Biogeochemical data in Argo (oxygen, pH, nitrate)

Southern Ocean Carbon & Climate Observations & Modeling (SOCCOM)

Ken Johnson, MBARI
input from
Orens de Fommervault, LOV
Catherine Schmectig, LOV
SOCOMM is launched!

The SOCCOM project has been awarded funding from the National Science Foundation and was officially launched on September 9, 2014.

Latest News

Southern Ocean Town Hall at AGU
Join us on Dec. 14th to discuss SOCCOM and other progress

SOUTHERN OCEAN CARBON AND CLIMATE OBSERVATIONS AND MODELING

The Southern Ocean Carbon and Climate Observations and Modeling project (SOCCOM) is an NSF-sponsored program focused on unlocking the mysteries of the Southern Ocean and determining its influence on climate.

Housed at Princeton University and administered by the Princeton...
Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM), 6 years, ~200 floats

Directorate
- Joellen Russell, U. Arizona
- Heidi Cullen, Climate Central

Theme I
- Jorge Sarmiento, Princeton
- Lynne Talley, SIO

Theme II
- Ken Johnson
- Steve Riser, U. W.
- Biooptics (Emmanuel Boss, Maine, Oscar Schofield, Rutgers)

Theme III
- Jorge Sarmiento, Princeton
- Lynne Talley, SIO
- Joellen Russell, U. Arizona
- Heidi Cullen, Climate Central
• NSF funding will enable ~30 to 40 biogeochemical (BGC) floats/y with pH, O$_2$, NO$_3^-$, ~200 total
• NOAA will provide half of the basic CTD floats
• NASA will provide biooptics (WETLabs FLBB or MCOM - ~FLBBBCDOM) for ~1/2 of floats
• Support for one Biogeochemical Argo data manager at UW (job search beginning) for real time and DM QC, data formatting. Intent is to send complete “B” files to DAC.
• CLIVAR quality calibration of chemical sensors at deployment
• Southern Ocean State Estimate (SOSE) with biogeochemical data assimilation of float data and error estimates
• Integrated biogeochemical modeling program linked to GFDL Earth System Model
• OSSE assessment of system design
• BGC floats will operate on a basic Argo mission
  – Apex and Navis floats at this point in time
  – 1000 m park depth
  – 2000 m (or nearly so) profile depth
  – 5 to 10 day cycle time, ~260 cycles
  – Goal is 4 to 6 year deployments
SOCCOM array will be circum-polar. Deployments will depend on collaborative cruise opportunities. Coordinated by Lynne Talley, SIO.
~10% Error in So. Ocn. CO$_2$ uptake

Figure 9. (a) Error estimates for the annual reconstruction of the Southern Ocean CO$_2$ uptake, in PgC, for varying number of floats. The error estimates are calculated as the standard deviation of the basin-integrated annual CO$_2$ flux from the reconstructed fields and the true model. (b) The percentage of the Southern Ocean, south of 30º S, where the monthly error estimate is larger than the threshold value of 1 mole m$^{-2}$ yr$^{-1}$. In both plots, different lines reflect reconstructions with varying levels of sampling error. The error in the estimate of total uptake is less sensitive to the sampling error than the percentage of exceedance.
Report from the SOCCCOM Data Management Meeting
University of Washington, Ocean Teaching Building
14 October, 2014
Report 21 Oct. 2014 v.2

Attendees (at UW)
Steve Diggs (SIO)
Ken Johnson (MBARI)
Bob Key (PU)
Steve Riser (UW)
Lynne Talley (SIO)
Dana Swift (UW)
Annie Wong (UW)

Attendees (virtual)
Emmanuel Boss (U.Maine)
Luke Colleti (MBARI)
Igor Heifetz (PEI)
Robert Hotinski (PU)
Laurie Juranek (OSU)
Matt Mazloff (SIO)
Josh Plant (MBARI)
Carole Sakamoto (MBARI)
Ariane Verdy (SIO)
Heidi Wells (PEI)

Agenda
Goals of meeting:
(1) Start discussion of complex issues (formatting, calibration, data products, web portals)
(2) Progress on institutional/individual responsibilities (i.e. fill in implementation plan), P16S pre-SOCCCOM data sets
• Biogeochemical Argo data require adjustment to be most useful (Oxygen, nitrate, pH...)

• Adjustments can be done in near real time

• Adjustment factors may change in time as more data is accumulated (e.g. air oxygen calibration)

• These adjustments might apply to whole data set, so a fair amount of reprocessing might be desired

• What is the protocol/policy for such reprocessing? How are reprocessed data sets identified? Users informed? Previous versions archived?
Example of GO-SHIP section and calibrated pH sensors from BGC floats
All BGC sensor data require some adjustment to be most useful.

1. What kind of adjustments are required?

<table>
<thead>
<tr>
<th></th>
<th>Gain</th>
<th>Offset</th>
<th>Drift</th>
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<tr>
<td>Salinity</td>
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<td>$O_2$</td>
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<tr>
<td>$NO_3^-$</td>
<td>&lt;10%</td>
<td>XX</td>
<td>XX</td>
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<tr>
<td>pH</td>
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<td>XX</td>
<td>XX</td>
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<tr>
<td>Biooptics (FL, BB)</td>
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SOCCOMViz 6.0 - Apex/ISUS Data Visualization for the SOCCOM program

ISUS nitrate sensors and Deep-Sea DuraFET pH sensors in Webb Research Apex profiling floats

What's new? Twelve floats were deployed in the Southern Ocean from R/V Revelle on the US Repeat Hydrography P16S cruise. Seven of these floats have pH sensors. This project is supported by the US NSF Polar Programs with some floats contributed by NOAA through the US Argo Program.

Quick Instructions

Float list and link to complete Ascii data files

Data Adjustments

Map of float tracks

Apex/ISUS description page

Select Output Type and Send Request:

Plot Text File

SEND

Raw Data or Adjusted Data:

Raw

Adjusted

Select Float (ctrl click for more than one)

5146SoOcn............N/O/d
5426DrakePass........N/O/d
6967SoAtlantic......N/O/FL
0088RossSea.........N/O/FL
5388SoOcn..........N/O/FL
7522SoOcn..........N/O/FL
751SoOcn............N/O/FL

Select One X Variable

Nitrate[muM]
Depth[m]
Date
Salinity
Temperature[°C]
DensityAnomaly
Oxygen[muM]
OxygenSat%
Chlorophyllum/"

Select Y Variables (ctrl click >1)

Nitrate[muM]
Depth[m]
Salinity
Temperature[°C]
DensityAnomaly
Oxygen[muM]
OxygenSat%
Chlorophyllum/"

Enter Ranges if Autoscale is Off (Min & max ranges default to 0 and 200 if Autoscale off and box is empty. Depth ranges are entered as negative values. Y Variables)

Autoscale X & Y axis:

On
Off
Adjustments described in a meta-notation in header of FloatViz QC files.

```
//0
//Oxygen, 1.209                comment
//Nitrate, 1,1,1.5,0            O2 gain
//Nitrate, 50, 1, 2, -1
//pH, 1, 0.0173, 0
```

Cycle #, Gain, Offset, Drift

Gain is Correct value / Raw value

Offset defined to be the offset relative to previous profile, or the correct value on first profile.

Drift is the rate of sensor drift per year.
Corrections should be done in raw measurement space – volts, not pH; phase, not O2. But that is almost impossible for nitrate. So just do nitrate changes.

range test, visual stuck value test, no automated spike testing (but we do so for published data).
Float 0276  SBE Navis float with MCOM.  2m resolution for BGC parameters except nitrate (due to power). Spike test not appropriate for backscatter (POC).
A Pacific FLBB (7647) and an Atlantic MCOM (0276)
Oxygen

- Calibration by air oxygen measurements.
- QC required for drift and calibration offset.
Air %Sat = 90.9 ± 0.9 % (N>200). Sensor gain correction is $1/0.909 = 1.100$ (1.106 when summer values filtered out).
As more air oxygen data come in, the gain factor will be revised and applied retroactively to the whole data set (all profile files recalculated).

How frequent is too frequent for recalculation?

How do you track versions?

Archive each version? DOI’s?

Version numbers??
Final reality check – compare float O2 to World Ocean Atlas gridded data for offsets or drift. But in So. Ocean, agreement won’t be so pretty.
Oxygen action items

• Who computes air oxygen gain??
• How frequent to update the gain value and reprocess the adjusted data??
• Use all air oxygen values or only when surface ocean close to saturation??
• We’ll need to archive air oxygen – not an Argo requirement (yet), but should be in netCDF files somewhere.
• We need to ensure this works for all SOCCOM optode foils. Older 3830 foils don’t look quite so good. Is that because newer foils are better characterized for temperature? Or because the pre-SOCCOM floats got unusually good foils?
• How do we do this with Navis floats as their sensor never sees air (in CTD flow stream)?? Request SBE add a pre-deployment air calibration step?
• Who does long term QC check for sensor drift?
• What O2 climatology? WOA?
DuraFET, an Ion Sensitive Field Effect Transistor (ISFET) pH sensor ‘chip’ produced by Honeywell

Redesigned at MBARI to operate in the ocean at high pressure, the Deep-Sea DuraFET

Ready for deployment

License to Sea-Bird Scientific in process
pH sensor calibrated for absolute pH, T and P coefficients at MBARI. pH within 0.03 and we believe we’re getting better at calibration.
SBE implementation of MBARI Deep-Sea DuraFET on Navis float off Kona coast – 2 m resolution in pH!!

<0.01 pH adjustment
pH action items

• Who computes pH sensor offset and gain??
• How frequent to update the gain value and reprocess the adjusted data??
• What pH climatology for deep pH? GLODAP V2? Gridded?
• Change pressure correction computation from polynomial to a great big look-up table???
The challenge, an accurate, affordable, pressure tolerant pH sensor.
Team DuraFET™

Bob Carlson, Honeywell, Inc.
Ken Johnson, Monterey Bay Aquarium Research Institute
Todd Martz, Scripps Institution of Oceanography
+Sea-Bird Scientific (Hochstein, Murphy, Brown...)

XPrize pH sensors
- ISFET chip produced by Honeywell
- Redesigned by MBARI
- Tested by SIO
- Commercialization by Sea-Bird Scientific
$2 million prize for ‘best’ pH sensor.

All Team Durafet Team Members hereby agree that Honeywell International Inc. .... shall donate any and all Wendy Schmidt Ocean Health XPRIZE winnings (less any tax or prize receipt obligations) to an ocean health non-profit organization such as the Argo Array

The intent is to help equip Argo with pH. Why? We need a long-term pH observing system.
Long-Term Nitrate Measurements in the Ocean Using the in situ Ultraviolet Spectrophotometer: Sensor Integration into the APEX Profiling Float

KENNETH S. JOHNSON, LUKE J. COLLETTI, HANS W. JANNASCH, AND CAROLE M. SAKAMOTO

Monterey Bay Aquarium Research Institute, Moss Landing, California

DANA D. SWIFT AND STEPHEN C. RISER

School of Oceanography, University of Washington, Seattle, Washington
Nitrate offsets/drift almost always constant with depth (Johnson et al., JAOT, 2013)
Float 6401. We have argued (Johnson et al., JAOT, 2013) that these drifts/offsets can be corrected to within 10%. I.e. 4 uM drift can be correct to within about 10% of correct value.
Float 6401. Corrected nitrate in upper 30 m: 0.40 ± 0.24 µM
Surface (0 to 30 m) data from float array at Station Papa after adjustment using (mostly) 1000 m data.
Raw Station Papa data.
Nitrate QC & Data Adjustments at LOV

Orens de Fommervault

(PhD. Student in Fabrizio D’Ortenzio’s group)
In situ experiment

The SUNA sensor was embedded in a Niskin bottle mounted on a CTD-rosette.

- Downcast the bottle was open (Temperature, Salinity and Pressure variable)
- Upcast the bottle was close (Temperature and Salinity fixed, Pressure variable)
Pressure dependence of bromide spectra is suspected. Correction may be applied to the extinction coefficient of seawater:

$$E_{SW}(\lambda, T_{is}, P) = E_{SW}(\lambda, T_{is}) \cdot \left(1 - f \cdot \frac{P}{1000}\right)$$

Extinction coefficient of seawater corrected from insitu temperature (Sakamoto et al., 2009)

An empirical value of 2% per 1000 dbar is proposed for the correction factor (f).
Additional Pressure adjustment?

- Difference of 20% at depth (deep nitrate value ~ 8µM)
Difference of 35% at depth (deep nitrate value ~ 6µM)
Additional Pressure adjustment?

North Atlantic float

- Difference of 3% at depth (deep nitrate value ~ 25µM)
A bias in the TCSS correction is induced because SUNA and the CTD are not sampling the same water. On PROVBIO-V2 (which are used in NAOS), SUNA are located around 1.5m under the CTD intake.

Temperature and salinity from the CTD are linearly interpolated at the depth of the SUNA. This allow measurement errors and spike to be corrected, especially in depth of strong temperature and salinity gradient.

\[
S(z + \text{lag}) = S(z) + \text{lag}. \frac{S(z+\Delta z)-S(z)}{\Delta z}
\]

\[
T(z + \text{lag}) = T(z) + \text{lag}. \frac{T(z+\Delta z)-T(z)}{\Delta z}
\]
World Ocean Atlas

WOA 2009 Annual Climatology 5x5° (Garcia et al., 2010)  
(http://www.nodc.noaa.gov)
Possible QC of the “reference value” using the number of point and the standard error given by the WOA
Mediterranean Sea

- Low concentrations at depth: around 8µM in the Western basin and 5µM in the Eastern basin

Data obtained from MEDAR-MEDATLAS (Maillard et al., 2005), MATER (Maillard et al., 2002) and SESAME programs as well as from specific
Regional range test

Using WOA
Value at 1000m-depth

\[
\begin{align*}
R_{\text{Min}} &= \text{Clim} + 3 \cdot \text{std} \\
\text{RangeMin} &= \min\left(-2, \max\left(-2, \frac{\text{Clim} - 3 \cdot \text{std} + 2}{1000 - 250} \cdot (P + 250) - 2\right)\right)
\end{align*}
\]

Note from KJ – if I did this, it would be to the adjusted data, not raw. And is 3 SD enough???
http://seasiderendezvous.fr/
Drift correction

Long-term drift was determined from the slope of a linear regression of the nitrate concentration at depth (average value between 800m and 1000m-depth) versus cycle number.

Drift versus time, and drift versus cycle were compared. Most often the correlation was higher considering cycle number compared to time.