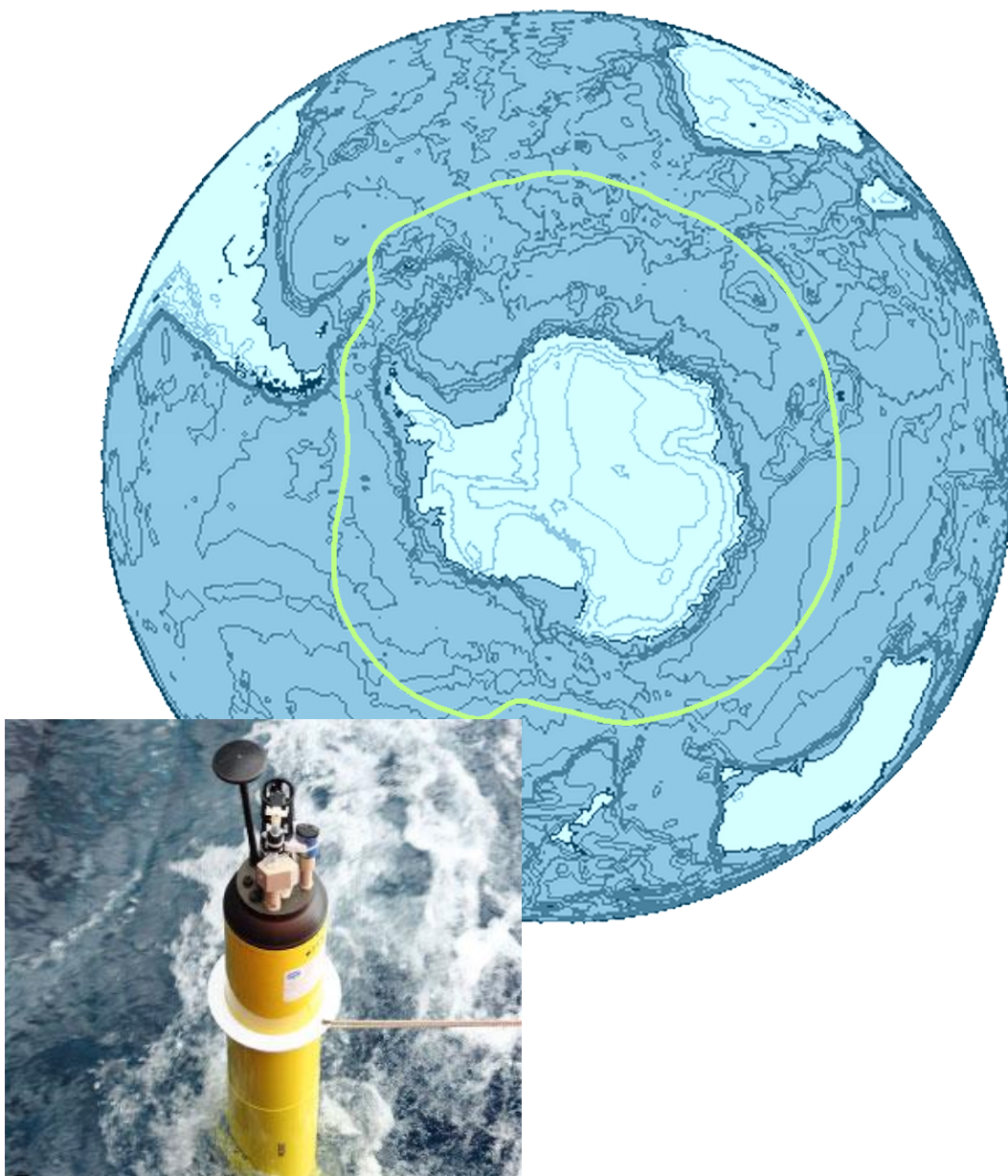


An evaluation of pH and NO₃ sensor data from SOCCOM floats and their utilization to develop ocean inorganic carbon products

A summary of discussions and recommendations of the Carbon Working Group (CWG) of the Southern Ocean Carbon and Climate Observations and Modeling project (SOCCOM)



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An evaluation of pH and NO₃ sensor data from SOCCOM floats and their utilization to develop ocean inorganic carbon products

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Recommendations and findings:

The Carbon Working Group (CWG) of the Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM) project is tasked with providing recommendations for acquisition and quality control of data from biogeochemical sensors on SOCCOM floats:

CWG Findings

- The NO₃ and pH sensors on floats are in development stage but rapidly reaching the point of providing quality data to study key biogeochemical processes in the Southern Ocean.
- There is an improved understanding and remedies of issues causing drift in the biogeochemical sensors.
- The transition from an ad hoc adjustment procedure of pH and NO₃ to a systematic approach handled by data centers is well laid out and progressing.
- The accuracies of float O₂, NO₃ and pH data after appropriate adjustments are 2 μmol kg⁻¹, 0.5 μmol kg⁻¹, and 0.01, respectively.
- NO₃ and pH data from the profiling floats in SOCCOM can be adjusted as needed using Multi Linear Regression (MLR) algorithms based on quality bottle data from 1000-2100 dbar in the region (see eqns. 3 and 4) to within the level of current instrumental uncertainties.

CWG Recommendations

- All samples brought back to shore from float deployment validation casts should be analyzed for total dissolved inorganic carbon, DIC, in addition to pH and total alkalinity, TALK.
- Continued acquisition and assembly of high quality inorganic carbon data from CTD/bottle casts is critical for quality control of float sensors, model validation and algorithm development/improvement.
- A consistent set of dissociation constants and a chemical model should be used for calculating inorganic carbon system parameters as described in Table 4.
- It is imperative that the temperature and pressure dependence of pH sensors, and their correspondence to the appropriate pH scales is further studied in detail.
- Continued study and improvement of adjustment approaches and incorporation of these efforts into a routine approach following Argo guidelines is needed.
- Continued study and improvement in deployment procedures, physical configuration of sensors, sensor design and quality control is needed.
- Accommodation is needed for updated protocols in Argo to process the biogeochemical and biological data using separate files and data acquisition centers prior to merging of physical and biogeochemical data.

1. Introduction

i. Purpose of document

The Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM) project is revolutionizing our efforts to investigate the Southern Ocean. The new approaches, in particular the utilization of biogeochemical sensors on floats, require a careful uncertainty analysis and clear procedures to create useful products. The carbon system working group (CWG) of SOCCOM is charged to address these issues with regards to the measured and derived inorganic carbon system parameters: total alkalinity (TAlk), total dissolved inorganic carbon, (DIC), partial pressure of CO₂ (pCO₂), and pH. The only inorganic carbon system parameter acquired from the SOCCOM floats is pH, the others are calculated through different means as described below. This document is an authoritative overview of procedures to adjust sensors for offsets and drift, and to use of the float data to create products, such as regional fields of inorganic carbon parameters.

ii. The CWG and SOCCOM objectives

The carbon working group activities are part of the overall objectives of SOCCOM. SOCCOM is focused on unlocking the mysteries of the Southern Ocean and its influence on climate. SOCCOM is a well-structured program with three major themes of observation, modeling and broader impacts. The CWG addresses the observation theme with focus on creating fields of carbon system parameters, such as carbonate mineral saturation states. A full description of the charge of the CWG is provided in Appendix A. The recommendations and implementation will also benefit the carbon cycle models of the Southern Ocean through improved constraints. The CWG will have significant broader impacts as the procedures and approaches described can be utilized to improve the quality and products resulting from floats equipped with biogeochemical sensors ocean-wide.

iii. Outline of document

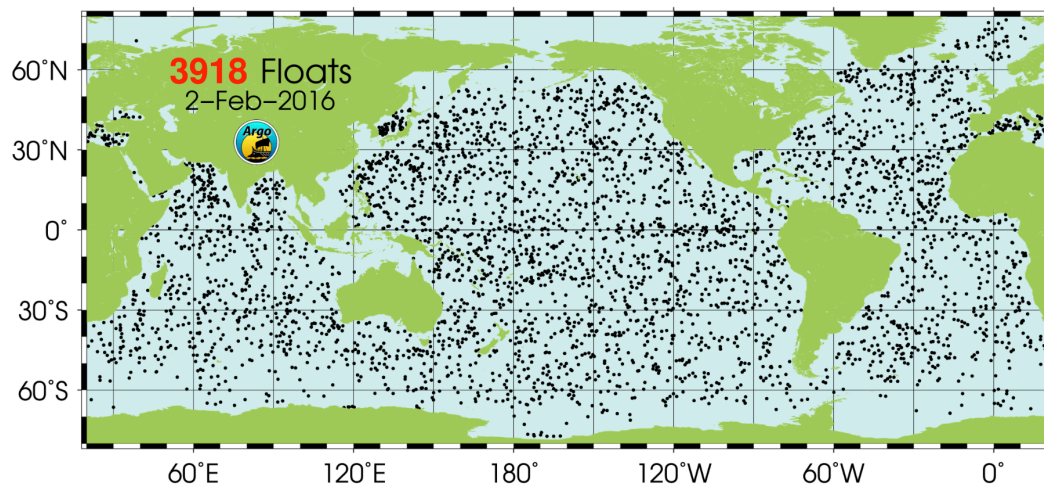
This document provides recommendations and guidelines to adjust and check data from biogeochemical sensors on profiling floats, in particular pH and NO₃ sensors based on empirical approaches and models. The adjusted data along with models of different levels of sophistication are used to determine the larger scale fields of the biogeochemical parameters of interest.

The first section of the document describes the sensors on floats and their pre-cruise calibration and typical behavior when first deployed with focus on the NO₃ and pH sensors. This is followed by a description of the pH measurement and the derivation of carbon system parameters and their uncertainties. Adjustment procedures of the NO₃ and pH sensors are described based on multiple linear regression (MLR) algorithms derived from the validation cruises and other high quality bottle data. The final section touches upon the carbon products that will be produced as part of the SOCCOM project using different empirical approaches.

2. Biogeochemical sensors on floats

The Argo profiling float program started in the early 1990's with an ambitious goal of deploying a global array of floats equipped with temperature (T), salinity (S), and pressure (P) sensors. Its primary objective was to determine changes in ocean heat content in the upper 1500 m. The overall vision of Argo is to greatly expand our knowledge of changes in the ocean with "greatly improved collection of observations capabilities inside the ocean through increased sampling of old and new quantities and increased coverage in terms of time and area"¹. The current program has well-defined objectives along with good dissemination, quality control, and data management protocols, and data from the Argo program is now used in over scientific 200 publications per year. The great success of Argo, the urgent need to study trends in other variables in a changing ocean, and rapid advances in sensor technology have inspired researchers to incorporate novel sensors onto the profiling float platforms. Oxygen sensors were the first to be used extensively (Körtzinger et al. 2004) and are now deployed on about 5 % of the global float array (see Figure 1 for float positions). The sensors are well behaved and with proper precautions yield data believed to be accurate to within 1 % ($\approx 2 \mu\text{mol kg}^{-1}$). Oxygen data processing protocols are close to routine but Argo biogeochemical sensor data still follow a different quality control path than core Argo data.

The biogeochemical sensors of primary interest to this discussion are NO_3 and pH. We also consider properties that are estimated or calculated from these and other Argo measurements (e.g. aragonite saturation Ω_A , TAlk, and DIC). The O_2 sensors are also discussed as O_2 data are used extensively to estimate the carbon system parameters. The O_2 sensors serve as an example of a comparatively mature effort to deploy novel biogeochemical sensors on the Argo platform.



¹ <http://www.argo.ucsd.edu>

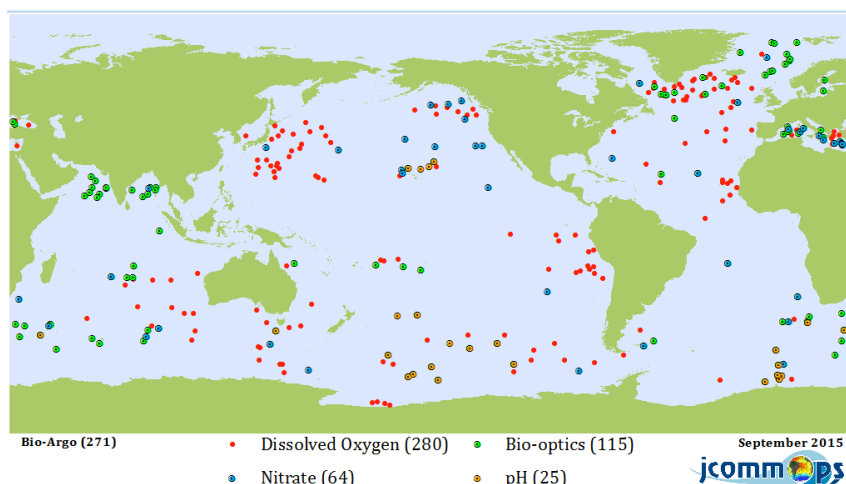


Figure 1. Locations of all floats reporting through the World Meteorological Organization’s Global Telecommunications System (GMS) for January 2016² (top) and floats equipped biogeochemical sensors as of September 2015³ (bottom)

Types of floats

Five types of floats are commonly deployed in the Argo program (APEX, Navis, SOLO II, Provor, and NOVA). SOCCOM exclusively uses APEX and Sea-Bird NAVIS floats at time of writing. The NAVIS floats with biogeochemical sensors are a standard product of Seabird Electronics and can be purchased with user specified configurations. They are in the late stages of development and not yet considered fully mature (as of the end of 2015). The Teledyne Webb Research (TWR) APEX floats are deployed by the University of Washington (UW) and are the primary platform for deploying the biogeochemical sensors described below. However, the APEX float with the BGC sensors used in SOCCOM is not a standard product of TWR and is not commercially available. SOLO II floats are extensively deployed by WHOI and SIO for the core Argo array, but they have not yet been adapted to carry a variety of BGC sensors. The platforms have no appreciable effect on the data from the biogeochemical sensors, other than that some floats have pH, Nitrate and O₂ sensors in a pumped water circuit⁴. This may impact sensor operation. Oxygen sensors in the pumped stream preclude O₂ air calibrations and anecdotal evidence suggests more fouling issues with the nitrate sensors when they are in a pumped loop.

² <http://www.argo.ucsd.edu/statusbig.gif>

³ <http://argo.jcommops.org/maps.html>

⁴ The placement in a pumped water circuit is to minimize fouling. However, some results suggest that, to the contrary, this is not optimal for the pH and NO₃ sensors. They are being repositioned to have direct exposure to seawater.

Details of sensors on SOCCOM floats⁵

Temperature (T), Pressure (P), and conductivity/"salinity"(C/S) sensors are the core sensors on the Argo profiling floats and have high accuracy. All of the Argo and SOCCOM floats carry Sea-Bird (SBE) pressure, temperature and conductivity sensors. Conductivity sensors sometimes experience slow drift rates that are corrected for in the delayed quality control (QC) process using salinity climatologies⁶.

The temperatures in the Argo profiles are accurate to $\pm 0.002^{\circ}\text{C}$. Pressures are nominally accurate to ± 2.4 dbar, but they may also drift. Pressure values are adjusted, if needed, in near real-time based on the known pressure when the sensor is at the surface. For salinity the accuracy is 0.005 based on propagation of uncertainties in conductivity and temperature. The factory specifications of the SBE sensors are provided in Table 1.

Table 1. Accuracy and drift of the temperature, Pressure, and conductivity sensors as provided by the manufacturer (Sea-Bird SBE)^a.

Sensor	Calibration Standard	Initial accuracy	Typical drift
T ($^{\circ}\text{C}$)	ITS-90	0.002	0.0002 $^{\circ}\text{C y}^{-1}$
C (S/m)	IAPSO/OSIL	0.0005	0.0002 (S/m) y^{-1}
P (dbar)	Deadweight & P ref	2	0.8 dbar y^{-1}

^a: based on a presentation by S Riser to the CWG on 9/15/2015.

Three types of O_2 sensors are currently deployed on SOCCOM floats that all work on the same principle referred to as optodes. These optical O_2 sensors consist of a semi-permeable membrane, sensing element, light-emitting diode (LED) and photodetector. The sensing element contains a luminescent dye that is immobilized in a gel matrix. When exposed to blue light from the LED, the dye either luminesces or is quenched by interaction with O_2 . Some sensors also emit a red light as a reference to enhance stability. This red light is simply reflected back by the dye. The intensity or lifetime of the returned luminescence is measured by a photo-detector. Because the intensity of response drifts relatively quickly SBE 63s and Aanderaa optodes only use the decay lifetime to calculate the dissolved oxygen concentration. The quantity measured is closely related to the partial pressure of O_2 and the sensor can measure the O_2 in air as well, therefor offering a unique way to calibrate the sensor when the float surfaces (Johnson et al., 2015).

⁵ From http://sio-argo.ucsd.edu/RG_Climatology.html) and http://www.argo.ucsd.edu/Data_FAQ.html

⁶ <http://www.jcommops.org/Apps/WebObjects/Argo.woa/wo/OR63C76oBdZD8I3Gtma1g/1.0.0.41.1.1>

For the floats deployed during SOCCOM the SBE 63 and Aanderaa Optode 3830⁷ and 4330 models have been used. As shown in Table 2 below they have similar characteristics. The important difference is that the SBE 63 is plumbed into the water loop that also houses the conductivity sensor and therefore cannot make oxygen measurements in air when it surfaces.

These air measurements offer an accurate calibration value if atmospheric pressure and water vapor pressure are known at time of surfacing. Air immediately above the ocean is generally at 100 % relative humidity, so that the water vapor pressure can be calculated from air temperature, salinity, and atmospheric pressure. These opportunistic calibrations in air when the float surfaces offer a means to adjust for small drifts (Bushinsky et al., 2016). The air calibrations have improved accuracies to 2 $\mu\text{mol kg}^{-1}$ compared to the factory specifications in Table 2. The accuracy is limited primarily by knowledge of the barometric pressure at the location the float reaches the surface.

Table 2. Summary of float O₂ sensor performance based primarily on manufacturers' specifications^a.

Sensor	Response Time	Accuracy [claimed]	Precision	Stability
SBE 43-IDO	< 1 sec	2% of sat.	1 $\mu\text{mol/kg}$	2%/1000 hr [170 profiles]
Optode 3830 (Aanderaa)	< 25 sec	< 8 $\mu\text{mol/kg}$	< 1 $\mu\text{mol/kg}$	Good
Optode 4330 (Aanderaa) (UW Apex)	8-25 sec	< 8 $\mu\text{mol/kg}$	< 1 $\mu\text{mol/kg}$	Good [0.3%/year]
SBE 63 (SBE Navis)	< 6 sec	$\pm 2\%$	< 1 $\mu\text{mol/kg}$	Good [0.3%/year?]

^a : From a presentation of S. Riser to the CWG (9/15/2015)

The NO₃ sensors on APEX floats are In Situ Ultraviolet Spectroscopy (ISUS) sensors built and calibrated at MBARI. The NAVIS floats have SUNA sensors built and calibrated by Satlantic. The SUNA V2 (Submersible Ultraviolet Nitrate Analyzer) is a chemical-free UV nitrate sensor based on the ISUS nitrate measurement technology developed at MBARI. ISUS and SUNA have the same main optical components, but SUNA has the optical path configured differently. The description below is adopted from Johnson et al. (2013). Nitrate absorbs light in the ultraviolet with peak absorption maximum near 200 nm with a

⁷ The 3830 sensors were used in the 12 "pre-SOCCOM" floats deployed during P16S in 2014. They are no longer used in SOCCOM floats

moderately strong molar absorptivity. The deep UV absorption spectrum of seawater is dominated by the combined signal from nitrate and bromide, with a much smaller contribution from dissolved organic matter that is separated by measurements at multiple wavelengths. The ISUS makes a single UV spectral scan with the lamp on (light scan) and lamp off (dark scan). The light and dark scans are used, along with reference spectral intensities from similar scans of deionized water made in the laboratory, to compute the absorbance spectrum from 200 to 400 nm. The absorbance spectrum is used with the concurrent temperature and salinity to compute nitrate using the temperature compensated, salinity subtracted algorithm (SW with T/S corr.). The observed salinity and temperature are used to predict the UV spectrum due to bromide. The corrected spectrum then contains only components due to nitrate and an approximately linear baseline due to organic matter and instrumental drift. All spectral data is telemetered to shore such that nitrate concentrations can be recomputed as necessary. The accuracy of the sensor is about 2 μM , and this can be improved through in situ adjustments. Errors in nitrate concentration are constant offsets over the entire vertical profile such that the error at the reference depth can be added back to the entire profile and a much higher-quality set of nitrate data can be obtained. The adjusted data have accuracies on the order of 0.5 μM , relative to the reference value.

Table 3. Accuracy of the SUNA Nitrate sensor in seawater ^{a, b}

	with T/S corr. ^b		without T/S correction
Detection limit	0.5 μM		2.0 μM
Accuracy (greater of)	$\pm 2 \mu\text{M}$	or $\pm 10\%$ of reading	
Precision (short term)	0.3 μM		1.0 μM
Drift (per hour lamp time) ^c	0.3 μM		2.4 μM

^a : From http://satlantic.com/sites/default/files/documents/2015_datasheet_SUNAV2.pdf

^b : These values are with appropriate corrections for salinity and temperature

^c : During a typical profile the lamp is activated 70 seconds or a total of 5.5 hours for a 5-year deployment

The (SBE/Satlantic) pH sensor is a new biogeochemical sensor and it is the first inorganic carbon system parameter routinely deployed on profiling floats. To date the pH sensors on the SOCCOM APEX floats have all been built at MBARI as part of a technology transfer agreement. To ensure a smooth transition from sensors constructed at MBARI to commercial versions, the MBARI sensors will be gradually substituted with commercially built sensors of similar design, beginning with the deployment of SBE pH sensors on Navis floats.

Measurement of pH using Ion Sensitive Field Effect Transistor (ISFET) technology is summarized in Martz et al. (2010) and briefly described here. The ISFET is a metal oxide semiconductor field effect transistor (MOSFET). The conduction channel is covered by a

thin insulating layer of amphoteric material. The pH of the solution at the insulator/solution interface controls the site-binding protonation/deprotonation state of the insulator material and, hence, the surface charge at the interface. The interfacial charge determines the strength of the electric field in the conduction channel of the FET, located between the source and drain. The ISFETs used in SOCCOM are operated by applying a constant drain source current. A conventional reference electrode is used in conjunction with the ISFET. It is a solid-state chloride ion-selective electrode (Cl-ISE) with very little pressure hysteresis. The approximate salinity sensitivity for the FET|Cl-ISE is $0.013 \text{ pH salinity}^{-1}$ (Martz et al., 2010).

The ISFET sensor deployed on profiling floats is called the Deep-Sea DuraFET pH sensor. The pH is reported on the total proton scale (pH_T). It can operate at pressures to 2000 m depth in the ocean. Therefore the system must be calibrated for pH measurements through large temperature and pressure gradients. The integrated Deep-Sea DuraFET includes a pressure tolerant, solid-state AgCl reference electrode Cl-ISE described above.

The output of the sensor is a voltage, V_{RS} that is related to H^+ ion activity, temperature and pressure by:

$$V_{RS} = k_0 + k_2 (T-273.15) + f(P,T) - RT/F \ln(a_{\text{H}^+} a_{\text{Cl}^-})_{T,P} \quad (1)$$

$$= k_0 + k_2 (T-273.15) + f(P,T) - RT/F [\ln(m_{\text{H}^+} m_{\text{Cl}^-}) + \ln(\gamma_{\text{H}^+} \gamma_{\text{Cl}^-})_{T,P} + \bar{V}_{\text{HCl}} P/RT] \quad (2)$$

k_0 is the reference potential. k_2 is the temperature dependence of V_{RS} . $f(P)$ is the pressure coefficient of the sensor. Unlike a conventional electrode, the k_0 and k_2 values of the ISFET contain terms associated with FET design, semiconductor processing and power application values. Therefore the k_0 and k_2 values must be determined for each individual sensor.

Given the uncertainty of coefficients in eqn. (2) over the range of T and P in the ocean the uncertainty can translate to a 0.01 pH error due to pressure at 2000 dbar pressure and 0.015 due to temperature. As a result, the estimated pH_T values can have biases on the order of 0.02 at pressures near 2000 dbar, based on propagation of possible errors due to uncertainties in T and P dependence.

Initial deployments of floats with pH showed a mean rate of drift, diagnosed as the change between pH observed below 1000 m depth and the expected pH at this depth, of $-0.036 \text{ pH yr}^{-1}$. However, with appropriate sensor conditioning, in particular equilibration of the AgCl reference electrode(Cl-ICE) with bromide in seawater, this drift can be decreased by 5-fold. (K. Johnson, pers. com.).

Frequency of profiling measurements

The pH and NO_3 sensors are logged on the upcast of the float with a default 10-day cycle. Approximately 65 measurements are taken on the upward profile with the APEX floats. This rate is determined by power requirements of the NO_3 sensor and limitations of the electronics. The measurement spacing is variable to capture relevant features with

nominally 100-m intervals from 1500 to 1000 m; 50 m from 1000 to 400 m; 20 m from 400 to 360 m; 10 m from 360 to 100 m; and 5-m intervals from 100 m to 5 m. The associated T, S, and O₂ data are provided at the same depths in the data files. The NAVIS floats, with more modern electronics, are capable of much higher vertical resolution. They provide pH, oxygen and bio-optical measurements at 2-meter spacing in the upper 1000 m. Nitrate remains at the same resolution obtained with APEX floats. Examples of two profiles of O₂ and pH from SOCCOM APEX float 9254 are provided in Figure 2.

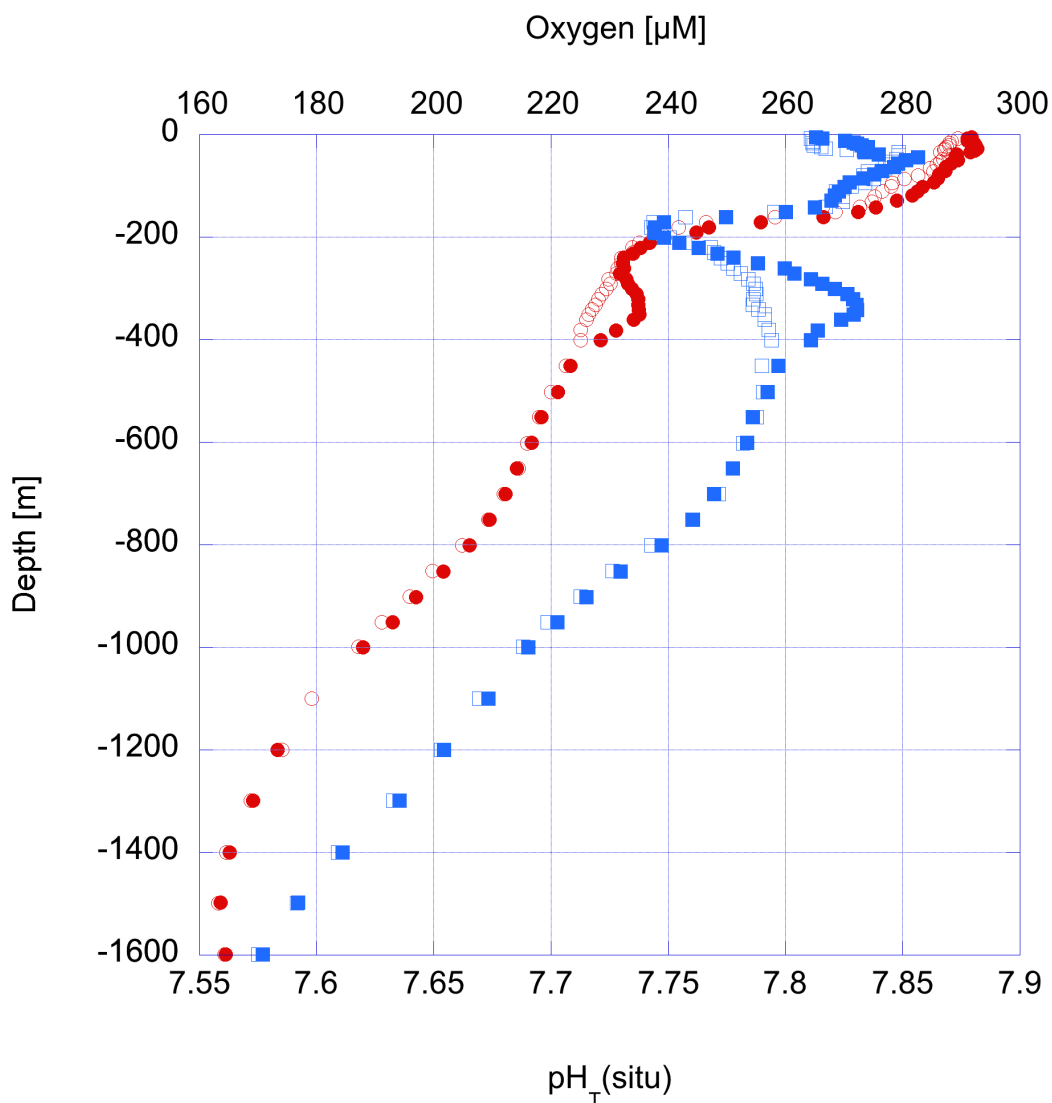


Figure 2. Profiles of oxygen (blue) and pH_T (red) from float 9254 at 39°S, 155°W, for 11/21/2015 (open symbols) and 12/01/2015 (closed symbols), illustrating the depth resolution, and the rapid but coherent changes in biogeochemical parameters in the upper

water column during the Austral Spring/Summer (data obtained on 12/05/2015 from <http://soccom.princeton.edu/soccomviz.php>).

3. Performance of sensors

Based on information on the sensors provided above and the measurements in the field to date we can provide an assessment of the performance of the sensors. This is not exact, as only limited *in situ* validation is possible. Moreover, sensors and the shoreside preparations and calibration routines are still being improved. Table 4 provides an assessment of current estimates of performance of the sensors based on manufacturers specifications and calibrations in laboratory and other venues.

Table 4. Sensor response and current estimates of accuracy of sensors during deployment

Parameter	Accuracy	Stability (drift)
P	2 dbar	0.8 yr ⁻¹
T	0.002°C	0.0002 yr ⁻¹
S	0.005	0.01 yr ⁻¹
O ₂	2 µmol/kg	0.6 µmol yr ⁻¹
NO ₃	0.5 µmol	0.3 µM yr ⁻¹ (a)
pH	.01	-0.036 yr ⁻¹ (b)

(a): Based on a 1-hour total lamp usage over a year (≈ 52 profiles) (see Table 3).

(b): From Martz et al. (2010), new conditioning approaches have decreased this drift to less than 0.007 yr⁻¹

There are slight differences in setups and types of the instruments deployed but overall they should have similar performance. An important difference is if the sensors are plumbed into a water circulation system or exposed directly to the ocean water. The circulation system precludes the air calibration of the O₂ sensor, but should improve the response time of the sensor. The circulation loops have an anti-fouling agent but the Nitrate (optical sensor) appears to have other fouling issues in the loop. Currently all the biogeochemical sensors on the APEX floats are being tested with sensors directly exposed to seawater.

4. Sensor deployments, calibration, validation and checks

Laboratory calibration of sensors has been challenging due to difficulties recreating the environment at sea when the sensors are deployed. O₂ sensors are routinely checked in the laboratory. For the APEX floats the O₂ sensors are compared side-by-side with a calibrated laboratory sensor of the same make and model. pH sensors are checked prior to deployment in artificial seawater but due to differences in chemical constituents between artificial seawater and real seawater, appreciable adjustments are necessary. NO₃ sensors are checked in the laboratory as well but while overall response and general behavior of the sensor can be checked, most data require an adjustment once deployed.

The validation CTD/bottle casts that are part of the usual SOCCOM protocol at the time of float deployment are an important means to check the sensors when they are deployed and to determine appropriate adjustments. The first profile from the float often does not correspond well with the bottle data from the cast because the sensors sometimes experience drift during their initial profile, notably the NO₃ sensor. The O₂ sensors generally do not undergo a check against the calibration cast, in part because the sensors show good agreement between lab based calibration values and the deployment values. However, for the sake of consistency, similar checks and adjustments should be made for O₂, pH and NO₃ sensors. The deployment cast is a good qualitative check for drift and offsets but currently adjustments to pH and NO₃ sensor values are performed based on the MLRs developed from deployment casts and other high quality bottle data in the Southern Ocean (see section 7).

The pH and NO₃ sensors routinely need a "soaking time" of a few profiles during which there is appreciable drift. The drift is attributed to several factors. For NO₃ it appears that the optical window could be dirtied by organics during storage and transport. For pH the AgCl in the reference electrode reacts with Br in seawater until equilibrium between AgCl and AgBr in the electrode is obtained. Cleaning procedures of optical windows and longer soaking times of pH sensors in real seawater in the laboratory are currently being investigated as a viable means to decrease initial drift.

Once the NO₃ sensor stabilizes from large drift there is a smaller residual drift (see Table 3). Thus the NO₃ sensor adjustment often involves an adjustment for offset soon after deployment followed, at a later time, by correction for a longer time drift. The adjustments are done in an opportunistic fashion based on knowledge of climatologies and stoichiometries between parameters. The primary adjustments are done at depth based on the World Ocean Atlas WOA, other climatology, or as recommended for SOCCOM by a MLR algorithm (section 7). For NO₃ sensors deployed in subtropical regions (e.g., near BATS) where summer time nitrate values in the surface are zero, a second calibration check is based on the zero concentration in the mixed layer. Drift over time is determined and corrected based on comparison of float and MLR algorithm at depth (1000-2100 m) where nitrate is linearly regressed against temperature, salinity, pressure and oxygen: $NO_3 = a + bT + cS + dP + eO_2$, where the coefficients are determined from cruise data in the area.

5. Recommended constants for inorganic carbon system parameters

Adjustment of pH sensors is significantly more challenging than for other sensors and requires information on the dissociation of the inorganic carbon species in seawater. This CO₂ system information is also necessary to create inorganic carbon products from the pH float data. pH sensors on the floats measure the pH at in situ temperature and pressure which is different from the calibration and validation samples which are analyzed at constant temperature and 1 atm. The sensors measure the free H⁺ ions and it is most appropriate to express the pH on the free scale (K. Johnson, pers. com.). The pH samples from CTD/Bottle casts are measured at constant temperature (usually 20 or 25 °C) on the total scale in a ship's laboratory. On select occasions pH is not measured on board but rather determined along with TAlk on bottle samples shipped to the shoreside laboratory

of A. Dickson of SIO. To compare the bottle data with the sensor data and apply adjustments to the sensor data, carbonate dissociation constants and a chemical model need to be applied. Details of the basic inorganic carbon chemistry and recommended analysis procedures can be found in Dickson et al. (2007).

Here we focus on using discrete bottle samples at fixed temperature and 1 atm pressure to adjust in situ pH sensor data. Excel[®] and MATLAB[®] routines are readily available to perform the conversions. The temperature and species conversions require a chemical model and two inorganic carbon system species (DIC, TAlk, pH, or pCO₂) (e.g. Pierrot et al. 2006). The recommended constants for SOCCOM efforts are provide in Table 5. They are considered the most consistent based on current knowledge, but the main purpose of the recommendation is for consistency. That is, all SOCCOM products should be based on the same constants such that disagreements in results or interpretations are not caused by products being developed using different constants.

Table 5. Recommended constants for calculating inorganic carbon system parameters in SOCCOM, including temperature and pressure normalizations.

Carbonate dissociation constants⁽¹⁾

pH _T ⁽²⁾	Total scale (mol kg ⁻¹ seawater)
pK ₀ ⁽³⁾	Solubility Weiss & Price (1980)
pK ₁ and pK ₂ ⁽⁴⁾	Lueker et al. (2000) using pH _T

Associated constants⁽⁵⁾

pK(B)	Dissociation constant boric acid Dickson, (1990)
pK(HF)	Dissociation constant for hydrofluoric acid of Perez & Fraga (1987)
pK _{2P} , pK _{3P} ⁽⁶⁾	2 nd and 3 rd dissociation constants phosphoric acid Dickson et al., (2007)
Pressure ⁽⁷⁾	Pressure corrections for various acid-base dissociation constants as implemented in CO2SYS
T _B	Total boron in seawater parameterized with salinity Lee et al., (2010)
K _{H2SO4} ⁽⁸⁾	Dickson (1990)
Ω _{Ar} , Ω _{Ca} ⁽⁹⁾	Aragonite and Calcite saturation states as provided in CO2SYS.

- (1) The CO2SYS program has been adjusted by D. Pierrot to accommodate these constants. (CO2SYSv2.2). The footnotes notes below are adapted from A. Dickson, pers. com.
- (2) Spectrophotometric measurement using purified m-cresol purple at 25 °C as reference (Liu et al., 2011). These have been verified in the laboratory (at 25 °C and S = 35) of A. Dickson, SIO and they agree with Liu et al. to 0.002 in pH. However, the resulting pH is not necessarily in perfect agreement with the way pH is defined in the definition of the various acid-dissociation constants. Preliminary work suggests a discrepancy of about 0.006 in pH. If this discrepancy is accounted for then pH, TAlk, and DIC are internally consistent within likely uncertainties.
- (3) pK₀ based on Weiss (1974), as implemented in the appendix of Weiss & Price (1980)

- (4) pK_1 and pK_2 based on data of Mehrbach et al. (1973), converted to total hydrogen ion concentration scale (Lueker et al., 2000).
 - (5) To convert total alkalinity to carbon alkalinity needed in calculations, and to estimate the hydrogen ion activity from non-carbonate species in seawater. Values are valid for $S \approx 20-38$, $T \approx -2$ to 40 °C)
 - (6) pK_{2P} , pK_{3P} for H_3PO_4 dissociation are based on Millero (1995) corrected to pH_T scale (see Dickson et al., 2007)
 - (7) Pressure corrections for acid-base dissociation constants as implemented in CO2SYS, This pressure dependence is based on original work by Culbertson et al. (1968) on the equivalent of the free pH scale with subsequent approximations of the ΔV of HCO_3^- based on that of HSO_4^- (K. Johnson, pers. com.).
 - (8) Waters and Millero (2013) and Khoo et al.(1977) show values of K_{HSO_4} that are twice as high as the recommended K_{HSO_4} of Dickson (1990) . The effects of pressure and temperature are different for the various K_{HSO_4} values that will lead to differences in pH of ≈ 0.01 for the different K_{HSO_4} values on the free scale
 - (9) Note, some current biogeochemical models (e.g. TOPAZ) do not reproduce calculated values from CO2SYS using TAlk and DIC. This appears to be an issue how Ca^{2+} is determined. In CO2SYS, $Ca^{2+} = 293.84 * S$.
-

For checks of other CO₂ system codes the following two examples are provided.

Test cases using CO2SYS V2.2 and constants in Table 5:

Sample 400217 Station 40, P16S (2014)

Input values

P = 1000.3 dbar

S = 34.319

T(in situ) = 5.720 °C

TAlk = 2286.4 $\mu\text{mol kg}^{-1}$

DIC = 2169.1 $\mu\text{mol kg}^{-1}$

$pH_T(20, 0)^{(a)} = 7.7366$

$PO_4 = 1.82 \mu\text{mol kg}^{-1}$

$SiO_3 = 17.8 \mu\text{mol kg}^{-1}$

output using TAlk and $pH_T(20, 0)$

$pH_T(5.72, 1000) = 7.9104$

$pH_F(5.72, 1000)^{(b)} = 7.9593$

DIC = 2167.8 $\mu\text{mol kg}^{-1}$

$fCO_2(5.72, 1000) = 493.4 \mu\text{atm}$

$\Omega_{Ar}(5.72, 1000) = 1.14$

$\Omega_{Ca}(5.72, 1000) = 1.79$

Sample 400210 Station 40, P16S (2014)

P = 1999.5 dbar

S = 34.581

T(in situ) = 2.626 °C

TAlk = 2350.6 $\mu\text{mol kg}^{-1}$

DIC = 2264.3 $\mu\text{mol kg}^{-1}$

$pH_T(20, 0) = 7.632$
 $PO_4 = 2.37 \mu\text{mol kg}^{-1}$
 $SiO_3 = 82.4 \mu\text{mol kg}^{-1}$
output using TAlk and $pH_T(20, 0)$
 $pH_T(2.62, 2000) = 7.8062$
 $pH_F(2.62, 2000) = 7.8459$
 $DIC = 2265.9 \mu\text{mol kg}^{-1}$
 $fCO_2(2.63, 2000) = 576.5 \mu\text{atm}$
 $\Omega_{Ar}(2.63, 2000) = 0.74$
 $\Omega_{Ca}(2.63, 2000) = 1.15$

- (a): $pH_T(20, 0)$ is the pH on the total scale at temperature of 20 °C and pressure of 1 atm.
 (b): $pH_F(5.72, 1000)$ is the pH on free scale at temperature of 5.72 °C and pressure of 1000 dbar (98.7 atm). pH_F is calculated from DIC and TAlk where DIC in turn is determined from TAlk and $pH_T(20, 0)$.

6. pH comparisons between bottle and float data

For the SOCCOM effort, use of the total pH (pH_T) scale is recommended. The other scales commonly used in seawater are the seawater scale (pH_{sw}) and free scale (pH_f)⁸. A comprehensive description of the metrology of pH can be found in Dickson et al. (2016). The Deep-Sea DuraFET pH sensor measures the free hydrated hydrogen ions and pH_f would be the best scale for this sensor in particular because the pressure dependence of bisulfate ion in seawater is not well known causing an uncertainty in the calibration of the pH data at depth compared to the surface reference. However, the DuraFET sensors are calibrated and validated on the pH_T scale as this is the scale of choice for spectrophotometric bottle pH measurements in seawater.

Table 6 provides an overview of the calculated pH at 25 and 0 °C and at both the surface and 2000 dbar using different pH scales. This table shows that the numerical values of pH_T and pH_{sw} are quite similar, due to the fact that hydrofluoric acid has a small contribution to hydrogen ions in seawater, but the difference with the free scale is appreciable. Of particular note is that the temperature and pressure dependence of the pH_f and pH_T scales differ which is a cause of ambiguity in the DuraFET pH values reported. With the advances in pH sensor technology a careful evaluation of the temperature and pressure dependence of pH in seawater is urgently needed.

Table 6. Comparison of pH scales for different temperatures and pressures ^a

S	T (°C)	P (dbar)	pH_{sw}	pH_T	pH_f
35	25	0	7.514	7.523	7.635

⁸ $pH_f = -\log\{H^+\}$, $pH_T = -\log(\{H^+\} + \{HSO_4^-\})$, and $pH_{sw} = -\log(\{H^+\} + \{HSO_4^-\} + \{HF_0\})$, where $\{H^+\}$ indicates the activity of free hydrated hydrogen ions.

35	0	0	7.876	7.883	7.824
35	25	2000	7.443	7.452	7.552
35	0	2000	7.793	7.799	7.839

^a: calculated using the CO2SYS V2.2 program where TAlk=2300 $\mu\text{mol kg}^{-1}$; DIC=2230 $\mu\text{mol kg}^{-1}$; $\text{PO}_4 = 2 \mu\text{mol kg}^{-1}$; and Si =50 $\mu\text{mol kg}^{-1}$

An example of the magnitude of corrections of pH for a depth profile of a calibration station, Station 40 on P16S, 2014 where a SOCCOM floats was deployed, is shown in Figure 4. The red line is the pH_T measured from CTD/Bottle samples (20 °C, 1 atm) and the green line is the calculated pH_T at in situ temperature and pressure which would be similar to a pH profile obtained from a SOCCOM pH sensor. At a pressure of 1600 dbar and in situ temperature of 3.15 °C the difference between the validation data at 20 °C, 1 atm and in situ pH data is 0.188 of which 0.242 is associated with the temperature difference and -0.065 is the pressure effect on pH. In comparison, the difference between measured pH_T (20, 0) and calculated $\text{pH}_T(20, 0)$ from TAlk and DIC for the shipboard measurement is -0.005.

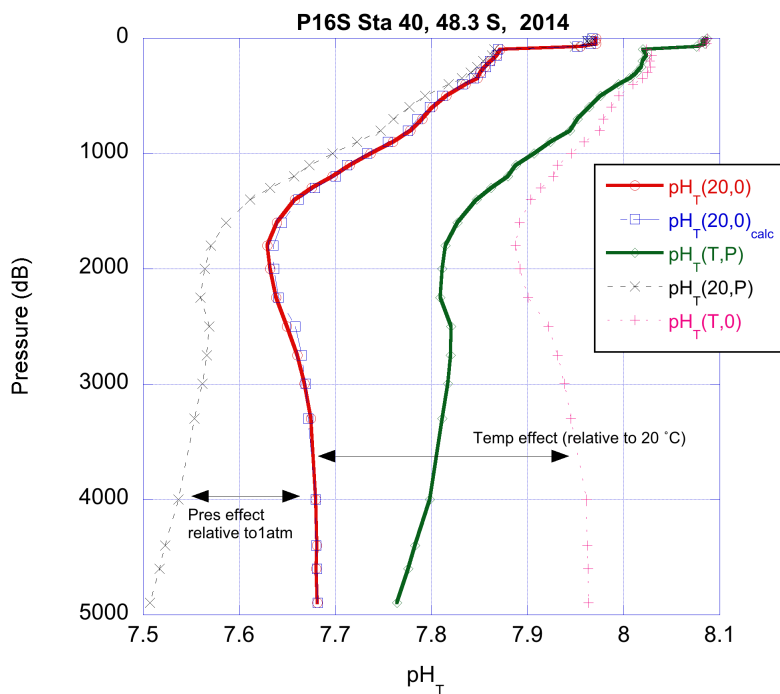


Figure 4. Example of pressure and temperature effect on pH based on a CTD/bottle cast on cruise P16. The red line is the interpolation of the pH_T measured by spectrophotometry (open red circles). The blue open squares are the pH_T values calculated from TAlk and DIC. The green line is the calculated pH_T at in situ temperature and pressure mimicking a float profile.

The dashed line with crosses is the effect of pressure relative to the measured data, and the dashed line with plus symbols is the effect of temperature relative to 20 °C.

Both temperature and pressure are appreciable corrections that are sensitive to the dissociation constants used. To calculate the effect of temperature on pH requires DIC or TAlk as a second inorganic carbon parameter but the accuracy of the measurement of the inorganic carbon parameter has little effect on the estimate. For instance, a 1 % uncertainty in the IC parameter (DIC or TAlk) will translate to a negligible uncertainty of 0.0005 in the pH for a conversion from 20 °C to 0 °C. Thus for validation samples taken to shore for the purpose of comparing pH, the TAlk measurement need not be of high accuracy. The temperature effect on pH is about 0.2 % °C⁻¹ on log scale. The pressure correction is about -0.04/1000 dbar. Only one set of constants is available for this correction, and its uncertainty is unknown. Since there are uncertainties in the constants and conversions from in situ pH from the float to spectrophotometric pH measurements it is prudent to attain the highest quality DIC and TAlk measurements as these measurements can provide an independent estimate of pH.

7. Utilizing multiple linear regressions to adjust pH and NO₃ sensors on SOCCOM floats

Several approaches can be applied to adjust the pH and NO₃ data from sensors on the floats but robust means to do so in situ are limited. During the first years of SOCCOM it was realized that applying multiple linear regressions (MLR) developed from high quality shipboard data in the region is a powerful means to discern offsets in float sensors at depth. The pH and NO₃ sensors appear to vary in a consistent manner within the pressure and temperature ranges over which they profile. This makes it possible to adjust the profile based on sensor-offsets obtained by comparing the sensor measurements at depth with MLRs created for depths of 1000- 2100 dbar.

The MLRs for NO₃ and pH are created with the same independent/predictor variables: P, T, S, and O₂ as these variables are measured on each of the floats that carry the pH and NO₃ sensors. Therefore, each float contains the information for checks of the NO₃ and pH sensors on board. The overall approach to create the MLRs is described in Juranek et al. (2009) with consideration of cross correlation and overfitting issues that can plague MLR approaches.

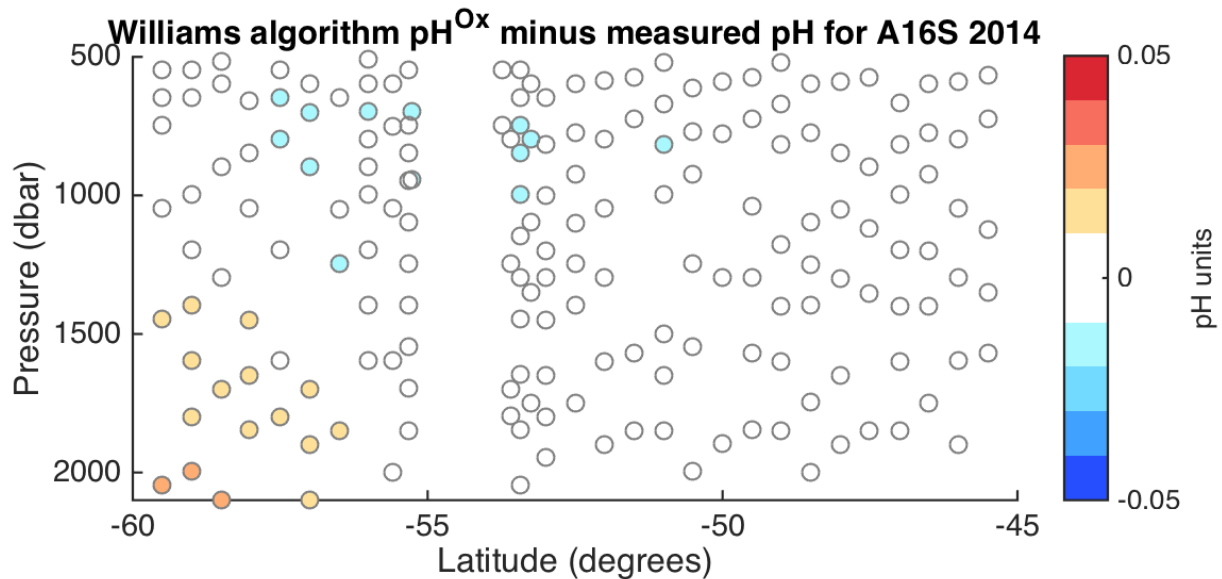
The empirical multiple linear regression relationships are developed from cruise data in 2011 (S04P) and 2014 (P16S) in the South Pacific south of 45 °S for depth from 1000 to 2100 dbar. The depth range and associated narrow parameter space increases the goodness of fit and avoids spurious results that can occur when independent/predictor variables are related as often is the case for biogeochemical and physical parameters in the ocean.

The MLR algorithms determined over the 1000 to 2100 m range are:

$$pH_T(T, P) = 1.380 + 1.8020 \times 10^{-3} O_2 + 0.17859 S + 7.4820 \times 10^{-3} T - 3.966 \times 10^{-5} P, r^2 = 0.98, s. d. = 0.004 \quad (3)$$

$$NO_3 = 544 - 0.108 O_2 - 11.4 \sigma_\theta - 4.92 S - 2.69 T - 3.14 \times 10^{-4} P, r^2 = 0.85, s. d. = 0.3 \quad (4)$$

Details on the algorithms can be found in the supporting information of Williams et al. (2016). Algorithms for pH_T utilizing NO_3 instead of O_2 have been developed as well with similar uncertainties but since the O_2 sensors on the floats are more plentiful and more accurate, the algorithms with O_2 will be used exclusively for the purpose of float pH adjustment. For the pH algorithms the discrete pH measurements at 20 or 25 °C at the surface were corrected to in situ values using the dissociation constants in Table 4. The outputs from algorithms have been compared with independent cruise data in the South Pacific (P18S-2007), Southern Indian Ocean (S04I-2012), and Atlantic Ocean (A16S-2014) and differences are generally within the limits of 0.01 for pH and 0.5 $\mu\text{mol kg}^{-1}$ for NO_3 (Figure 5). At the geographic limits and in areas of deep-water formation the differences tend to increase and this should be taken into consideration when float data are adjusted in these regions.



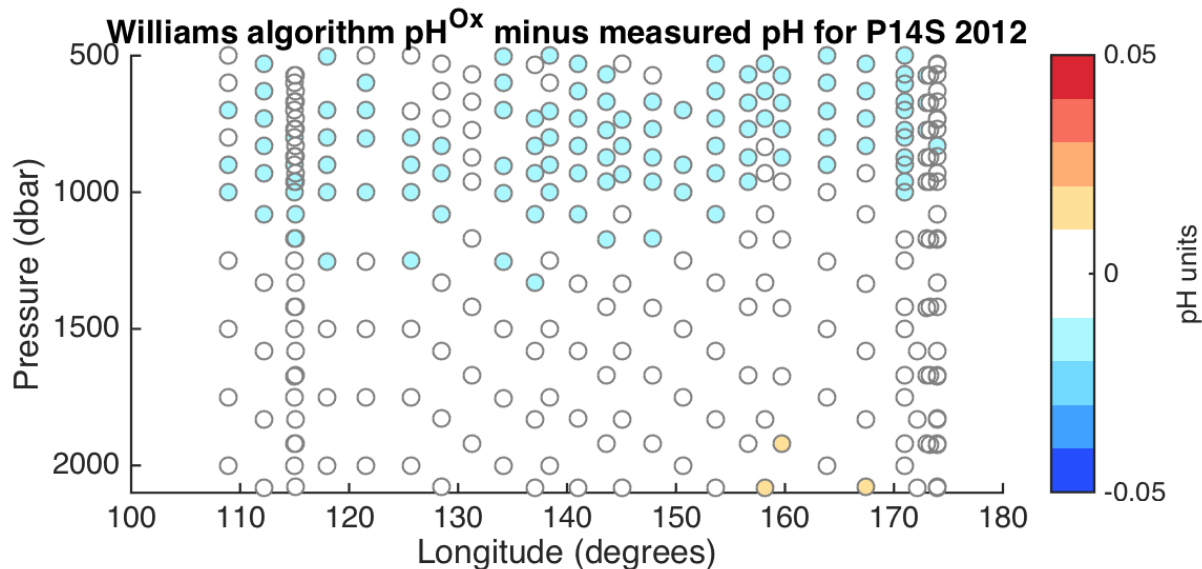


Figure 5. Comparison of the MLR output for $pH_T(T,P)$ with measured values not used in the MLR development in the Southern Ocean. A16S is a meridional line in the South Atlantic and P14S is a zonal line ($\approx 62^\circ S$) South of Australia. The circles depict the sampling depth and those with colorless centers indicate that the MLR output is within the uncertainty limits of 0.01 of the analysis.

For SOCCOM all pH and NO_3 sensor data are adjusted based on the algorithm listed above. Adjustments are performed based on pH and NO_3 float data acquired at depth. For pH an additive adjustment is made to the reference potential k_0 (see eqn. 1) to reach correspondence with the algorithms values. For NO_3 the adjustment is additive to its reported concentration value.

8. Data management, quality control and adjustments

Successful full implementation of the SOCCOM float program requires improved efficiencies and protocols in data acquisition and management. Continued interactions with Argo data acquisition centers (DAC) are a must to assure full incorporation of biogeochemical sensors and biological sensors into the Argo data suite. This is particularly true if the SOCCOM effort is considered a precursor of a global biogeochemical and biological sensor array. The challenges of making a developmental effort like SOCCOM, which requires flexibility and adaptations but also the more rigid requirements of the more mature array are significant. At the same time piggy-backing on the Argo array is a great benefit for lessons learned and established infrastructure.

The SOCCOM biogeochemical parameters measured on floats O_2 , NO_3 and pH will be transitioned from investigator based management (K. Johnson and S. Riser lead) to a streamlined and consistent approach managed by the University of Washington (S. Riser). The biogeochemical data will be processed in parallel with the core Argo data following agreements with the Argo steering group.

The Argo processing is as follows⁹. There are three relevant files that are created for each float: a core-Argo, B-Argo and M-Argo profile and trajectory files. The core-Argo profile and trajectory files contain only the CTD data. The parameters included in a core-Argo file are pressure, temperature, salinity, and conductivity. The B-files, where B stands for biogeochemistry or biology, will include all other parameters except temperature, salinity, and conductivity. They will include all intermediate parameters that are necessary for calculating parameters of interest such as the UV spectra for NO₃ and luminescence decay time for the O₂ optodes. The core and B files are created primarily for ease of calculating and, when necessary, adjusting parameters. The core and B files are then merged into M-files which will be of most interest to investigators. They will contain all ocean variables that the float measures. This file will contain the concentration of interest for the core parameters and parameters found in the B-file but not the intermediate parameters. The transition to this new data processing scheme (called version 3.1) will be challenging and possibly slow down the release of biogeochemical data from floats while the protocols are being implemented.

9. Product development

A priority for SOCCOM is to utilize the large increase in high-resolution data in the Southern Ocean to estimate the state of biogeochemical properties, and the processes and rates involved. In particular, the magnitude and causes of seasonal variability will be established for the first time. The year-round presence of the profiling floats and ability to sample under ice will offer seasonally and spatially unbiased results.

Two approaches can be followed for determining fields and processes involving inorganic carbon parameters based on the float and additional data. The first approach is to determine TAlk empirically from float data or other means. The derived TAlk and measured pH from the float can then be used with the thermodynamic relationships and constants (Table 4) to determine any of the other carbon system parameters of interest such as DIC, pCO₂, Ω_{Ar} or Ω_{Ca} . Robust relationships of TAlk and salinity and temperature have been derived for surface water (Lee et al., 2006; Takahashi et al., 2014) based on the conservative behavior of TAlk on regional scales. For subsurface, remineralization and mixing precludes simple relationships and more sophisticated algorithms are established based on the global ocean water column carbon dataset (GLODAP-2, Key et al., 2004). Carter et al. (2016) developed an algorithm (and associated MATLAB code) to estimate alkalinity globally, referred to as “locally interpolated alkalinity regression.” Specific algorithms will also be developed for the Southern Ocean as part of SOCCOM (Williams, pers. com.)

⁹ www.argo.ucsd.edu/Data_FAQ.html

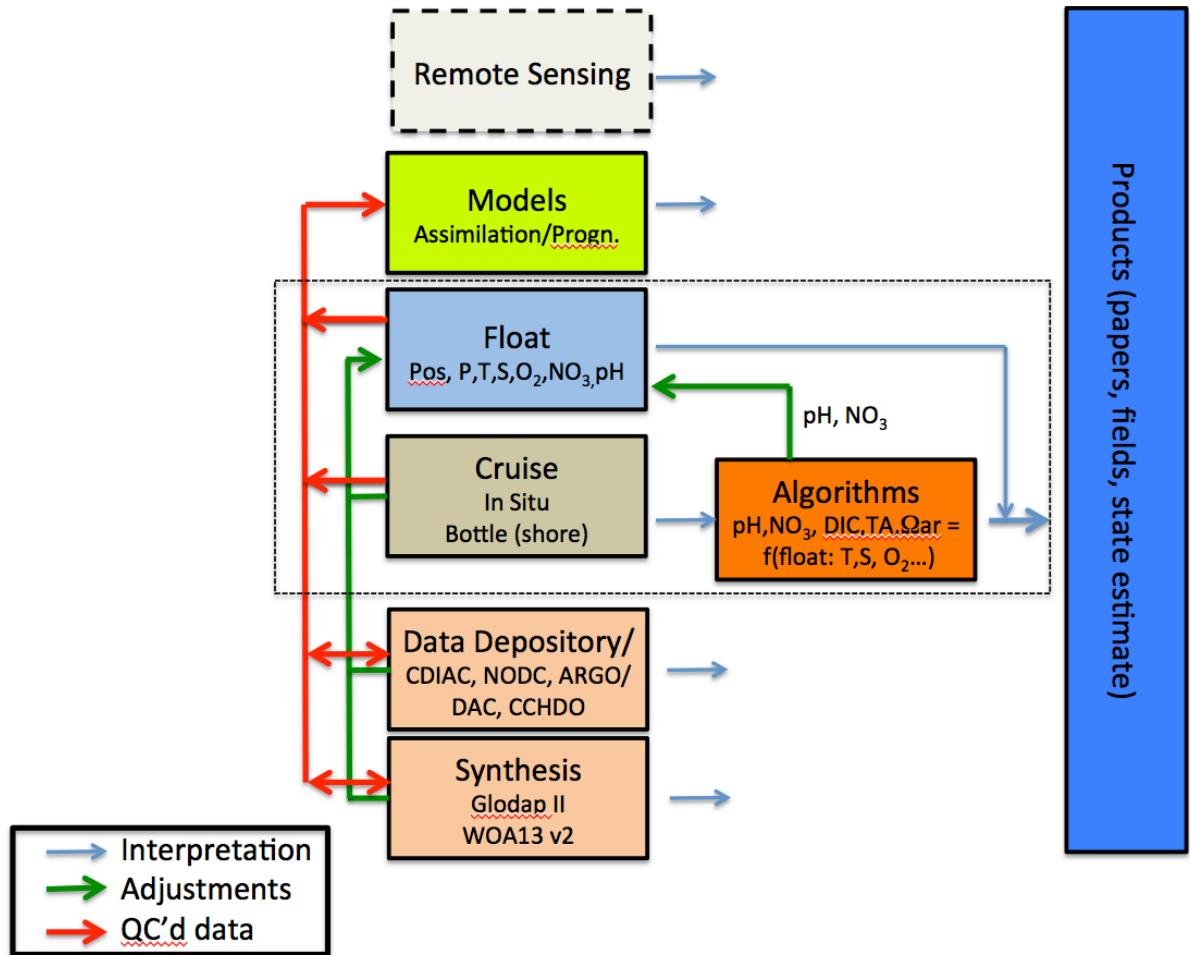


Figure 6. Diagram of pathways for data flow and quality checks. The blue lines indicate the data streams used for interpretation, the green lines are the pathways used to adjust the float data and the red lines are the pathways of quality controlled data flow. The double arrows indicate that the data repositories both ingest and contribute to the quality control. The procedures in the dashed rectangle are the focus of this report. Note that most depositories have multiple functions.

A second approach is to establish empirical relationships with the parameter of interest and predictor variables that can be measured on floats, or determined from bottle data from cruises and applied to float data. This approach is similar to the MLR algorithms used to adjust the pH and NO₃ data at depth for floats. This method does not necessarily depend on pH data or TALK estimates. However, it does assume that the MLR with predictor variables that are not inorganic carbon system parameters can faithfully predict the inorganic carbon system parameters of interest on scales that are relevant to the carbon cycle, from sub-mesoscale to mesoscale and beyond; and time scales, from seasonal through interannual to decadal and beyond. Any process that changes the carbon system parameters with respect to those properties used in the MLR will degrade the estimates of

the evolving carbon system parameters. For example, in the surface mixed layer functional dependencies can change rapidly due to gas transfer and biological productivity and often cannot be well represented by MLRs. On decadal scales anthropogenic CO₂ increases will invalidate MLRs predicting DIC, pCO₂ or pH. While both approaches need to be investigated in full, it is probable that parameters that can be better predicted in the surface layer such as TAlk along with measured float pH will have some advantages over large-scale MLR approaches not using inorganic carbon system parameters in the surface mixed layer.

10. Outlook

The SOCCOM effort is in its infancy and making the necessary preparations to fully utilize the observations and models when fully in place. As of February 2016, 37, or 18 % of the planned 200 total, floats are deployed; this number will be close to 50, or 25%, by the end of May 2016. Implementation of robust data management and biogeochemical data adjustment schemes is underway but will require continued close interaction with Argo and significant resources from SOCCOM. As described above, creative and robust approaches using multiple linear regressions from CTD/bottle data are used to correct NO₃ and pH data to within 0.5 μM and 0.01, respectively, which is within current instrument specifications. Continued checks and improvements of the algorithms utilizing CTD/bottle data and bottle synthesis products that will be delivered during the SOCCOM project are advisable. Further, the program must rigorously assess sensor performance and failures to ensure that sensor reliability, accuracy and precision are continuously improved. This will minimize the dependence on adjustment procedures and result in data of ever greater utility.

Biological data from the profiling floats, "bio-optics", are not addressed in this report but will require a similar scrutiny on sensor performance and approaches to adjust sensor values. As many of the bio-optical parameters are not state variables and sometimes are operationally defined this will be a much greater challenge. Uncertainty estimates will also be greater and applicability to some of the large-scale questions raised in SOCCOM will be limited. However, their use in study of seasonality of the biological cycle and spatial heterogeneity (both in the horizontal and vertical) of biological parameters, and their influence on the inorganic carbon cycle will be invaluable. Moreover, the bio-optical parameters link closely to several of the space borne measurements offering the possibility to expand the 2-D view of the ocean surface from space to a 3-D or even 4-D view that includes time and depth dimensions.

A major focus of SOCCOM as part of unraveling the mysteries of the Southern Ocean is to vastly improve our understanding of biogeochemical processes and associated estimates of biogeochemical fields in the Southern Ocean as a whole. The measurements and tools to tackle this large scale problem are being developed and deployed over the full 6 year time scale of the grant, but it is critical that initial estimates be made as early as possible with a small subsets of the array in order to identify and address as early as possible important issues such as those addressed in this report. Similar questions have to be addressed with respect to models that will improve throughout the SOCCOM period.

Even with limited float deployment to date several nuggets or "firsts" can be obtained from the quality-controlled data. This pertains particularly to some of the first biogeochemical observations in wintertime when conditions are such that ship-based observations are challenging and ability to sample under ice. Under ice processes as pertaining to biogeochemistry in seasonal sea-ice regions can now be determined. Biogeochemical state estimates can be validated by float measurements particularly for the wintertime. Observing System Simulation Experiments (OSSEs) for network design can be checked with the floats currently deployed and the validity of the assumption used in the OSSEs can be verified.

The next major development for biogeochemical investigation in SOCCOM will be the development of so-call carbon products, or fields of carbon parameters such as TAlk, DIC, Ω_{Ar} and Ω_{Ca} using a variety of approaches ranging from interpolation of float data, to regression analyses and numerical models. By producing these fields through time key processes such as net community production, calcification, and respiration can be inferred. Moreover, the temporal evolution of pCO₂ patterns and saturation horizons can be studied and the role of the Southern Ocean as a major anthropogenic CO₂ sink.

Appendix A. Charge for the carbon working group (CWG) of SOCCOM

CHARGE FOR THE SOCCOM INORGANIC CARBON SYSTEM WORKING (CSW) GROUP
[Original July 11, 2015; Edited December 2, 2015]

RATIONALE-

A major objective of SOCCOM is to assess the changing carbon sink and associated changes in inorganic carbon in the Southern ocean through utilization of new autonomous technology. For many properties, such as aragonite saturation or dissolved inorganic carbon, the autonomous sensors do not directly measure the parameters of interest. In particular, for the inorganic carbon system, SOCCOM currently measures only pH. In addition to the observed pH, a second carbon parameter must be obtained in order to solve the full inorganic carbon system. This will be accomplished by using stoichiometric and/or statistical relationships derived from the bottle datasets available. These algorithms will then be applied at the location of the float measurements using the in situ [float] data. Such relationships may also be used to generate pH and other tracer estimates that can be used to quality control and adjust sensor data. The overall approach will provide a dataset with a resolution of that of the float observations. Time resolution will be on the order of a week and spatial resolution will be 100's of km in the horizontal and meters in the vertical down to 2000 m.

Several groups within SOCCOM are developing and applying these novel empirical approaches to determine the inorganic carbon system parameters of interest from the autonomous sensors. A working group within SOCCOM is desired to exchange ideas; to provide a mechanism to share results; and to apply the approaches in near real-time utilizing the autonomous sensors. The working group aims to facilitate rapid dissemination of results with sound interpretation, providing clear confidence intervals and specifying appropriate caveats and limitations.

GOALS-

The working group will address several specific questions with the principal goal to obtain a measurement-based estimate of the full inorganic carbon system including pH(measured and calculated), DIC, TAlk, $p\text{CO}_2$, CO_3^{2-} , and Aragonite and Calcite saturation indexes.

The working group will engage in the following activities:

1. Assess quality and issues with the independent [float based] variables including drift and hysteresis:

- Nitrate,
- Oxygen
- pH

- Temperature
- Pressure

Priority task: create an interpolated estimate of the oceanic pH using algorithms from high quality shipboard/laboratory inorganic carbon system measurements and related parameters that can be used to test the behavior of the pH sensor.

2. Develop a streamlined approach for initial QC and adjustment of float-based variables and a documented approach for users to suggest adjustments and flags.

3. Document uncertainty and validity (time, distance, depth range) of algorithms. A particular focus will be on distribution of error/uncertainty in time and space.

Priority task: Provide an interpolated estimate of alkalinity that can be used with the pH sensors data to produce a first set of papers on the carbon system as determined using the floats (including estimate of uncertainty)

Longer-term objective: Examine all aspects of the carbon system measurements and calculations so as to produce the highest quality estimates of DIC, pCO₂ and pH,

4. Create a best practices manual for ad-hoc float sensor validations and checks

*[5. Provide advice to the SOCCOM exec on the coordination of manuscripts and presentations]

*[6. Assess quality and issues with the variables from optical sensors on floats to measure chlorophyll and backscatter.]

* Possible activities at a later point

SOCCOM Carbon Working Group members:

Briggs, Ellen: surface water pCO₂, ice effects

Bushinsky, Seth: float sensors (oxygen)

Carter, Brendan: Alkalinity algorithm development and application

Dickson, Andrew: shore based discrete inorganic carbon system measurements

Feely, Richard: P16S inorganic carbon data

Gray, Alison: algorithm development and application

Johnson, Ken: float data

Juranek, Laurie: algorithm development and application

Key, Bob: Bottle data assembly, including historical data; hydrography

Riser, Steve: float data

Talley, Lynne: P16S measurements, CTD hydrography

Williams, Nancy: algorithm development and application

Sarmiento, Jorge: model application

Russell, Joelle: model application

Verdy, Ariane: Biogeochemical Southern Ocean State Estimate (SOSE)

Wanninkhof: Coordinator

APPROACH:

- Bi-Weekly teleconferences with assignments of tasks & reports
- Protected site for sharing data algorithms and preliminary findings
- Inquiry to [outside] experts on regimes, approaches, methods, & analyses

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