter pair). A single 10-liter cubitainer™ was used to collect water from surface casts. Two 5-liter cubitainers were used to collect samples on Intermediate and Deep casts. Samples were acidified to pH~2 (20ml 6M HCl for 5-liter samples and 40 ml for 10-liter samples), caps were parafilm, and the cubitainers were double bagged prior to storage.

We collected 10-liter samples from the McLane pump depths at 10 stations for on-board processing by Mark Stephens of the Po/Pb group. Two liter samples were collected and stored for Si isotopes (M. Brzezinski at UCSB) at almost every Full/Super station.

In addition, 5-liter water samples were collected at Super Stations (~10 samples/station) for high precision Uranium isotope measurements by Larry Edwards group at the University of Minnesota. Twenty-liter samples were collected at 8 stations for Tim Kenna (LDEO) to make artificial radionuclide measurements (Pu isotopes and ²³⁷Np).

4.5.2 Intermediate and Arriving Fish water samples

Filtered water (details from Cutter on filters, 0.45 and 0.2µm?) was collected in a 60 liter tank from the surface fish. Ten-liter samples were collected at intermediate stations, and upon arrival

at Full/Super/Demi stations for Th isotopes, ^{231}Pa and Nd/REE. Twenty-liter samples were collected at arriving stations where Tim Kenna was getting samples for artificial radionuclides.

4.5.3 Cross-Flow Filtration and Anapore Filter Colloid samples

At Super Stations, Janelle Steffen processed samples at 12 depths from the GTC system for colloidal Th isotopes and Pa. We received 60 ml samples filtered through a $0.02\mu\text{m}$ Anapore filter, and a pair of 1 liter samples (permeate and retentate) from the Texas A&M Cross-Flow Filtration system. Samples were acidified with 6M HCl ($250\mu\text{l/sample}$ for 60 ml samples and 4ml/sample for each 1 liter sample).

4.5.4 Summary of water collected

	Leg 1	Leg 2	Total
5 liter (Rosette)	387	580	967
10 liter (Rosette, Fish)	186	174	360
20 liter (Rosette, Fish)	57	65	122
1 liter Colloids (CFF Permeate/Retentate)	50	72	122
60 ml Anapore Colloids	24	36	60

4.5.5 Monocore sediment samples

We were very successful coring on this cruise. Seventeen of 20 deployments (before Station 39) were successful. Core lengths ranged from 7cm to 25 cm. On Leg 1, John Calderwood was very helpful with making modifications to the cloaking device that made the corer virtually invisible to the altimeter mounted on the rosette. On two occasions, the line that attached the corer to the rosette was in disarray n recovery; once preventing two bottles from closing properly.

Mistakenly, the new 25 meter line for attaching the corer to the rosette was made with a “floaty” rope, Amsteel Blue. To keep this from happening multiple shackles were tiwrapped to the line along it’s length to ensure that the line sank during the coring process at the seafloor.

Clear changes in lithology and sediment sources are visible in the suite of cores collected.

4.6 Total ^{234}Th (Particulate and Dissolved) Collection and Analyses

PI: Ken Buesseler, Woods Hole Oceanographic Institution

Shipboard collection and analyses: Jennifer Kenyon and Steven Pike, Woods Hole Oceanographic Institution

Total ^{234}Th samples were collected at all stations. For shallow depths, typically less than 1000 m, total ^{234}Th samples were collected from the PigRaTh (pigments, radium, and thorium) cast and the Demi ODF cast where applicable. For deeper depths, seawater was collected from 30 L Niskins incorporated into the McLane pump casts at depths that coincided with pump depths. In the event where 30 L Niskins on the pump casts miss-tripped, samples were collected from the corresponding depths during the appropriate intermediate and/or deep ODF casts. Typically, 13 water depths were collected during shallow ODF casts and 8 water depths collected per pump cast. Shallow cast seawater samples were collected at depths that coincided with the 8 shallow pump depths, as well as 4 additional depths selected on the basis of interesting features observed on the station's CTD data. Intermediate fish seawater samples were also collected for total ^{234}Th analyses.

Seawater samples were collected into approximately 2 L FLPE Nalgene bottles from each Niskin. Each sample was spiked with 1 mL of a 50.03 dpm/g ^{230}Th standard for future recovery calculations. Total ^{234}Th was precipitated via additions of KMnO_4 and MnCl_2 onto QMA filters. Precipitate samples were counted onboard using RISØ Laboratory anti-coincidence beta counters for preliminary first and second counts, with third counts to be completed onshore. Total ^{234}Th samples will be coupled with particulate ^{234}Th data (as well as other particulate trace metal and isotope data) in order to produce flux calculations. In summary, 701 total ^{234}Th , 392 small-size fraction (<51µm) particulate ^{234}Th , and 392 large-size fraction (>51µm) particulate ^{234}Th samples were collected and processed onboard. See section on pump operations for more detail on particulate analyses.

4.7 Ra Isotopes

PIs: Matt Charette and Willard Moore

At Sea: Paul Henderson (leg 1) and Emilie Le Roy (leg 2)

4.7.1 Surface sampling for Ra isotopes

At all GEOTRACES and Repeat Hydrography stations, ~1500 L of surface water was collected and filtered through Mn-oxide coated acrylic cartridges to collect Ra isotopes. In total, 36 samples were collected. Water was collected using a Surface pump with tubing deployed over the port side of the R/Vf Roger Revelle to ~3 m depth. At sea, these surface samples were processed in a similar manner to the MnO_2 pump cartridge samples. They were analyzed for short-lived Ra isotopes on the ship-board RaDeCC systems by Paul Henderson and Emilie LeRoy.

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

MnO_2 -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. ^{224}Ra ($t_{1/2} = 3.7$ d) and ^{223}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 Paul Henderson and Emilie LeRoy. 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 ^{226}Ra , 20–25 L seawater was passed over a column of MnO_2 impregnated acrylic fiber on deck, which removes radium at 100% efficiency. These filter samples were bagged and will be analyzed for ^{226}Ra through its daughter, ^{222}Rn back in land-based laboratories. Efficiency filter samples were collected by Jennifer Kenyon and processed by Paul Henderson and Emilie LeRoy.

4.8 Dissolved Cobalt and Underway Proteomics

PI: Mak Saito

At sea: Rebecca Chmiel

Shipboard analysis of dissolved total cobalt (samples were UV irradiated prior to analysis) and dissolved labile cobalt (samples were not UV irradiated) was performed by Rebecca Chmiel. Duplicate 60 mL samples were collected in acid-washed LDPE bottles using the GEOTRACES trace-element rosette and the trace-element clean towfish. Samples were filtered using a 0.2 μM Acropack filter. One duplicate was run within 3 days of collection for shipboard dissolved cobalt analysis, and the other duplicate was kept in an oxygen depleted sealed container for future verification and analysis. Dissolved cobalt was measured using a hanging mercury drop electrode following the cathodic stripping voltammetry method outlined in Saito et al. 2001. In total, 1042 dissolved cobalt samples were analyzed during the cruise: 719 dissolved total cobalt samples from 36 stations and 323 dissolved labile cobalt samples from 22 stations. At least one intra-laboratory seawater standard was run once per day and at least one D1 and GSC 2 GEOTRACES intercalibration standard was run once per week during shipboard analysis. Triplicate technical replicates were run on every sample to determine the precision of the method, and duplicate depths from different rosette casts were run when available. Blank analysis was completed with each new batch of reagents, and the blanks were found to be within acceptable limits of <10 pM.

Filtered particulate samples for proteomic and genomic analysis by the Saito lab were collected from the underway seawater system by Rebecca Chmiel. Particulate samples were first filtered through a 51 μm Nitex filter (not collected). Samples were collected first onto a 3 μm Versapore filter and then onto a 0.2 μm Supor filter. The volume of seawater filtered varied between 15 L and 58 L, depending on the oligotrophy of the seawater. Both size fractions of filter were sub-sampled into proteomics samples and DNA samples, with 1/8 of the filter collected for DNA analysis and 7/8 of the filter collected for proteomic analysis. Samples were stored at -80°C . 100 particulate samples were taken in total from 25 stations, including all full and super stations.

4.9 Ultrafiltration/Colloids

PI: Jessica Fitzsimmons

At sea: Janelle Steffen

Two ultrafiltration methods were used to separate the truly dissolved, “soluble,” metal fraction from the colloidal fraction in various samples: 1) a cross flow filtration system (Pellicon XL) and 2) a membrane filtration system (Anodisc). All membrane filters had a pore size of 20 nm, while two separately sized cross flow filters had pore sizes of 3 nm (10 kDa) and 9 nm (300 kDa), respectively. Ultrafiltered samples from all three systems, along with the $<0.2\ \mu\text{m}$ dissolved samples collected using the GTC rosette, will be analyzed in the Fitzsimmons laboratory at Texas A&M University using ICP-MS techniques for Fe, Mn, Cu, Cd, Zn, Ni, Pb, and Sc concentrations. The four size fractions will then be analyzed together from a single depth to reveal the relative contributions of small (3-9 nm), medium (9-20 nm), and large (20-200 nm) colloids to the dissolved metal fraction. In addition to the analysis at Texas A&M, the total dissolved concentrations ($<0.2\ \mu\text{m}$) from super stations will be measured by Claire Till (Humboldt State University) using a separate, non-isotope dilution, multi-element method for intercalibration.

858 total dissolved ($<0.2\ \mu\text{m}$) 250 mL samples were collected from the GTC rosette. Additionally, 702 x 60 mL samples were collected through the Anopore membrane system ($<20\ \text{nm}$). 594 x 60 mL samples were collected through the 10 kDa cross-flow filtration system (3 nm) - one permeate 60mL bottle and one retentate 60mL bottle from each of 297 sampling depths. 342 x 60 mL samples were collected through the 300 kDa cross-flow filtration system (9 nm)—again, one permeate 60 mL bottle and one retentate 60 mL bottle from each of 171 sampling depths.

In addition, ultrafiltered samples were provided collaboratively to several other groups. 206 x 500 mL total dissolved ($<0.2\ \mu\text{m}$) samples were collected from the GTC rosette for Claire Till for the intercalibration of total dissolved concentrations for Fe, Mn, Cu, Cd, Zn, Ni, Pb, and Sc mentioned above. 52 x 60 mL Anodisc filtered ($<20\ \text{nm}$) seawater samples and 102 x 1 L cross flow filtered ($<3\ \text{nm}$) samples from the super stations were provided to Marty Fleischer and Bob Anderson (Lamont-Doherty Earth Observatory) to calculate the partitioning of Th isotopes into soluble and colloidal fractions. 48 x 1 L cross flow filtered ($<3\ \text{nm}$) samples were provided to Seth John (University of Southern California) for measurement of Ni and Cu isotopes. 122 x 1L cross flow filtered ($<3\ \text{nm}$) samples were provided to Tim Conway (University of South Florida) 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.

Lastly, 168 x 500 mL dissolved ($<0.2\ \mu\text{m}$) samples were provided to Laramie Jensen (Fitzsimmons lab, Texas A&M), 122 x 500 mL dissolved ($<0.2\ \mu\text{m}$) samples were provided to Randie Bundy (University of Washington) and Kristen Buck (University of South Florida), and

57 x 500 mL dissolved (<0.2 μ m) samples were provided to Matt Hurst (Humboldt University) for measurement of organic Fe-binding ligand concentration and strength by electrochemistry.

4.10 Trace element organic speciation (“Ligands”)

PI: Daniel Repeta, WHOI

At sea: Lydia Babcock-Adams (Leg 1), Jingxuan Li (Leg 2)

We processed water and particulate matter along the GEOTRACES meridional transect for molecular analyses of trace element organic matter. Water from the GEOTRACES trace metal clean rosette and underway “fish” system was filtered, and the filtrate pumped through extraction cartridges. 4 L of filtered (Acropak 0.2 μ m for rosette) seawater is collected into PC bottles (acid-cleaned but re-used). Dissolved ligands are concentrated from seawater using solid phase extraction onto hydrophobic and hydrophilic resins. Twelve samples from a cast are processed at the same time. The samples are pumped through the ENV (polystyrene based, for moderately nonpolar and nonpolar ligands) cartridge to a second set of bottles. For some casts, these samples are acidified to pH 2 and pumped back through the ENVI-Carb column (graphitized non-porous carbon packing, for very polar ligands) into the original sample bottles to be discarded. Approximately 1000 ENV column, and 300 ENVI-Carb column are loaded with samples. These cartridges were frozen and returned to our laboratory for mass spectral analyses.

In addition, we collected particulate matter from the ODF Niskin rosette that will be used for companion genomic analyses. We also collected samples for ligands in the particulate phase, in collaboration with the pump team. Finally, we collected large volume particulate and dissolved organic matter from the ship’s underway seawater system to collect material for targeted organic matter analyses. Once the samples are returned to our laboratory, we will extract the organic matter, recover the organic compounds by washing the cartridges with methanol, and measure the distribution of iron, copper, and other trace elements using inductively coupled mass spectrometry. Samples will then be screened by high resolution electrospray ionization mass spectrometry and the two datasets merged to identify each iron, copper, or other trace metal compounds. The distribution of trace metal organic complexes will be assessed in relation to the physical and biological features that characterize the sampling region.

On Leg 1, approximately 351 GTC samples, 162 ODF samples, and 16 Fish samples were collected (see table). In addition, 4 incubations were conducted. On Leg 2, 440 GTC samples, 246 ODF samples, and 20 Fish samples for ligands were processed on board. 3 incubations (water taking from unfiltered fish) were also conducted, and 117 Pump filters (provided by pump team) were collected.

Table of organic ligand samples collected from towfish on GP15

Fish samples Station	4L Ligands (filtered)	4L Genomics (unfiltered)	20L Ligands (filtered)	Incubation (unfiltered)	20L for culture work at WHOI	Fish samples Station	4L Ligands (filtered)	4L Genomics (unfiltered)	20L Ligands (filtered)	Incubation (unfiltered)
1	y					Loihi				
2	y					19	Y	Y	Y	
3	y	y				20	Y	Y	Y	
4	y	y				21	Y	Y	Y	
5	y			y		22	Y	Y	Y	
6	y	y		y		23	Y	Y	Y	
7						24				
8	y	y		y		25	Y	Y	Y	
9	y					26				
10	y	y	y		Y	27	Y	Y	Y	
11	y		y			28	Y		Y	
12		y	y			29	Y	Y	Y	Y
13	y		y			30	Y		Y	
14	y	y		y		31	Y	Y	Y	
15	y		y			32	Y		Y	
16	y	y	y			33	Y	Y	Y	Y
17	y		y			34	Y		Y	
18	y	y	y			35	Y	Y	Y	
						36	Y		Y	
						37	Y	Y	Y	Y
						38	Y		Y	
						39	Y			

4.11 Helium isotopes

PI: William Jenkins

At sea: Kevin Cahill (Leg 1), Zoe Sandwith (Leg 2)

Helium samples were collected from every station and every depth from the ODF Shallow, Intermediate, and Deep casts. A sample was also collected at every surface niskin of the ODF PigRaTh casts. There were a total of 891 discrete samples collected. Almost all were collected in duplicate, save for 6 samples where 1 of the 2 duplicates was compromised during sealing.

Sampling method:

Samples were collected using the copper tube method. In this method 2 ~45" sections of tygon tubing is attached to a 29.5" section of 5/8" soft copper refrigeration tubing (Cambridge-Lee Industries, LLC) that has been straightened, sectioned, deburred, and marked into 2x12" sections with 2.75" spare length at each end. Both sections of tygon tubing have a clamp placed ~18" from the copper tube. While flushing with sample water, the copper tube is thumped with a bat to remove bubbles from the walls of the tube. After flushing roughly 1 liter of water through them, the clamps are closed. The sample filled copper tube is then cut into the 2 predefined 12" lengths using pneumatic jaws. This means that each sample is collected in duplicate. The samples are then rinsed and cleaned thoroughly with fresh water to inhibit corrosion on the copper surface during storage.

Samples will be analyzed at the Helium Isotope Lab at Woods Hole Oceanographic Institution.

4.12 ^7Be

PI: David Kadko

At sea: Mark Stephens

Samples of seawater, aerosols and particles were collected for ^7Be analyses. Seawater was sampled at all full stations and superstations (20 Be-7 casts, 118 seawater samples total). Water for ^7Be was pumped into vertical tanks on deck (600-700L) with a centrifugal pump and 1.5 inch pvc hose. Typically six depths were sampled per station, up to a maximum depth of 130m. A profiling CTD (Seabird 19plus) was attached to the hose inlet to determine exact depths. The water was then pumped out of the barrels through Fe-coated acrylic fibers. 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 at FIU. In order to expedite analysis of Be-7 (half life 53 days), samples from leg 1 (RR1814) were shipped to Miami from Hawaii at the midpoint of the cruise.

4.13 ^{210}Pb — ^{210}Po

PIs: J. Kirk Cochran and David Kadko

At sea: Mark Stephens

We are measuring the activities of the natural radionuclides ^{210}Po and ^{210}Pb in water and particulate samples. Water samples of ~10L were taken, filtered through Acropak filters and acidified to pH ~2. Further processing was completed on board as follows: ^{209}Po , stable Pb and Fe were added, and Po and Pb were co-precipitated with $\text{Fe}(\text{OH})_3$ by raising the pH to ~8 with NH_4OH . The precipitates were filtered and subsequently dissolved in HCl. Po isotopes were plated onto silver disks for return to the laboratory and determination of the alpha activity of ^{210}Po . In addition, particulate samples were taken by P. Lam and Y. Xiang using in situ pumps deployed at the same depths as the water samples. Aliquots of the filters were returned to Cochran's laboratory for analysis on shore. The following stations were sampled by us:

Leg	Station	Number of Depths
1	1	5
“	3	9
“	8	25
“	14	25
“	18	17
“	18.3 (Puna Ridge)	8
2	18.6 (Loihi)	4 (8 samples, filtered & unfiltered)

“	21	17
“	23	25
“	29	25
“	35	25
“	39	25

4.14 Methane

PI: Alan Shiller – University of Southern Mississippi
At sea: Laura Whitmore (leg 1), Virginie Sanial (leg 2)

4.14.1 Continuous surface seawater methane analysis

Dissolved methane concentration was continuously measured at the surface (~ 5m) using the ship's seawater intake. 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 methane concentration was also measured regularly. Typically, equilibrated air was measured for 120 minutes, then bow air measured for 10 minutes. The exception to this pattern was when we were on station, only equilibrator air was measured as contamination from the ship is more likely for the bow air. These measurements, combined with ship windspeed data, were used to make flux estimates for the section (Fig. 4.14-1).

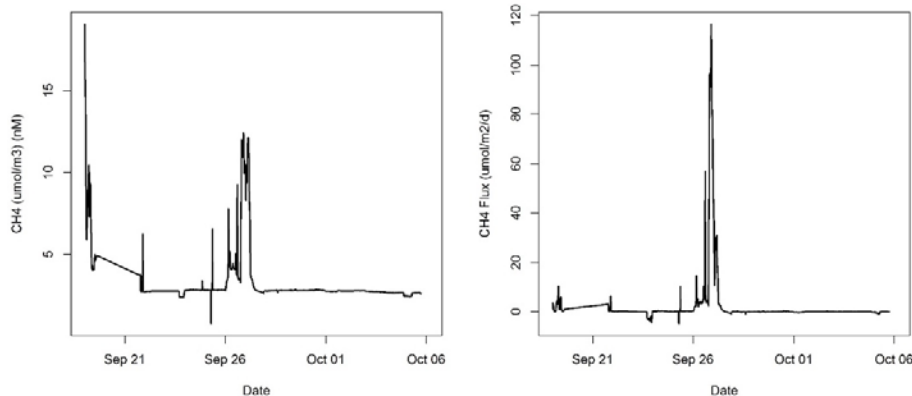


Figure 4.14-1. Methane concentrations of surface waters from September 16th to October 6th (Panel A). Concentration data are paired with atmospheric measurements and ship MET data to calculate flux (Panel B). Note that the data are preliminary and have not been QA/QC'd.

The continuous system was calibrated by regularly measuring air standards with different methane concentrations. Additionally, several discrete seawater samples were collected from the ship's flow-through and run separately following the discrete analysis method (see below) to validate the methane concentration from the continuous system. Discrete samples from surface Niskin bottle (5 m) were also compared to the continuous system (Fig. 4.14-2).

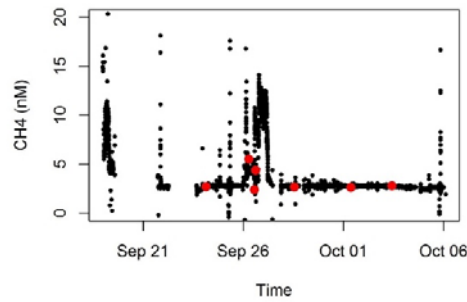


Figure 4.14-2. Comparison of discretely collected surface samples from the <5 m Niskin bottle (red dots) to underway system measurements.

4.14.2 Water column discrete methane analysis

Seawater samples were collected from the ODF rosette to determine dissolved methane concentration throughout the water column. This method involves seventy-milliliter samples collected into 140-mL syringes with 3-way gas-tight Luer-Lock valves. Samples were prepared for head-space equilibration by adding 70 mL methane-free gas to the sample syringe. Samples were equilibrated for approximately 30 minutes. The equilibrated headspace was then measured on a Picarro methane analyzer (G2301).

The Picarro methane analyzer for measuring the discrete samples was calibrated the same way as the continuous system, i.e. by frequently measuring air standards of different methane concentration. In addition, ship intake underway samples were collected in triplicate to check the reproducibility. Three samples were collected in duplicate from the Niskin bottles (at stations 21, 33, and 39) as well.

Partial (demi stations) or full (full and super stations) depth profiles were collected at stations 1 to 39 from the ODF rosette. Samples were also collected from the underway seawater sinks in conjunction with the intermediate fish (surface samples) at 42 stations. During leg 2, additional samples were collected from the ODF PigRaTh cast and compared to the ODF shallow cast to provide information on temporal variability of methane concentration in surface and subsurface waters (Fig. 4.14-3). In total, 1234 discrete seawater samples were collected and processed aboard ship (including replicates).

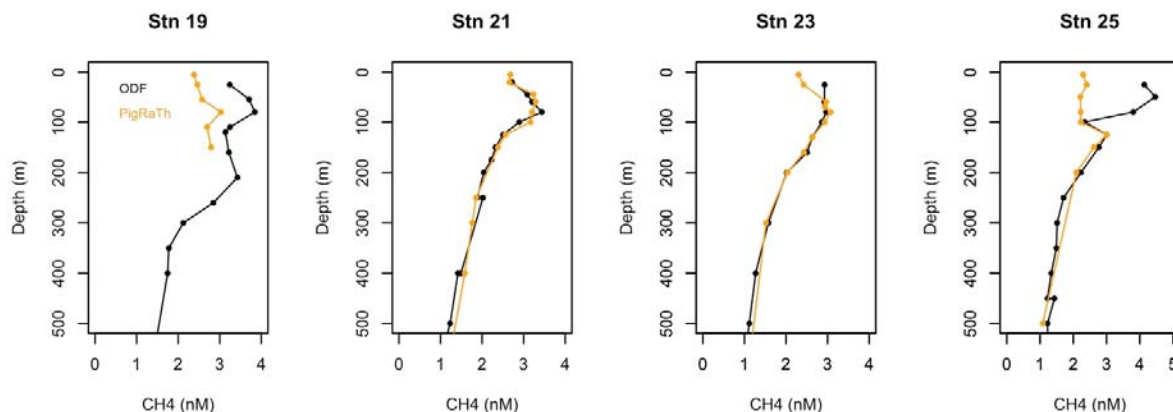


Figure 4.14-3. Example of vertical profiles of dissolved methane concentrations measured on samples collected from ODF shallow cast and PigRaTh cast.

Preliminary results show that methane concentrations and shape of the vertical profiles agree well with other published oceanic methane data. There is a broad methane enrichment in the first 300 m of the water column associated to productivity. Then, the methane concentration decreased with increasing depth (Fig. 4.14-4). Lower methane concentrations are observed south of the Equator. High methane concentrations (up to 27 nM) were measured over the Alaska shelf (Fig. 4.14-4), as well as at the bottom of station 18.6 (Loihi station) showing a potential hydrothermal methane signal.

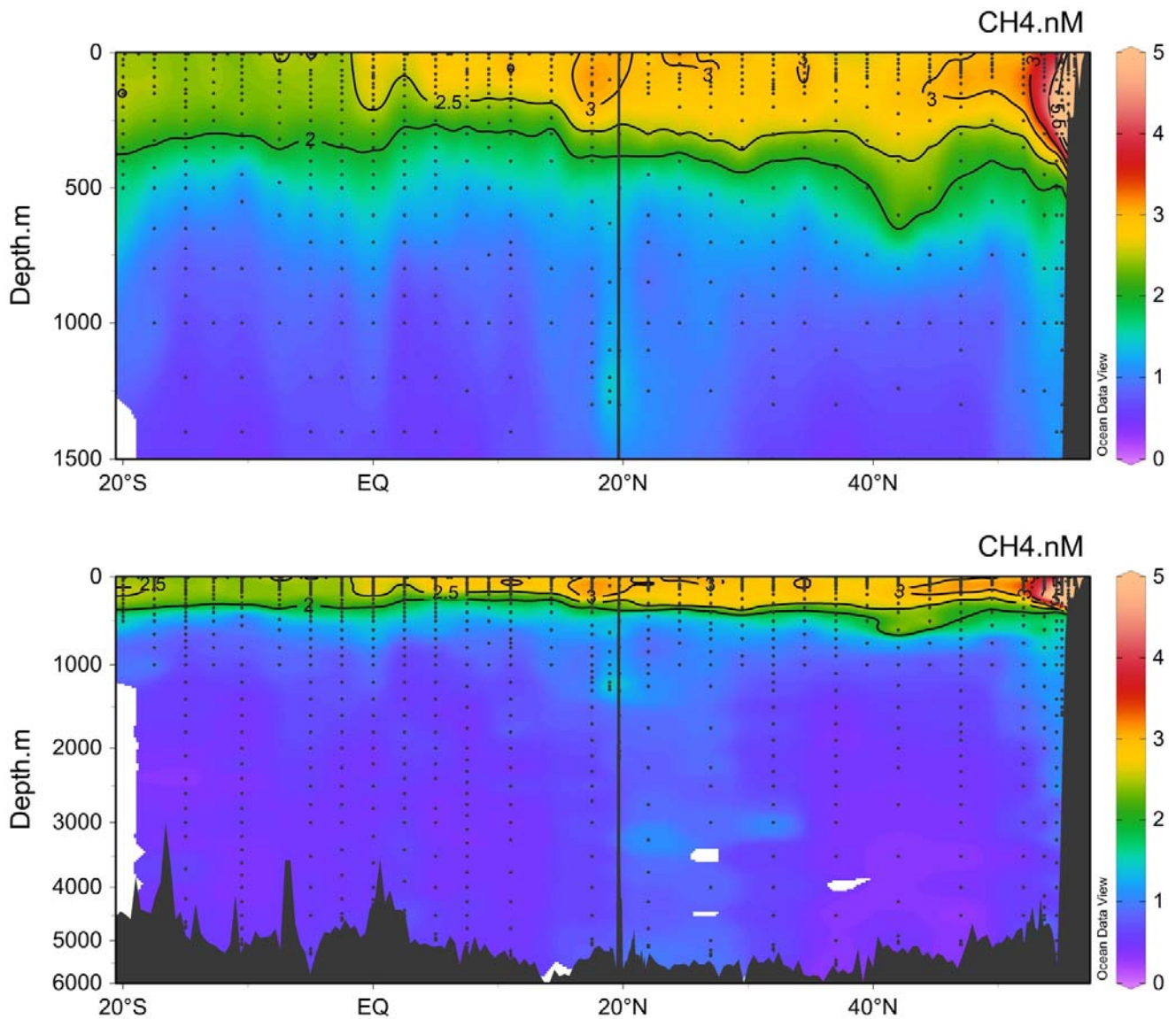


Figure 4.14-4. GP15 section of methane concentration from Alaska to Tahiti. Note, that the data need to be QA/QC'd

4.15 DIC and dissolved gases

4.15.1 Dissolved Inorganic Carbon Isotopes (C. Stump)

Dissolved Inorganic Carbon ($^{13}\text{C}/^{12}\text{C}$, ^{14}C) samples (for Quay lab) were collected at 34 stations (Repeat Hydrography and Geotraces stations). There were 91 total ODF casts sampled and a total of 988 DIC samples were taken from those ODF casts. Station 1 and 2 and the two test stations were not sampled. In addition 32 DIC samples were collected from the underway seawater line as a comparison with surface seawater from the ODF Pigrath (pigment, radium, thorium) cast.

All samples were 250 mL total volume and were poisoned with 100 μL HgCl_2 . A total of 1010 DIC-isotope samples were collected throughout the duration of the cruise. Samples will be processed at University of Washington and other institutes.

4.15.2 Dissolved Gases (N_2/Ar) (C. Stump)

250 ml dissolved gas samples were collected for Paul Quay at 32 stations from either the ODF Pigrath (pigment, radium, thorium) cast or from a surface seawater Niskin on demi stations. A 6 – 8 sample profile was done on the 20 Pigrath casts comprising depths from the surface to 200 meters. In addition 30 N_2/Ar samples were taken from the underway seawater line as a comparison with surface seawater from the ODF Pigrath (pigment, radium, thorium) cast. In addition 35 duplicate O_2 samples were collected at the same time from the underway seawater line, also as a comparison to the surface seawater from the ODF Pigrath cast.

All samples were 250 mL total volume and were poisoned with 100 μL HgCl_2 . A total of 193 N_2/Ar samples and 70 O_2 samples were collected throughout the duration of the cruise. Samples will be processed at University of Washington and other institutes.

4.15.3 Underway Gas and Nutrient Sampling (C. Stump)

During the length of the cruise, both a MIMS Prisma Plus(membrane inlet mass spectrometer) quadrapole mass spectrometer and a Picarro G2131-i cavity-ring-down laser system were continually run using the underway seawater line and a Weiss-type equilibrator was used to generate an equilibrated headspace to sample the water. A reverse flow column of N_2 gas was used to dry the sampled headspace before entering the two analyzers. A script allowed for seven hours of sampling. After each seven hours, a Valco valve switched to either deck air collected from the bow of the ship or an air standard. Each was analyzed for one hour. The MIMS mass spectrometer read the ion currents of oxygen, nitrogen, argon and the real-time O_2/Ar data. The Picarro G2131-i read the concentrations of pCO_2 , $\delta^{13}\text{C}$ of dissolved CO_2 and CH_4 . In addition an Aanderaa Optode was placed in a container being overflowed with the underway seawater. Once a day the Optode was air calibrated for one hour. A fluorometer was also in line with the underway seawater as well as a SUNA nitrate analyzer. The SUNA nitrate analyzer was only employed from 56N to 35N and from 5N to 5S.

4.16 Shipboard analysis of Dissolved Al, Fe, and Mn

Dissolved Al, Fe, and Mn (dAl, dFe, and dMn) samples were obtained from the GEOTRACES trace metal rosette equipped with 24 Teflon-coated, 12L General Oceanic GO-FLO bottles. The University of Hawaii group (Hatta and Weiss) performed shipboard determinations on 0.2µm Acropak filtered subsamples from these bottles taken by the subsampling team. Subsamples were collected into 125mL acid washed PMP bottles and acidified to 0.006M HCl and microwaved for 58 seconds/125mL of sample. These samples were subsequently analyzed shipboard for dissolved Al, Fe, and Mn using flow injection analyses (Resing and Measures, 1994; Measures et al., 1995; Resing and Mottl, 1992 respectively). A total of 846 trace metal samples were collected at 41 GEOTRACES water column stations (including two test stations). This total includes the surface samples collected by the GEO Tow Fish, which collected surface seawater at a nominal depth of 5m. The surface samples collected by tow fish were also filtered through a 0.2 µm Acropak filtered and acidified and microwaved as described above. Additionally, 47 samples were obtained from the ODF rosette at the Puna (station 18.3), Loihi (station 18.6) and one superstation (station 35) and were also filtered through a 0.8/0.45µm Acropak 500 capsule filter. The precision of each of the methods was determined by replicate determination of the same sample at the beginning of the day's run, with typical values of 1.5% for Al at 2.8nM; 1.8% for Fe at 1.4nM, and 0.9% for Mn at 1.3nM.

Dissolved Al, Fe, and Mn concentrations were determined from samples obtained from both the GEOTRACES and ODF rosettes at the Puna and Loihi stations for comparison. The preliminary concentrations of dAl and dMn were comparable between the two rosettes; however, dFe concentrations were slightly higher for the samples from the ODF rosette compared to the ones from the GEOTRACES rosette. We did see the differences between the cast, which could be temporally variable between the two casts. Elevated dFe and dMn value were seen in the vicinity of the shelf stations (stations 1 & 2) and in the vicinity of hydrothermal activity at 1100-1300 m at the Puna (station 18.3) and at Loihi (station 18.6). Elevated dAl value was seen in the EUC (station 29) and in the mixed layer between 27°N to 2,5°N. Also, elevated dAl were seen in the deep-water value (below 4000m depth) from 27°N to the south.

4.17 Hydrogen Sulfide

PI: Gregory Cutter, ODU

At Sea: Nicole Buckley (ODU graduate Student)

Samples of 0.2 µm-filtered water from the GTC system and tow-fish pump, and particles from the McLane pumps were collected for sulfide analyses. ODU graduate student, Nicole Buckley, made shipboard measurements on sulfide speciation and pH at 34 stations. In total, she analyzed over 1,000 samples for total dissolved sulfide (TDS), free (uncomplexed) sulfide, particulate acid volatile sulfide (pAVS), and pH.

Approximately 425 total dissolved sulfide samples were collected and measured in duplicate or triplicate analyses. Concentrations of TDS were higher on the shelf and slope stations, typically between 75-150 pM through station 5, with station 2 having greater concentrations between 150-

250 pM. The water column TDS concentrations decreased as we transited south. Most stations had concentrations that did not exceed 50 pM.

Approximately 250 pAVS samples were measured in single analyses of Supor filters supplied by the Pump/Lam group. Particulate acid volatile sulfide concentrations were greatest near the shelf and decreased as we proceeded southward. In the open ocean water column the greatest pAVS concentration rarely exceeded 3 pM. Approximately 250 samples of QMA filters from the McLane pumps were placed in heat-sealed Tedlar bags with oxygen scrubbers and stored at -80°C. These will be returned to the ODU lab via a LN2 dry shipper for subsequent determinations of particulate chromium-reducible sulfur (pCRS, typically $\text{FeS}_2 + \text{CuS}$).

Approximately 350 pH samples were collected and were typically measured in single analyses using the spectrometric method of Carter et al. (2013). Based on preliminary calculations, the pH values tabulated from Leg 1 are close to the values that were collected along 152°W in the North Pacific in 2006 and reported by Byrne et al. (2009).

References

- Carter, B. R., Radich, J. A., Doyle, H. L., and A.G. Dickson. 2013. An automated system for spectrophotometric seawater pH measurements. *Limnol. Oceanogr.: Methods*, 11: 16-27.
- Byrne, R. H., Mecking, S., Feely, R. A., and Xuewu Liu. 2009. Direct observations of basin-wide acidification of the North Pacific Ocean. *Geophys. Res.*, 37, L02601, doi: 10.1029/2009GL040999, 2010.

4.18 Biogeotraces

PIs: Dreux Chappell, Paul Berube, Sophie Clayton, Ginger Armbrust, Benjamin Twining

At sea: Sveinn Einarsson

Single cell preservation samples and DNA samples were collected at all tow-fish sampling points, arriving and intermediate points, and from the DCM at full and super stations. DCM samples were collected from the ODF CTD. Single cell preservation samples were preserved and frozen (-80) and DNA samples were collected by filtering seawater through sterivex filters (6 liters/per filter for tow-fish sample, ~4.5 liters/filter for DCM samples). DNA preservation solution was added to sterivex filters and frozen (-80). 313 total single cell preservation samples were collected and 158 total sterivex filters were collected. Samples will be analyzed at Old Dominion University (Chappell and Clayton), Massachusetts Institute of Technology (Berube), and the University of Washington (Armbrust).

SeaFlow flowcytometer was sampling at all times when the ship flow through system was turned on. Data generated will be analyzed at UW (Armbrust).

Samples for Synchrotron X-ray Fluorescence (SXRF) and were collected at 8 vertical profile stations. Unfiltered water samples were taken for SXRF analysis from tow-fish. Samples were preserved with 0.25% trace metal clean buffered glutaraldehyde and centrifuged onto C/formvar-coated Au TEM grids. Stations 4,6,8 and all super stations were sampled for SXRF, and samples will be analyzed at Bigelow (Twining). Total of 32 SXRF samples were collected.

4.19 Shipboard determinations of dissolved Zinc (dZn)

PI: Gregory Cutter, ODU (management grant)

At Sea: Lisa Oswald, ODU

Samples were collected from the trace metal clean rosette at stations 1, 2, 5, 6, 10, & 12 for shipboard zinc determinations. All samples were filtered (0.2 µm AcroPak Supor), acidified (0.024 M q-HCl) and then analyzed shipboard for dZn using analysis using a Lab-on-Valve, GlobalFIA MiniSIA-2 analyzer and FloZF software, as described in Grand *et al.* (2016). Data generated onboard served primarily to validate the sample collection methods by highlighting any potential contamination sources in near real-time. Samples were collected from all bottles in a given cast to access bottle replicates. While the MiniSIA-2 provides excellent precision (generally better than 1% RSD), the accuracy was in question. The preconcentration column necessary to quantify sub-nanomolar dZn measurements suffered from breakthrough at higher concentrations, making it difficult to quantify a profile of samples without multiple calibration curves. Ultimately, the precision of the system made it a good tool for assessing GO-FLO bottle contamination, but the method will need some revision to be useful for accurate sample quantitation in a timely manner.

References:

Grand, M.M., Chocholous P., Ruzicka J., Solich P., and Measures, C.I. 2016. Determination of trace zinc in seawater by coupling solid phase extraction and fluorescence detection in the Lab-On-Valve format. *Anal Chim Acta*, 923: 45-54

4.20 Nanomolar-level nutrient analyses

PI: Gregory Cutter, ODU (management grant)

At Sea: Lisa Oswald, ODU

Samples were collected from the uppermost 4 depths of the trace metal clean rosette and from the trace metal clean fish beginning at Station 25. Samples were held until ODF analyses determined whether the nutrient concentrations were below their detection limit of 0.02 nM. All samples were filtered (0.2 µm AcroPak Supor) into acid-cleaned 25 mL scintillation vials then refrigerated until analysis. Samples were to be analyzed on an Astoria-Pacific Segmented Flow Analyzer using World Precision Instruments Waveguides as detector cells with three channels: PO₄, NO₂, and NO₃+NO₂. Instrument issues were ongoing, including the x-y autosampler, the waveguides, and the peristaltic pump and Lisa was unable to complete the analyses.

4.21 Outreach

PI: Phoebe Lam, UCSC (management grant)

At Sea: Alex Fox

As part of the management grant, we hired a professional freelance science writer, Alex Fox, to be in charge of outreach for the cruise. Fox assisted in the creation of the GP15 website and social media accounts (Twitter, Facebook, and Instagram) in collaboration with the management team.

Per the statement of work, Fox created daily social media posts, weekly in depth blog posts, and conducted outreach to gain media coverage for the expedition. Fox created multimedia content (photos and video) to furnish social media accounts and to provide collateral materials for the cruise and its researchers.

Social media:

1. Instagram: 85 posts, 251 followers
2. Twitter: 331 followers
3. Facebook: 269 page likes

Blog:

10,382 page views; 2,523 visitors; 15 posts

1. The journey begins...almost! - By Karen Casciotti
2. Packing time! - By Karen Casciotti
3. Loading up and shoving off
4. What is GEOTRACES?
5. What's up with GP15?
6. Paperclips and duct tape
7. Not that kind of cruise: a GEOTRACES glossary
8. The North Pacific's "shadow zone" traps the oldest water in the ocean
9. 3 photo galleries from leg 1
10. Deep sea mining appears on GP15's radar
11. Super Station, Super Techs – part 1
12. Super Station, Super Techs – part 2
13. GUEST POST - Teamwork makes the dream work: the Scripps technicians of GP15 - By Melissa Miller edited by Alex Fox
14. Women in Oceanography
15. GP15 by the numbers

Coverage:

News stories from UC Santa Cruz, Stanford University and University of Hawaii.