$O_2$, $NO_3^-$ and pH real time processing, QC, adjustment

Ken Johnson
MBARI
Calibration & Quality Control to produce adjusted data sets

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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<tbody>
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<tr>
<td>$O_2$</td>
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<tr>
<td>$NO_3^-$</td>
<td>&lt;10% **</td>
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<td>XX</td>
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<tr>
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<tr>
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**Collaborating with SCOR WG 147 (COMPONUT) to adapt their nutrient standards for use in ISUS/SUNA calibration.
Step 1: Continue to improve sensors to minimize the need for data correction!

Step 2: Adjust oxygen with a gain correction determined from air (Johnson et al., 2015)

Step 3: Adjust NO3, pH data by comparing data around 1500 m depth with values predicted from a multiple-linear regression eqn fitted to a reference data set at depths 500 to 2000 m to determine initial offset and drift.
Air Oxygen Calibration of Oxygen Optodes on a Profiling Float Array

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Oxygen offset: more or less eliminated with air measurements

- Ken applies correction to oxygen sensor based on air oxygen
- With ongoing air calibrations there is confidence that this is stable
Fouling by organic flocs was a problem in pumped systems. Problem is much reduced by removing the sensor from the pumped stream.

Nitrate at 1000 m, Float 7553
How do we deal with remaining offsets and drifts in nitrate and pH?

Track change at 1000 to 2000 m depth and assume offsets at depth are a constant adjustment over whole profile.
Float 5145 near Hawaii. Offsets occur as a constant shift over whole profile.

Johnson et al., 2010
Float 7564 in the Greenland Sea.
What QC is required? Float 7564 in the Arctic. Nitrate sensor has property that an offset is constant over the whole profile (Johnson et al., in review). QC would apply this offset to all subsequent data.
What QC is required? Float 7564 in the Arctic. Nitrate sensor has property that an offset is constant over the whole profile (Johnson et al., 2013). QC would apply this offset to all subsequent data.
Rather than use WOA as deep reference values, fit multiple linear regression (MLR) in T/S/Z/O2 to high quality data set and use the MLR to predict pH or NO3.

Real-time estimation of pH and aragonite saturation state from Argo profiling floats: Prospects for an autonomous carbon observing strategy

L. W. Juranek,1, 2 R. A. Feely,2 D. Gilbert,3 H. Freeland,4 and L. A. Miller4

Robust empirical relationships for estimating the carbonate system in the southern California Current System and application to CalCOFI hydrographic cruise data (2005–2011)

Simone R. Alin,1 Richard A. Feely,1 Andrew G. Dickson,2 J. Martín Hernández-Ayón,3 Lauren W. Juranek,1, 4, 5 Mark D. Ohman,2 and Ralf Goericke2
pH and Nitrate Algorithm Update
Carbon System Working Group

9/4/2015
Nancy Williams
Laurie Juranek
Dick Feely
**deep NO3**

- [1450 1550 meters]
- float NO3 slope = -2.8653
- regressed NO3 slope = -0.1760

**NO3 anomaly (float - William's regression)**

- NO3 difference trend = -2.6892
Nitrate, 1, 1, 1, 0
Nitrate, 3, 1, -2,-3
-3 drift has probably stopped and should be ~0. How often to revisit this? Or make it automatic?
Nitrate sensor drift - Float 9095
Should we apply a similar technique to nitrate data?

3 umol/kg contours
3 umol/kg contours

Nitrate sensor drifting downward
Float 9095  upper 50 meters of water column
# SOCCOM Data Reference - 02-Nov-2015 05:00:53

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Download a .zip file containing this table as text file

**KEY for SOCCOM DATA REFERENCES**
- ctdDATE, ctdTIME, ctdLAT, ctdLON - CTD taken near drop position, from Exchange format CTD file
- dropDATE, dropTIME, dropLAT, dropLON - Drop Time/Position, from Cruise Report or similar
- sensor - I = ice enabled; O = oxygen sensor; N = nitrate sensor; F = FLubb; p = pH; * = preceding sensor failed on deployment
How about pH? Sensor measures \( V_{RS} \), we compute pH

\[
V_{RS} = k_0 + k_2 \times t + f(P) - RT/F \times \ln(10) \times \log(a_{H^+}a_{Cl^-})_{T,P}
\]

If the sensor drifts, is it change in \( k_0 \), \( k_2 \), or \( f(P) \)?

Our correction scheme assumes the effect is all in \( k_0 \). Changing \( k_2 \) or \( f(P) \) alters profile shape. It’s not possible to change \( k_2 \) or \( f(P) \) to match drift at depth and have reasonable surface values.
Black = Corrected pH
Blue = MLR Algorithm
Green = Raw pH
Black = pH sensors on floats deployed at HOT (Hawaii), upper 40 m
Green = HOT shipboard data, upper 40 m

Measured on float
Estimated from ship data
Computed from pH and TAalk

MBARI Chemical Sensor Lab
Global Biogeochemistry
Carbon Working Group
LIAR Alkalinity regression

Brendan Carter
October 2015
Alk1 = C_1 + C_2\theta + C_3S

Alk2 = C_1 + C_2\theta + C_3S

Alk(1.5) = (Alk1 + Alk2) / 2

LIAR: Locally-interpolated alkalinity regression
pH performance might be improved by removing it from the pumped stream, as for nitrate.

But pH sensor is light sensitive!