SOCCOM Technical Report Series

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SOCCOM Biogeochemical Profiling Float Deployments from GO-SHIP P16S

Ship and Expedition ID: RVIB Nathaniel B. Palmer NBP1403

Dates: 20 March 2014 – 5 May 2014

Cruise identifier (CCHDO, CDIAC and SOCCOM): 320620140320

Technical Report 2014-1

National Science Foundation (EAGER) Polar Programs PLR-1353103 (UW) and PLR-1353177 (MBARI); ONR NOPP N00014-09-10052; U.S. Argo Program NOAA NA17RJ1232 Task 2; David and Lucile Packard Foundation.

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P16S (N.B. Palmer NBP1403): Argo and Argo-equivalent biogeochemical floats.

Principal investigators: Ken Johnson (MBARI) and Stephen Riser (U. Washington).

Report contributions also from Lynne Talley (SIO) and Tyler Hennon (U. Washington).

Float funding sources: NSF DPP (Eager grant) and NOPP

15 May 2014

Table 1. Deployment and profile Information as of 14 May 2014

	Float ID	P16S Sta. #	WMO number (Argo)	Equipped Sensors*	Reporting Sensors*	Deploy-ment date (UTC)	Lat.	Lon.	Days/ cycle	Max p	Number of profiles 5/11/14
1	6091	1	5904179	IONF	OF	26/03/2014	60 0.0 S	173 57.8 E	10	2000	5
2	7557	2	5904181	IONF	ONF	28/03/2014	63 29.27 S	176 00.66 W	10	1500	5
3	7567	3	5904182	IONF	OF	30/03/2014	65 41.17 S	161 55.34 W	10	1800	2 (4/21 most recent**)
4	7613	4	5904180	IONF	ONF	31/03/2014	66 30.64 S	155 59.47 W	10	1600	2 (4/11 most recent**)
5	7614	5	5904183	IONF	ONF	01/04/2014	67 00.82 S	149 59.97 W	10	1600	3 (4/22 most recent**)
6	9091	11	5904184	IONFp	ONFp	03/04/2014	63 59.55S	150 01.36 W	10	1400	4
7	9092	17	5904185	IONFp	ONFp	07/04/2014	59 59.54 S	150 01.18 W	10	1600	4
8	9031	27	5904396	ONFp	ONFp	11/04/2014	55 0.34 S	150 01.04 W	5	1500	7
9	9018	32	5904186	Op	Op	13/04/2014	52 29.33 S	150 0.61 W	5	1600	8
10	9095	37	5904188	ONFp	ONFp	14/04/2014	49 59.23 S	149 59.44 W	5	1600	6
11	9101	45	5904187	Op	Op	18/04/2014	44 58.43 S	149 59.55 W	5	1700	5
12	9254	53	5904395	ONFp	ONFp	20/04/2014	39 39.40 S	149 58.96 W	5	1600	5

*Sensors: I = ice enabled (software) O = oxygen N = nitrate F = FLbb p = pH

** Most likely ice-covered thereafter, will report after emerging from ice

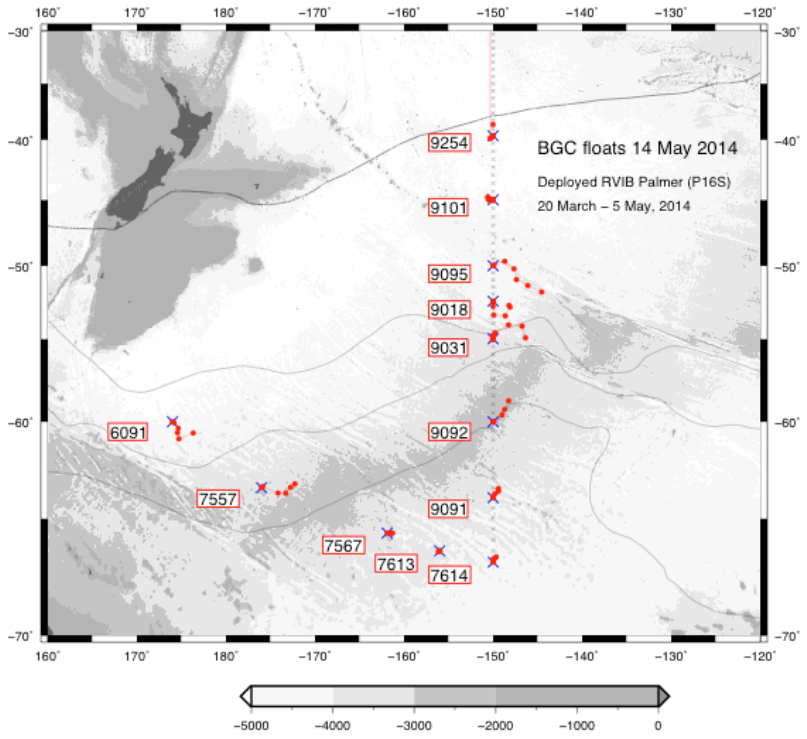


Figure 1. RVIB N.B. Palmer (NBP1403) float deployment locations and subsequent tracks (red), with P16S CLIVAR stations (black x's) (20 March – 5 May, 2014). Float ID numbers are listed in Table 2; WMO numbers for access to data on the Argo servers are listed in Table 2. Light curves are the standard Orsi fronts (subtropical, subantarctic, polar and southern boundary, from north to south). The Ross Sea lies south of the southern boundary, and sea ice has already advanced over the southernmost 3 floats.

Table 2. Float and calibration data servers

Server	url	Purpose
U. Washington Argo float server	http://runt.ocean.washington.edu	U.W. float summaries, diagnostics, engineering data, profiles
Floatviz (MBARI)	http://www.mbari.org/chemsensor/floatviz.htm	Float profile data including all sensors, quality controlled data
U.S. GODAE Argo GDAC	http://www.usgodae.org/argo/argo.html	Real-time and delayed-mode Argo data server (U.S.), high resolution T/S
JCOMMOPS Argo data server	http://argo.jcommops.org/ (links to US GODAE for data access)	Real-time and delayed-mode Argo data server (international), high resolution T/S
CCHDO (CLIVAR and Carbon Hydrographic Data Office)	http://cchdo.ucsd.edu/ (PI: Lynne Talley, SIO)	CTD and discrete rosette sample data (calibration) from GO-SHIP P16S
NASA Seabass	http://seabass.gsfc.nasa.gov (PI: Joaquin Chaves Cedeno, NASA GSFSC)	HPLC and POC discrete samples; IOP profiles

1. Deployments from RVIB NB Palmer (edited from the GO-SHIP P16S cruise documentation)

Twelve Argo-equivalent floats equipped with various combinations of state-of-the-art biogeochemical instrumentation and sea ice-avoidance software were deployed during the RVIB NB Palmer cruise (chief scientist Lynne Talley), 20 March - 5 May, 2014 (Table 1 and Figure 1). 4 of the floats were deployed along the great-circle transit from Hobart, Tasmania, to the initial station of the P16S section (67°S, 150°W), and the remaining 8 were deployed along 150°W from 67°S to 39°40'S. Six of the 7 floats along 150°W that included pH sensors were funded through an NSF Eager grant; the high resolution T/S data are reported to Argo. The other 6 are Argo floats that have been outfitted with additional sensors through a NOPP grant. Tyler Hennon, a U. Washington graduate student (advisor co-PI S. Riser), was responsible for all deployments and record-keeping on the cruise, with assistance from the Palmer's marine technicians for all deployments. The two SIO Oceanographic Data Facility nutrient technicians (S. Becker and M. Miller) and the SIO alkalinity technician (D. Cervantes from the A. Dickson laboratory) also assisted with several deployments to gain experience in the event that they will be on ships that deploy such biogeochemical floats in the future.

Typical deployment procedure was relatively simple. After finishing the CTD cast at a deployment location, the Palmer would relocate to ~1 km off station and then proceed at about 1-2 knots in whatever direction offered the most shelter to the deployment. Hennon, along with one NBP ASC marine technician and one additional assistant (either a second MT or an SIO chemistry technician), then would lower the float from the stern to the water with a rope. This proved to be moderately challenging, given that the sea state was usually quite rough. Following deployment, the ship made a wide arc back to its steaming direction, ensuring that it did not pass over the deployment location.

All 12 floats reported their first profiles on time and several profiles thereafter, with information and data posted on both http://www.mbari.org/chemsensor/floatviz.htm

(biogeochemical site, plots, data sets) and http://runt.ocean.washington.edu/ (float tracking, engineering data, profiles). All oxygen, pH and FLbb sensors and 8 of the 10 ISUS nitrate sensors (exceptions are floats 6091, 7567) are producing good data. Of the 49 floats with nitrate sensors built at MBARI, these are the first two that did not respond on deployment. Engineering data indicate that the nitrate sensor on float 7567 is not responding because the persistent power interface (PPI) on the float is not operating properly and the nitrate sensor is not receiving power. This float appears to have had a significant shock on launch, as several other subsystems operated abnormally on the first profile. Operation of the other subsystems was restored, with the exception of the PPI. Loss of the nitrate sensor on 6091 has not been understood, at this time. The sensor communicated properly during predeployment tests. All systems in the float itself are operating normally after deployment, but there are no communications being received from the sensor.

Individual float deployment concerns (no issues for floats not listed):

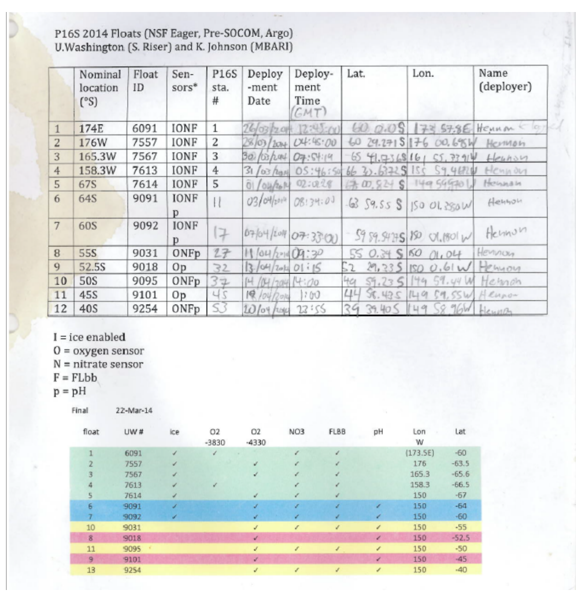
6091: The Palmer was steaming close to 3-4 knots to try to protect the back deck (deployment location) from bad weather. The nitrate sensor did not work for unknown reasons.

7567: A wave pushed float 7567 against the ship when the float was still attached to the deployment line. Initially this didn't cause concern, as there was not a violent collision. However, the data returned from the first profile (~12 hours after deployment) indicated severe problems and possible entry of saltwater into the float. Fortunately the 2nd profile was normal, with the exception of a nonfunctional nitrate sensor. Currently, it is unclear what caused the problems or if the float will continue operating normally. It is now presumably under ice along with two of the other floats and we will only learn more in the austral spring when they emerge.

7614: The line tangled during deployment. After a couple minutes we were able to shake the float free, but there were incidents of low speed (~10 cm/s) contacts between the iridium antenna and the ship's hull. The float has since reported back and is fully functional.

9031: Deployed in big swell, but there was no contact with ship to cause concern. The Palmer was steaming 4-5 knots during the deployment to protect the back deck from incoming waves. The bad conditions also prevented the ship from steaming off the CTD station until all the sampling was completed in order to limit the wash upon the deck (CTD sampling was outdoors at this point). This caused the float to be deployed about 2.5 hours after the conclusion of the CTD cast, but this is not a concern as the location was close, and the first float profiles are normally 12 to 24 hours later in any case.

Deployment Information (Original Log)



P16S 2014 Floats (NSF Eager, Pre-SOCOM, Argo)
U.Washington (S. Riser) and K. Johnson (MBARI)

	Nominal location (°S)	Float ID	Sensors*	P16S sta. #	Deploy-ment Date	Deploy-ment Time (GMT)	Lat.	Lon.	Name (deployer)
1	174E	6091	IONF	1	26/03/2014	12:45:00	60 0.0 S	173 57.8E	Hennon
2	176W	7557	IONF	2	28/03/2014	04:45:00	60 29.271 S	176 00.695W	Hennon
3	165.3W	7567	IONF	3	30/03/2014	07:54:19	65 41.7368	161 55.7391W	Hennon
4	158.3W	7613	IONF	4	31/03/2014	05:46:50	66 30.6372 S	155 59.4682W	Hennon
5	67S	7614	IONF	5	01/04/2014	02:02:28	67 00.824 S	149 59.970 W	Hennon
6	64S	9091	IONFp	11	03/04/2014	08:34:00	63 59.55 S	150 01.380W	Hennon
7	60S	9092	IONFp	17	07/04/2014	07:33:00	59 59.5427S	150 01.1801 W	Hennon
8	55S	9031	ONFp	27	11/04/2014	09:30	55 0.34 S	150 01.04	Hennon
9	52.5S	9018	Op	32	13/04/2014	01:15	52 29.33 S	150 0.61 W	Hennon
10	50S	9095	ONFp	37	14/04/2014	14:00	49 59.23 S	149 59.44 W	Hennon
11	45S	9101	Op	45	19/04/2014	1:00	44 58.43 S	149 59.55W	Hennon
12	40S	9254	ONFp	53	20/04/2014	23:55	39 39.40 S	149 58.96W	Hennon

I = ice enabled
O = oxygen sensor
N = nitrate sensor
F = FLbb
p = pH

Final 22-Mar-14

float	UW #	ice	O2 -3830	O2 -4330	NO3	FLBB	pH	Lon W	Lat
1	6091	✓	✓		✓	✓		(173.5E)	-60
2	7557	✓		✓	✓	✓		176	-63.5
3	7567	✓		✓	✓	✓		165.3	-65.6
4	7613	✓	✓		✓	✓		158.3	-66.5
5	7614	✓		✓	✓	✓		150	-67
6	9091	✓		✓	✓	✓	✓	150	-64
7	9092	✓		✓	✓	✓	✓	150	-60
10	9031			✓	✓	✓	✓	150	-55
8	9018			✓			✓	150	-52.5
11	9095			✓	✓	✓	✓	150	-50
9	9101			✓			✓	150	-45
13	9254			✓	✓	✓	✓	150	-40

2. Float data and engineering information (14 May 2014)

The data and performance information from the 12 floats deployed on NBP1403 are available in near real-time and delayed mode from four servers, each with a unique purpose (Table 2).

2.a. Temperature/salinity profiles reporting to Argo data servers

The high resolution temperature/salinity data (2 m vertical resolution above 1000 m) from all 12 floats are available according to Argo protocols from the U.S. GODAE and JCOMMOPS servers, listed in Table 3. (The U.S. GODAE server is the U.S. mirror site for JCOMMOPS.) The WMO numbers for each float are provided above in Table 2, and are also listed on the floatviz.htm website.

2.b. Float information and statistics to U. Washington data server

The U. Washington profiling float website tracks each of the Apex floats that have been built at U. Washington. This NBP1403 group of 12 is displayed with the Southern Ocean floats. Information about each float can be accessed by clicking on the float ID (Table 2 and Figure 1). This website provides plots (trajectories, profiles, and a large amount of additional information about each float's performance, that are not provided by the Argo data server websites. The U.W. website does not provide the data sets themselves.

2.c. T, S, oxygen, nitrate, pH, fluorescence (chlorophyll) and backscatter data to MBARI floatviz data server

The MBARI floatviz.htm website provides both the data sets and visualization tools for the biogeochemical and physical parameters collected by these floats, as well as many other floats outfitted by MBARI (K. Johnson). The complete data sets at the lower resolution of the chemistry data (~70 vertical samples on each profile) for each of the 12 floats are posted and are public. There are two versions of each data set: non-QC (raw data) and QC (adjusted data, with quality control flags). International and U.S. Argo are just beginning to decide how to work with and format data other than temperature and salinity; eventually the chemistry data posted at floatviz will be available through Argo.

3. Data quality

We have just begun assessing the quality of the new data sets. The NB Palmer P16S CLIVAR observations included a full suite of carbon-related measurements (DIC, alkalinity, pH), nutrients, oxygen, temperature and salinity, and many other chemical and physical quantities, all measured at the highest possible international standards of accuracy and precision. The pH and nitrate data from the floats are already being checked against the shipboard measurements. The CTD/rosette profiling included a fluorescence sensor, which can be used for comparison with the float fluorescence data. A full optical program was also aboard from

NASA, for ocean color satellite validation, and therefore high quality in situ data in the upper 200 m are also available for comparison with the float optical sensors (Wetlabs FLbb); water samples were collected for pigment analysis.

As discussed in Appendix A, it appears that the pH sensors were likely coated with TBT anti-foulant that biased the calibration and first profile of each float. The TBT was rapidly removed and subsequent profiles have been extremely stable. Surface pH values on profiles subsequent to the first are stable to about +/-0.005 pH (1 std. deviation for all data in the upper 50 m) for up to 6 profiles and one month in the water, as shown in Figure 3.

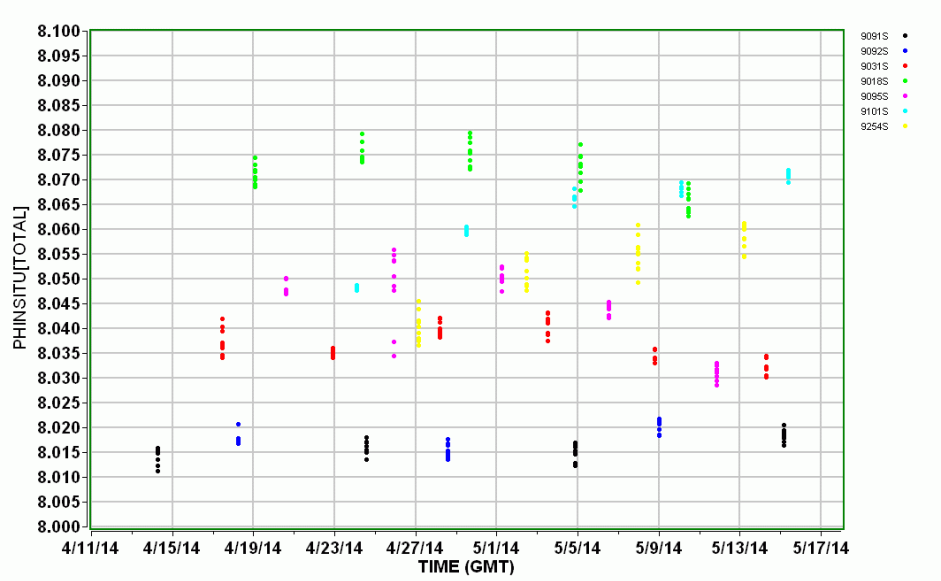


Fig. 2 In situ pH values in the upper 50 m for all float profiles except the first, from all 7 floats with pH sensors. The plot was generated from the FloatViz web site. Cooling without deep mixing drives pH up, while deep mixing lowers pH.

A full set of plots comparing the float and P16S insitu observations of oxygen, nitrate and pH is available as a powerpoint; an example for one float is shown in Figure 3. The profile shapes are excellent. Calibration offsets are being calculated and applied. As part of the learning curve, it appears that laboratory calibrations of the pH and nitrate sensors were affected by an inadvertent presence of antifoulant (see long email discussion from K. Johnson, Appendix A).

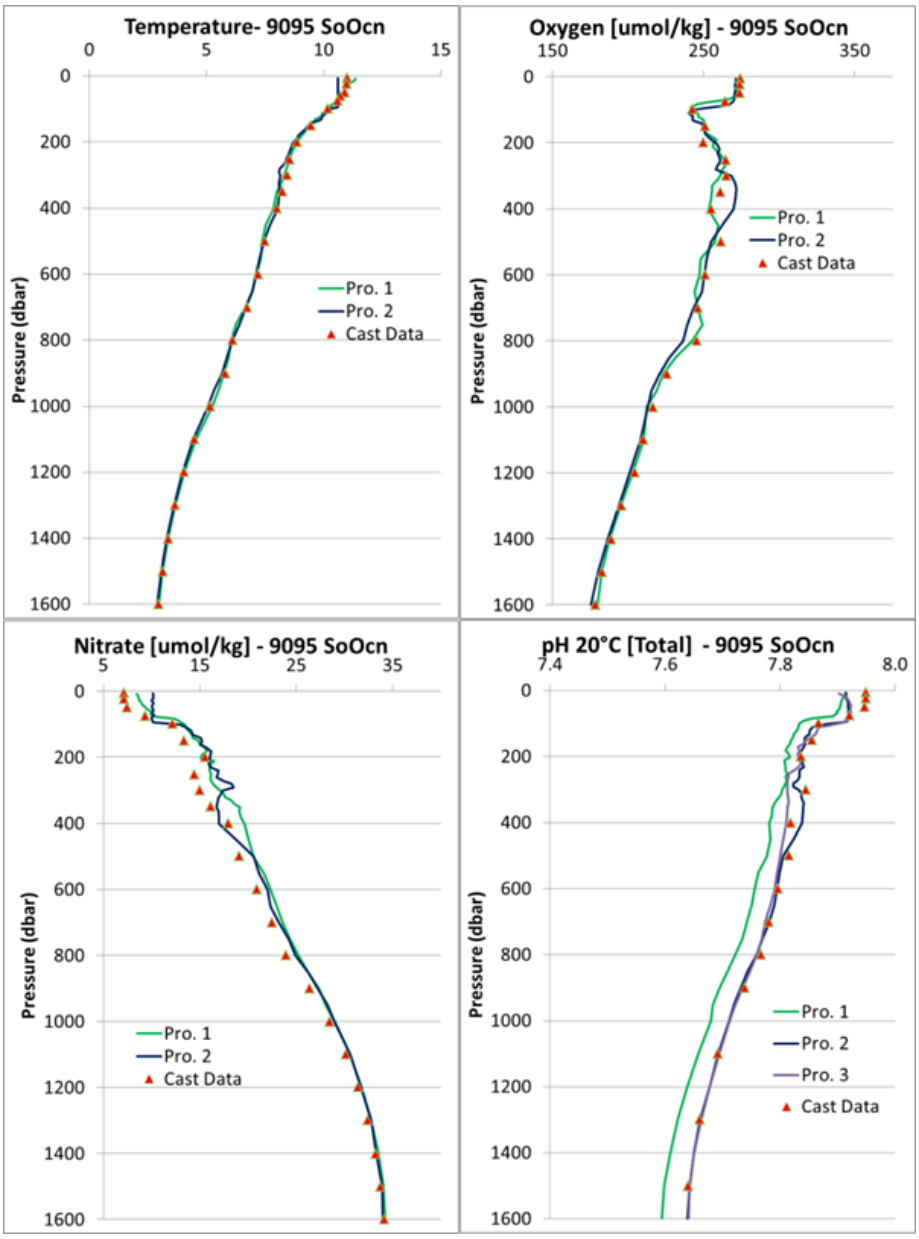


Figure 3. Comparison of shipboard measurements ("cast data") and (float measurements from the first two profiles of float 9095, as an example of the comparisons made as soon as profiles were available. Data were adjusted to match deep (1000-1600 m) data for nitrate and pH. Oxygen was adjusted so that the mean of all sensor measurements in air (one measurement is made on each profile) match air oxygen partial pressure. The first float profiles occur within 24 hours and several kilometers of the rosette cast. The initial offset of the pH profile is likely due to the presence of antifoulant during laboratory calibration and will not be an issue in the future.

Acknowledgments. This first deployment of biogeochemical floats for the Southern Ocean, prior to onset of the fully funded SOCCOM program, and the pH sensor development for the floats was funded by National Science Foundation (EAGER) Polar Programs PLR-1353103 (UW) and PLR-1353177 (MBARI) and ONR's National Oceanographic Partnership Program (NOPP) ONR N00014-09-10052. Some of the development was funded by the US Argo program, through NOAA grant NA17RJ1232 Task 2 to UW, and by the David and Lucile Packard Foundation. The floats were deployed from the U.S. GO-SHIP cruise P16S, which provided calibration measurements, principally funded by NSF's OCE physical and chemical oceanography programs, with support for carbon measurements from NOAA OAR, and bio-optical measurements from NASA GSFC.

Appendix A (Mis-)Calibration of the Deep-Sea DuraFET pH sensors (extracted and edited from an e-mail of May 7, 2014 from K. Johnson to P. Milne, L. Clough, L. Talley, J. Sarmiento)

There's a bit of a story about why our pH pre-deployment calibrations did not meet our expectations of being absolute. This is what we think happened. The float CTDs have a TBT anti-fouling plug in the circulating seawater line, which constantly pumps ambient seawater through the CTD. We do the final, absolute calibration of the sensor to pH with the whole sensor installed on the float endcap and plumbed into the CTD flow stream. Normally, the TBT anti-fouling plug on the CTD should be removed for pH/nitrate calibration because the flow stream is recirculated during lab calibration, with a dummy in its place. But a new employee didn't get the message and we received the CTD's with TBT loaded. That has been verified. It's hard for us to tell if the TBT is present because the dummy TBT plug would be installed to provide the same mass during ballasting at UW and it looks just like the real thing. In any case, the final calibration took place with a small volume of Tris buffer at pH 8.2 recirculating through the TBT plug and TBT concentrations would have been quite high. TBT is very surface active, it's an organic metal oxide with a strong affinity for the oxide on the gate of the pH sensor, and it would have coated the pH sensor, resulting in an offset calibration.

Coincidentally, we actually do two pH sensor calibrations. The first, for the sensor T and P response, is done in dilute HCl (the only solution we really know the proton activity properties of at high P) before the pH sensor is installed on the CTD and before the sensor would have seen TBT. The HCl and Tris calibrations normally produce very similar reference potentials for the sensor, but this time they did not. Unfortunately, we just did not do the comparison of the reference potential in HCl and Tris before we shipped the floats. It wasn't part of our protocol. The HCl calibration definitely has more error than the Tris calibration because its pH is so far from that of seawater (calibration at pH 2 to measure seawater pH near 8). When we applied the Tris calibration reference potential to the float data, the results for pH were way off, with

large but constant offsets. But the HCl calibration gave pH values that were just about right on. In some cases, they're just right, in some case a little bit of adjustment is needed to bring sensor pH into agreement with the ship pH. The only way we can explain the weird Tris calibration is that something had coated the pH sensing surface and altered the sensor output during calibration.

One other bit of evidence for contamination by TBT during the pH sensor calibration was that the first profile for each sensor had an even larger offset, that went away after one profile. Just as if something like adsorbed TBT was dissolving off the sensor. This also impacted the nitrate sensor and the first nitrate profiles are a bit odd too, with constant offsets that have since gone away. Coincidentally, TBT has a strong UV absorbance, which would affect the ISUS's spectrophotometric nitrate measurement. Normally, the TBT is not a problem when the float is deployed because levels are low as water constantly flows through the system, but during our lab calibrations it just recirculates and concentrations can build up. We're kind of picking on TBT, but it was the one anomaly in the calibration process that we can identify and the effects makes sense.

So we're now processing the data using the HCl calibrations, in some cases with a small, constant offset added to account for non-linearities in sensor response that don't matter when calibrated near the pH it's measuring. Because of the TBT issue, we've ignored the first profile for all the floats and are only looking at profile 2 and on.

The pH delta for pH from TA/DIC minus spectrophotometric pH has a standard deviation around 0.002 to 0.003 pH on each profile. The pH delta for sensor minus spectrophotometric pH is larger, about 0.007. Partly, that larger standard deviation is due to the problem of matching profiles at different times and in the upper ocean where gradients can be pretty steep. But even in the deeper water where concentrations should be more nearly invariant, the scatter for the sensor pH delta is a bit larger than the pH delta derived from measurements on a seawater sample. So we likely don't quite have the precision that the shipboard measurements do, but CLIVAR shipboard laboratory measurements of all properties are the "gold standard" and no autonomous sensors on Argo floats match the accuracy of these highest quality benchmark measurements. On the other hand, these floats will be out there for 5 years and will provide the first complete annual cycles of pH observed anywhere in Antarctic waters over many years, thus demonstrating, as for other sensors, the value of the combination of (i) high accuracy shipboard measurements against which to compare autonomous sensors with (ii) the many years of autonomous measurements that cannot be made from ships.