The 2008 North Atlantic Bloom Experiment

Calibration Report #3

Calibration of the Dissolved Oxygen Sensors on Float 48 and on The *Knorr* CTD with Winkler bottle samples

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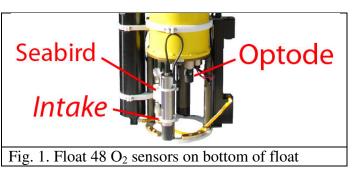
Summary

The Seabird SBE-43 oxygen sensor and the Aanderra optode on float 48 both require calibration and removal of various sensor errors. The optode is poorly calibrated in terms of dissolved oxygen, temperature and pressure. During times of low flow and a closed drogue it can have biases exceeding 10 uMol/kg probably due to oxygen consumption by the float. The SBE-43 exhibits mode-variable biases due to our attempts to reduce pumping energy. By intercomparing these sensors and comparing them with the Winkler bottle samples and SBE-43 sensor taken on calibration casts during Knorr cruise 193 adjustments are developed to bring both float sensors and the Knorr CTD SBE-43 sensor into agreement and into absolute calibration to an accuracy of better than 2 uMol/kg. These corrections are applied to v7 of the float data. The best float 48 oxygen data is obtained from the SBE-43 in all float modes and the optode in down and drift modes. The optode data from settle and up mode still contains systematic errors.

1. Oxygen Sensors, Mission and Errors

Float 48 (Fig 1) was the primary float in NAB08. It carried a SBE-43-CT sensors on the

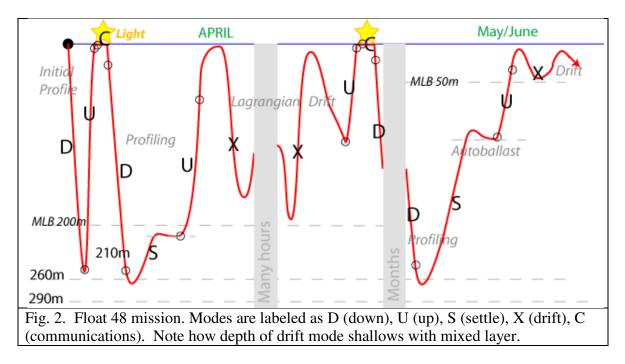
top (SN-3530) and bottom (SN-3529) endcaps with the entrances to the sensors separated vertically by 1.40 m. The bottom CTD also included an inline SBE-43 oxygen sensor (SN-100). Both sensors were pumped for about 2 seconds at 'slow' speed, approximately every 50 seconds to measure T and S. In addition, the bottom



sensor was pumped for each oxygen measurement for 17 seconds at 'slow' speed and 15 seconds at 'fast' speed at intervals of about 50 seconds during profiles and about 400 seconds during settles and drifts. An Aanderra optode (Model: 3835, SN545, Foil batch 3606), mounted to the bottom endcap with its sensor about 20 cm below the CT-O2 sensor intake, was sampled approximately every 50 seconds. Float 48 was deployed on April 4, 2008 (day 95), stopped sampling on May 25 (day 146) and was recovered on

June 3, 2008. Oxygen data taken before day 104.6 (April 13) is available only in subsampled form, which includes most of the SBE-43 data but only about 1/8 of the optode data. Oxygen calibration casts were made both on the Knorr process cruise (see section 4) and on the float deployment cruise, but only the former were of sufficient quality to be useful in sensor calibration.

The float executed a complex mission (Fig. 2) alternating between profiles (down, up modes), autoballasting (settle mode) and mixed layer Lagrangian drift (drift mode). During the former, the float actively controls its buoyancy to seek a depth and/or isopycnal goal. During the latter, it passively followed the currents in the mixed layer, adjusting its buoyancy to match the density of the surrounding water. The float drogue was generally closed during all modes except drift.



The SBE-43 oxygen sensor must be pumped to give accurate measurements. When the pump is turned off, the sensor consumes oxygen in the water near its membrane and reads a nearly anoxic value within a few seconds. When the pump is turned on again, the anoxic layer is renewed reaching an equilibrium value to within 1 uMol/kg in 20-30 seconds depending on the sensor and temperature. During up and down modes, the SBE-43 was sampled on every data cycle, nominally 50-60s, in order to maximize the resolution of the samples. The sampling is somewhat faster during down than up because some extra time is spent during each data cycle in up pushing out the ballasting piston to make the float go up. During settle and drift modes, the SBE-43 was only sampled every 8 data cycles, typically 400 seconds, in order to minimize the energy used in pumping. During this long off time the sensor could become more anoxic than during the short off times of the profiling modes. This resulted in a reduction of the measured oxygen value during drift and settle relative to up and down. Correction for this effect is the major issue in obtaining accurate data from the SBE-43 from this float.

The Aanderra 3835 optode requires no pumping because it does not consume oxygen. Its energy consumption is much less than that of the SBE-43 so it is sampled on every data cycle. However, the factory calibration is insufficiently accurate for our needs. Understanding its temperature, pressure and oxygen sensitivities is a major issue in obtaining accurate data. In addition, it is much slower than the SBE-43 so its data must be corrected for time response.

3. Intercalibration of the Optode and SBE-43 [DownCheck.m]

The best operation of both sensors occurs during down mode. The SBE-43 is sampling at its fastest speed and the float is sinking, thus leading to optimal flushing of both sensors. It is assumed that the pressure and temperature dependences of the SBE-43 are much more accurate than those of the optode. The optode is adjusted using the formula

 $[O_2] = A + B * [O_2] + C * (T_{OPTODE} - 9^\circ C) + D * P + T_{lag} \frac{d}{dt} [O_2]$ and the values of the 5 coeficients [A, B, C, D, T_{lag}] are found by minimizing the difference between the SBE-43 and the optode on all down casts. The time derivative is found by first differencing the optode data. Nearly optimal values are found to be [16.8794 uMol/kg, 1.0133, 1.29 uMol/kg/C, 0.00564 uMol/kg/dbar, and 152 s] respectively. Note that the factory calibration of the optode is significantly off in offset (A), in slope (B) in temperature coefficient (C) and in pressure coefficient (D). The time response is significantly slower than the quoted 43 seconds. There is probably room for some minor improvement in these coefficients and in the optode time response correction.

The intercalibrated optode and SBE-43 are compared in Fig. 3. The comparison of individual down casts is shown in Appendix 1. With these adjustments, the two sensors agree within a standard deviation of 0.8 uMol/kg and show no systematic variations with depth. Much of this difference is due to slow time variations of about 1.5 uMol/kg. It is unclear which sensor is responsible for these errors and no corrections have been made.

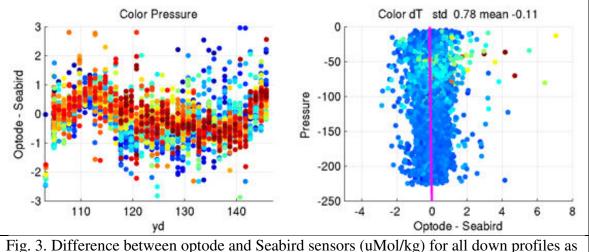


Fig. 3. Difference between optode and Seabird sensors (uMol/kg) for all down profiles as a function on left) yearday of 2008 and right) depth. Colors are depth and temperature difference between sensors, respectively.

3. Calibration with Winkler data [KnorrCheck.m]

Absolute calibration of the down data is achieved by comparing with Oxygen samples and the CTD/SBE-43 data taken on 6 calibration casts on *R.V. Knorr* cruise 193-03. Oxygen samples were processed by Jan Kaiser and Alba Gonzalez-Posada Most depths are sampled in triplicate and a mean and standard deviation of the bottles extracted. The data is of excellent quality with a mean standard deviation between triplicates of 0.25 uMol/kg.

A linear correction of the Knorr's SBE-43 was used to correct this sensor to the Winklers separately on each calibration cast. The offset varied from 6-10 uMol/kg, increasing during the cruise, and the average slope was about 1.07. The calibration constants used are listed in the first plot of Appendix 2.

Fig. 4 shows two sample casts. Data is compared with potential density as a vertical coordinate since this removes the effects of internal wave displacements. The error in the regression is shown by the width of the 3 red curves (as computed by MATLAB polyval()). The SBE-43 on the float (blue) is adjusted as described above. The bottles are shown by the black symbols with the two '+' giving their standard deviation. The cast in Fig. 4a shows excellent agreement. The cast in Fig. 4b shows larger differences because of the high variability in oxygen profiles near 27.4 kg m⁻³. All of the casts are plotted in Appendix 2.

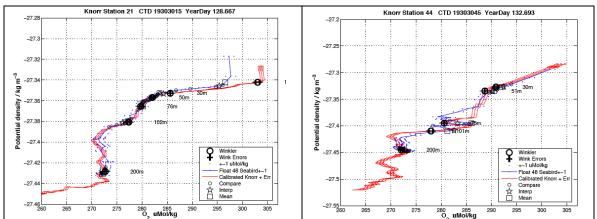
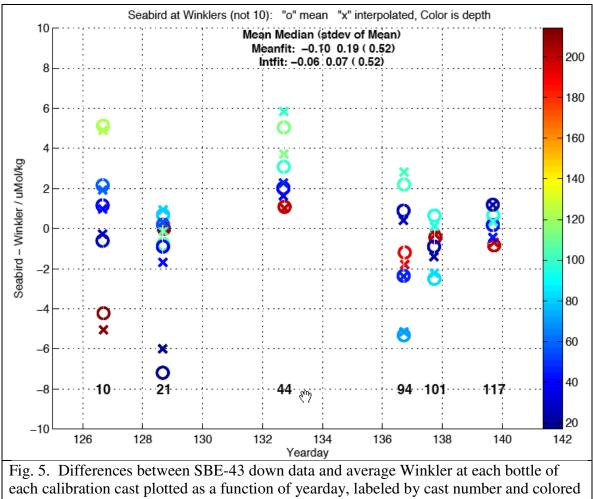


Fig. 4. Two calibration casts. Left: High quality cast. The CTD, bottle data and float data all agree to within 1 uMol/kg. Right: Cast with some problems. The two bottles near 100m occur in a region of high variability so that accurate intercomparison is difficult. Small circles show all SBE-43 points within 0.005 kg m⁻³ of Winkler; stars show interpolation to Winkler potential density; squares show their mean.

An absolute calibration of the SBE-43 down mode data was achieved by subtracting 0.9 uMol/kg from the factory-calibrated values. Fig. 5 summarizes these results. As in Fig. 4, the quality of the fits between bottle and float varies significantly. For the best casts (21 and 117), the SBE-43 data is within 2 uMol/kg; others are much worse. The mean difference between the bottles and the SBE-43 is nearly zero by construction, with the standard deviation of the mean well below 1 uMol/kg.



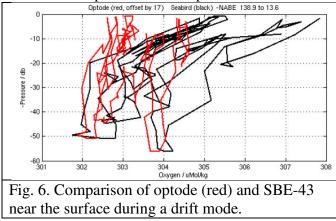
each calibration cast plotted as a function of yearday, labeled by cast number and colored by pressure. Seabird value is computed either by average over densities within 0.005 kg m^{-3} of the bottle (circles) or by interpolating to the density of the bottle (x). Cast 10 is plotted but excluded from the averages.

4. Seabird Mode Offsets

Measured SBE-43 oxygen values from the drift and settle modes are on average 2.7 uMol/kg lower than those from down and up modes due to the longer sampling interval, as explained above. This offset is applied to the drift and settle modes to eliminate the difference. The transitions between modes show intermediate values. The sampling interval is not constant for each mode. Samples are sometimes skipped, effectively doubling the interval. The sampling interval slowly increases through the mission, presumably because it takes more time to write to flash. No corrections for these effects have been made.

5. Wave Effects (WaveCheck.m)

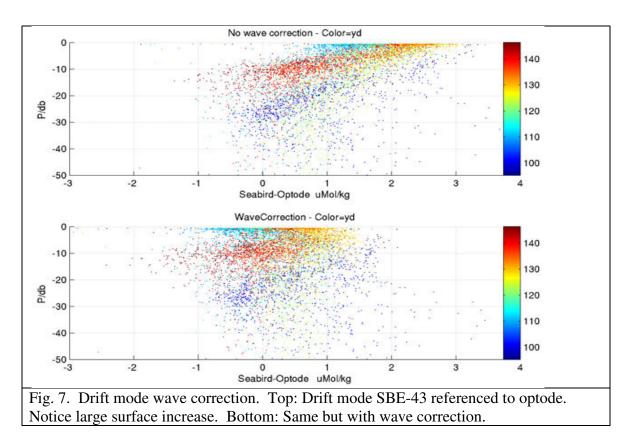
During drift mode, SBE-43 oxygen profiles increase near the surface, while optode measurements do not. An example is shown in Fig. 6. This is due to the extra flushing of the SBE-43 cell by wave action near the surface which reduces the degree of anoxia which develops between samples. Seabird has simulated this effect in the laboratory.



A correction for this effect is developed by fitting $[O_2] = [O_2]_0 + a * t + bt^2 + De^{-EP}$ to the upper 50m of drift mode data to form time series of D and E with a resolution of about 7 ks. The fit metric is the mean squared difference between SBE-43 and optode data plus $(D/D_{err})^2$, the latter term acting to minimize D. The values of D and E⁻¹ are limited to less than 2 uMol/kg and 5m

respectively. Not all segments yield good fits. The D and E values are then interpolated in time and the last term of the fit applied to remove the wave effect.

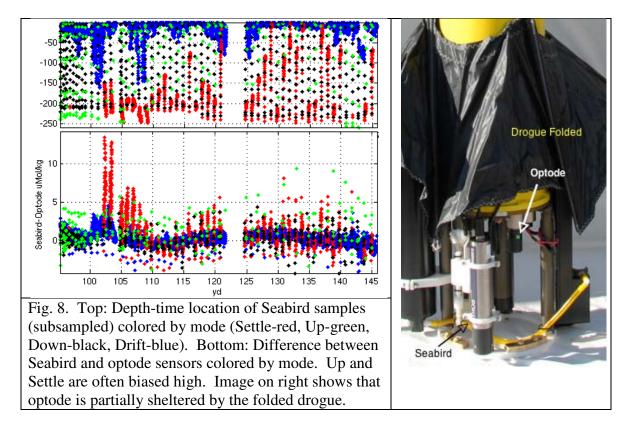
Fig. 7 shows the result. Most of the wave effect has been removed. The two sensors agree to about 1 uMol/kg. Much of the residual variance can be attributed to the slow time variation seen in Fig. 3a.



6. Other Errors

The optode was found to often read low at depth during settle and up modes as seen in Fig. 8. This occurs only when the float drogue is closed and the float is not moving. It seems likely that the oxygen levels are reduced in the water trapped by the drogue due to respiration in the water or on the float and the optode reads these lower oxygen levels. The Seabird sensor is further from the drogue and actively pumped, which makes it less susceptible to this effect. During these times, the optode shows 5-10 times more noise than the Seabird, also suggesting that the problem is with the optode. No correction for this effect has been made.

In regions of high temperature gradient, the optode often diverges from the Seabird, due to the inadequacy of our compensation for its time response. Thus although the optode data has a higher spatial resolution than the Seabird (see Appendix I), its accuracy is often lower in gradient regions. There thus appears to be no reason to use the optode data. No additional correction for this effect has been made.



7. Final Check (MLCheck.m DeepCheck.m)

A final check on these corrections is shown in Fig. 8 for data shallower than 14m and near 200m. The two sensors, the various SBE-43 modes and the Winkler bottles all agree to about 1 uMol/kg. Here, as in Fig. 5, there is a suggestion that the data is biased slightly low at depth relative to the surface.

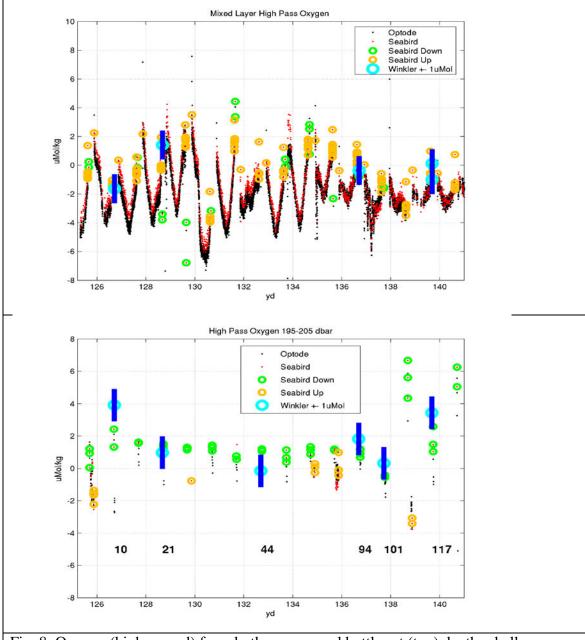
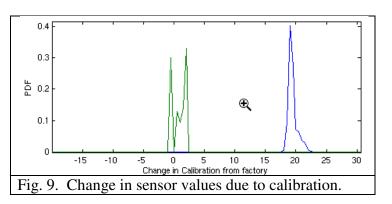


Fig. 8. Oxygen (high passed) from both sensors and bottles at (top) depths shallower than 14 dbar and (bottom) depths between 190 and 210 dbar. Colors indicate sensor and mode. Vertical bars on the Winkler samples show ± 1 uMol/kg.

8. Calibration shifts

Figure 9 shows the change in sensor oxygen values relative to the factory calibration caused by the calibrations developed in this report. The Seabird SBE-43 values during down mode are changed by only 0.9 uMol/kg. Other modes have larger changes. The 3835 optode factory calibration is off by about 19 uMol/kg, with a



spread caused by errors in the factory temperature, pressure and oxygen dependences.

10. Conclusion

The following function brings the float 48 oxygen sensors into agreement with each other and the Winklers during the Knorr cruise to about 1 uMol/kg. These corrections are applied to version 7 of the float 48 data. The highest quality data are the down modes from either the SBE-43 or optode. The oxygen variables are:

- seabird.oxycal0 Oxygen concentration computed from pre-cruise calibrations
- seabird.oxycal1 Offsets for each mode have been applied to oxycal0
- seabird.oxycal2 Wave correction has been applied to oxycal1
- seabird.oxy Best Seabird oxygen. Equals seabird.oxycal2 in this release
- optode.oxycal0 Oxygen calculation from factory calibration
- optode.oxycal1 Add linear dependence on oxycal0
- optode.oxycal2 Add linear dependence on pressure
- optode.oxycal3 Add linear dependence on temperature
- optode.oxycal4 Correct for response function
- optode.oxy Best optode oxygen. Equals optode.oxycal4 in this release

function [optode,seabird]=CorrectOxy4(optode,seabird);

% Corrections to float 48 NAB oxygen sensors

- % optode and seabird are data structure for each sensor
- % Seabird and Optode factory values are in *.oxycal0
- % final oxygen calibrations are in oxycal
- %

% EAD April 2010

% Convert to uMol/kg from uMol/L for both sensors

seabird.oxycal0kg=O2Conv(seabird.oxycal0,'umol/l','umol/kg',...

seabird.S(:,1),seabird.T(:,1),seabird.P,'Potential');

optode.oxycal0kg=O2Conv(optode.oxycal0,'umol/l','umol/kg',... optode.S(:,1),optode.T(:,1),optode.P,'Potential');

```
% Correct seabird
Seabird.profile_offset=-4.5;
Seabird.bias=4.05;
Seabird.drift_offset=-1.8;
```

gp=find(seabird.mode==0 | seabird.mode==2)+1; % The +1 seems important gx=find(seabird.mode~=0 & seabird.mode~=2)+1; gx=gx(find(gx<=length(seabird.mode))); seabird.oxycal1=seabird.oxycal0kg+Seabird.bias; % Average offset seabird.oxycal1(gp)=seabird.oxycal1(gp)+Seabird.profile_offset; % Extra Profile Offset seabird.oxycal1(gx)=seabird.oxycal1(gx)+Seabird.drift_offset; % Extra drift/settle Offset

```
if 1 % Do seabird wave correction
```

```
load('Wavefit.mat');
```

```
% Dwave Nwave Pminwave dtwave iterwave
% Errwave OPwave SBmOPwave flagwave ydwave
% Ewave Pmaxwave SBwave idwave
D=interp1(ydwave,Dwave,seabird.yd,'nearest');
E=interp1(ydwave,Ewave,seabird.yd,'nearest');
E=min(E,1/5);
D=max(D,2);
% Fix QL period
q=find(seabird.yd<min(ydwave));
E(q)=1./30;
D(q)=1.5;
seabird.oxycal2=seabird.oxycal1;
```

```
gx=find(seabird.mode>2 & ~isnan(D+E));
seabird.wavecorr=seabird.oxycal1*NaN; % NaN if no correction
seabird.wavecorr(gx)=-D(gx).*exp(-E(gx).*seabird.P(gx));
seabird.oxycal2(gx)=seabird.oxycal1(gx)+seabird.wavecorr(gx);
```

```
seabird.oxy=seabird.oxycal2; % save final cal in same variable
else
seabird.oxy=seabird.oxycal1;
```

end

% Correct optode

Optode_P=1.41/250; %2.5 % Pressure dependence Optode_lag=152; % time lag of sensor Optode_T=1.29; Optode_mn=1.61;

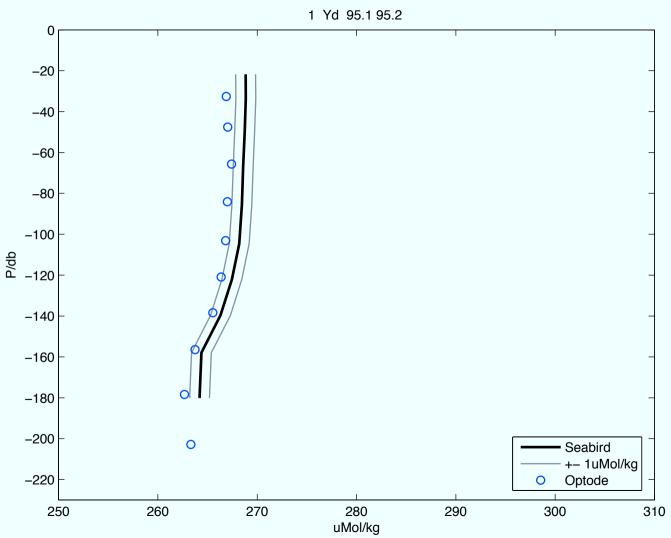
```
% Adjust Optode linearly
L1=[1.0133 1.6794+7.6+7.6+0.45];
```

```
optode.oxycal1=polyval(L1,optode.oxycal0kg);
% Pressure correction to optode
optode.oxycal2=optode.oxycal1+optode.P*Optode_P; %
% Correct optode for T
optode.oxycal3=optode.oxycal2-Optode_T*(optode.T(:,1)-9)-Optode_mn;
% speed up optode
df=[-1 0 1]'/2;
dO=conv2(optode.oxycal3,df,'same');
dt=conv2(optode.oxycal3,df,'same');
dg=find(dt<100); % But only if sampled sufficiently fast
optode.oxycal4=optode.oxycal3;
optode.oxycal4(dg)=optode.oxycal3(dg)+Optode_lag*dO(dg)./dt(dg);
```

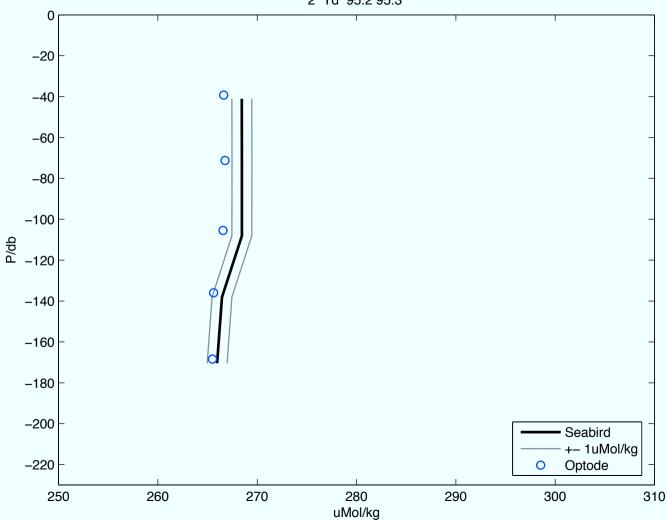
```
optode.oxy=optode.oxycal4; % save final cal in same value
```

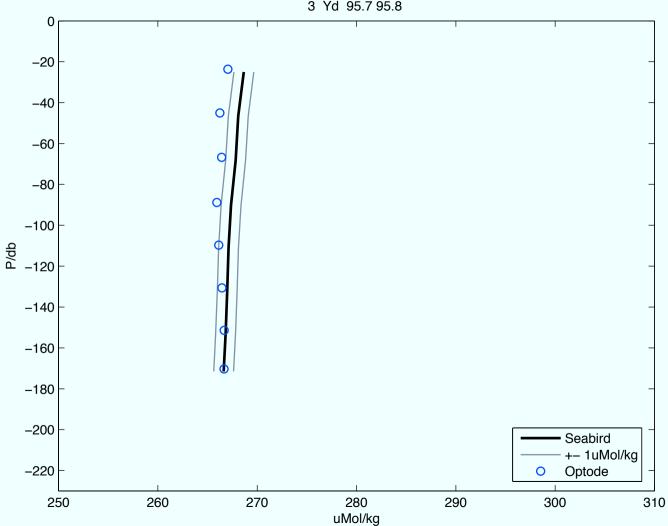
```
% Edit bad points
if 1
b=find(seabird.oxy<250);
seabird.oxy(b)=NaN;
end
```

APPENDIX 1

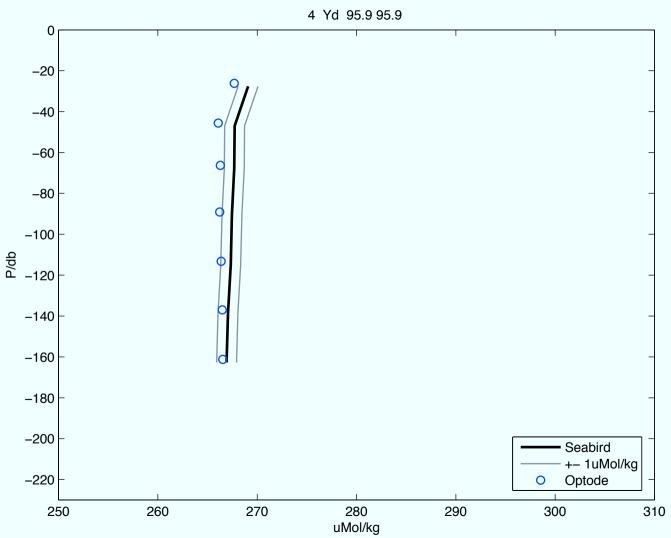


2 Yd 95.2 95.3

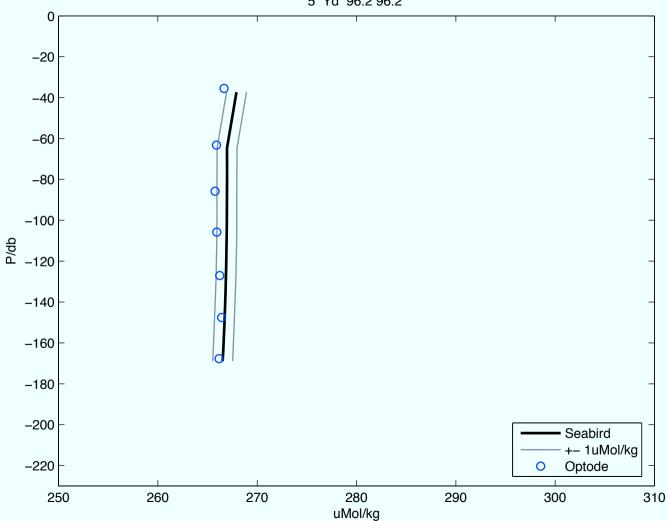


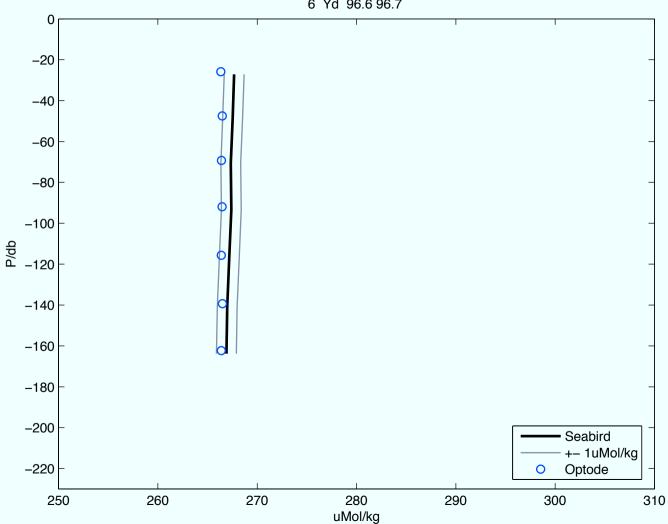


3 Yd 95.7 95.8



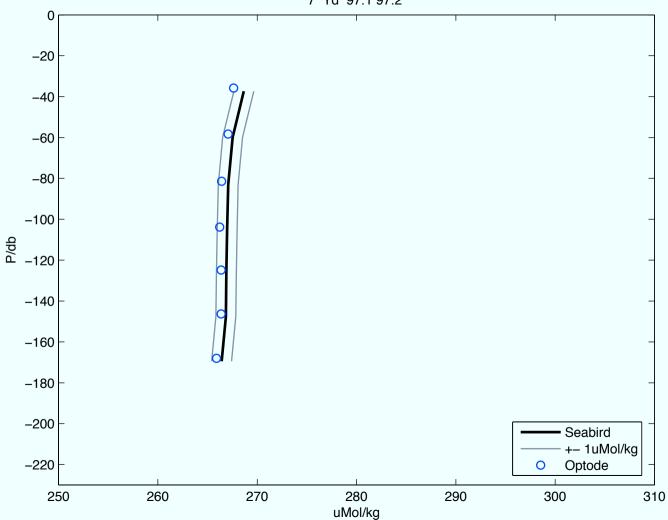
5 Yd 96.2 96.2

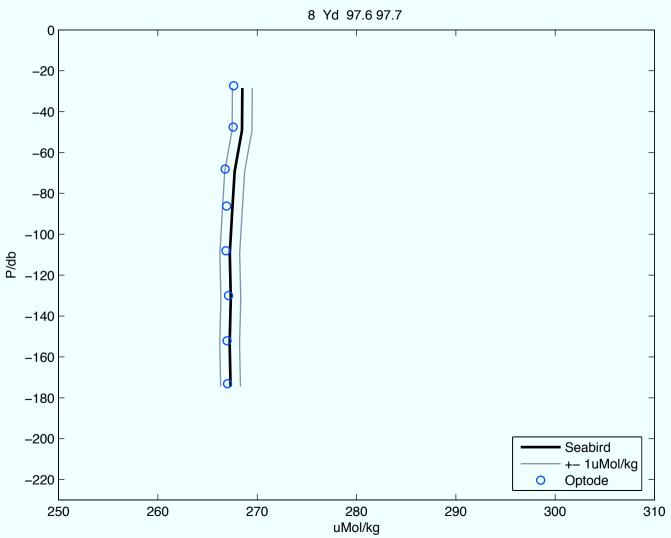




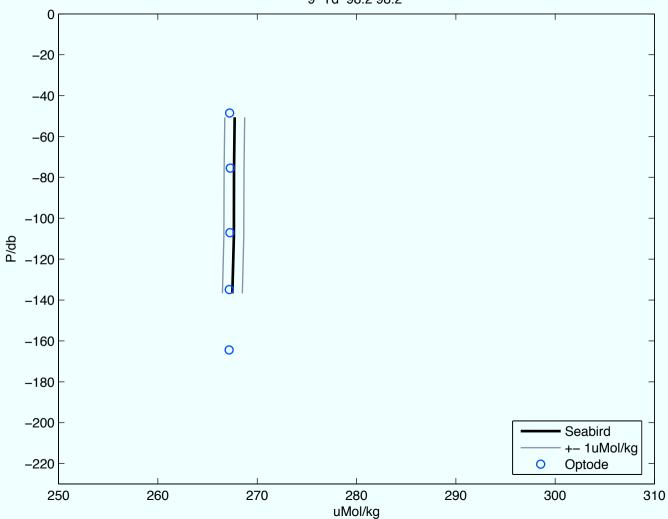
6 Yd 96.6 96.7

7 Yd 97.1 97.2

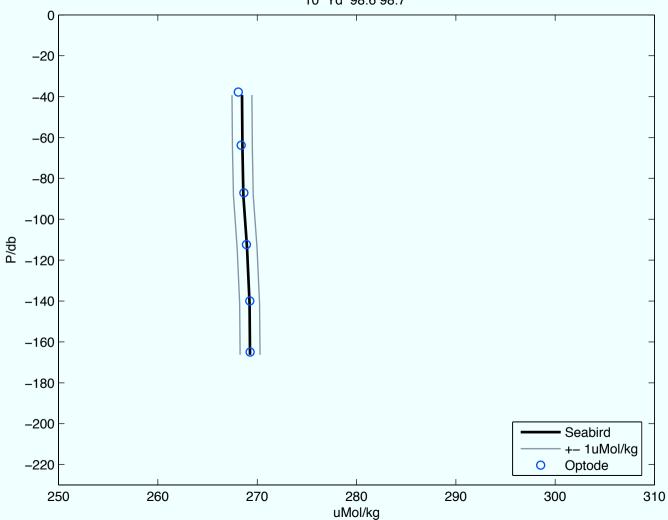




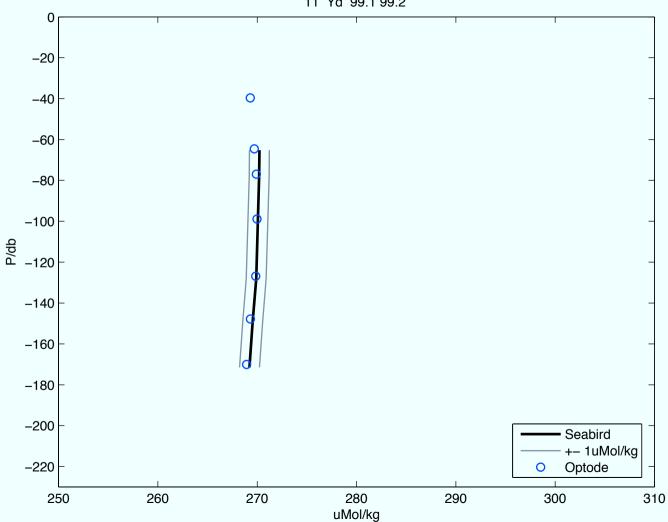
9 Yd 98.2 98.2

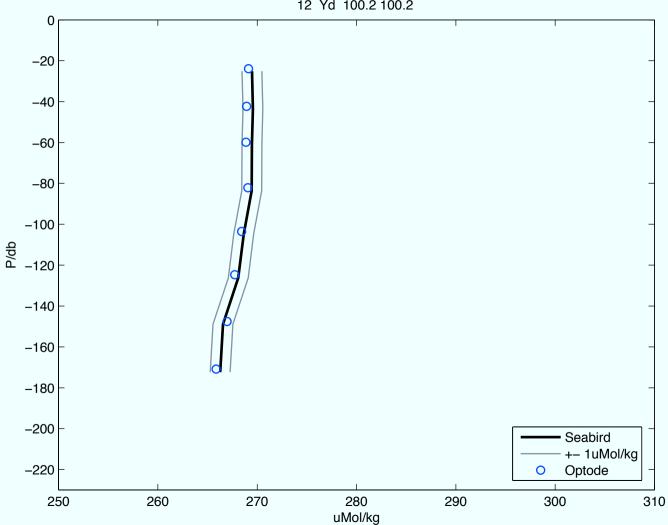


10 Yd 98.6 98.7



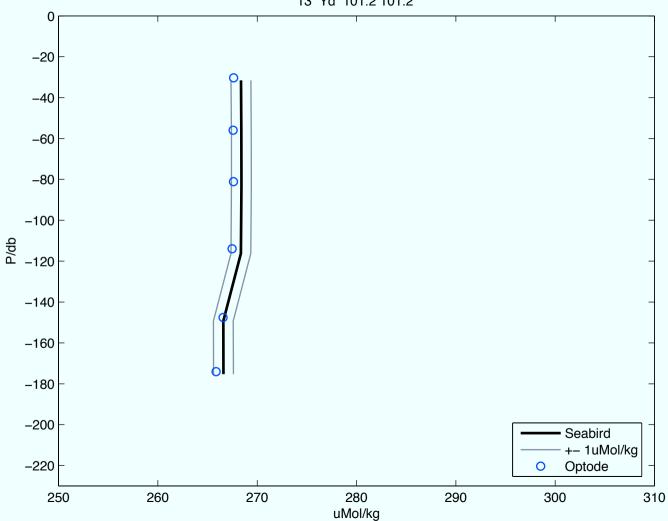
11 Yd 99.1 99.2



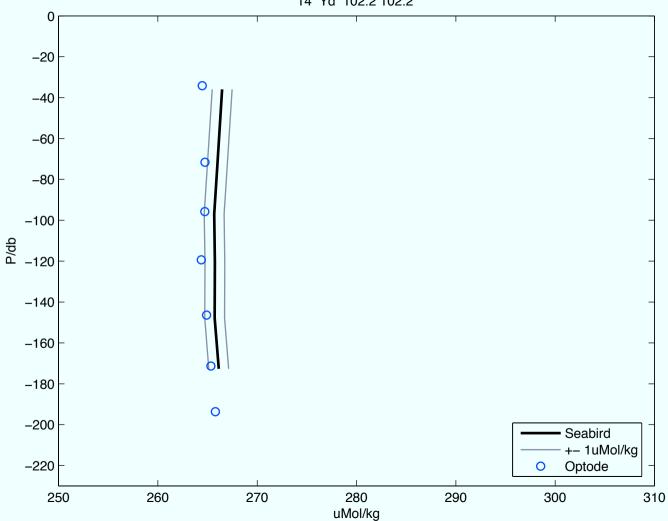


12 Yd 100.2 100.2

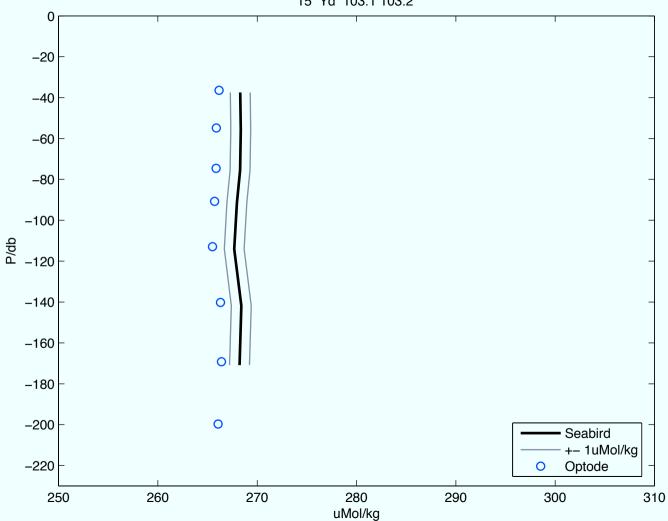
13 Yd 101.2 101.2

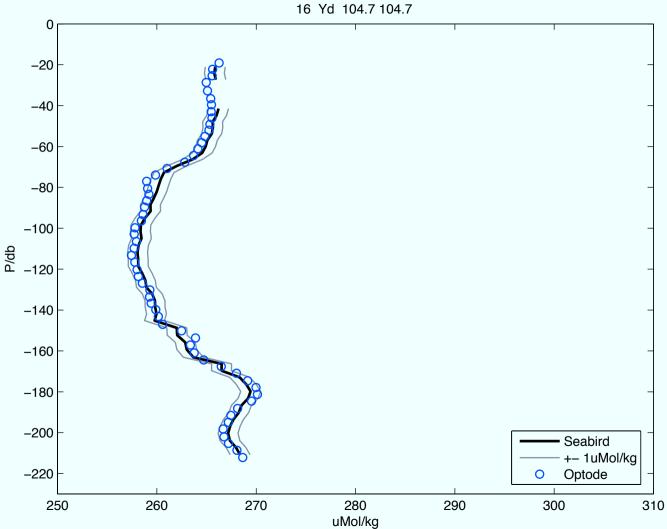


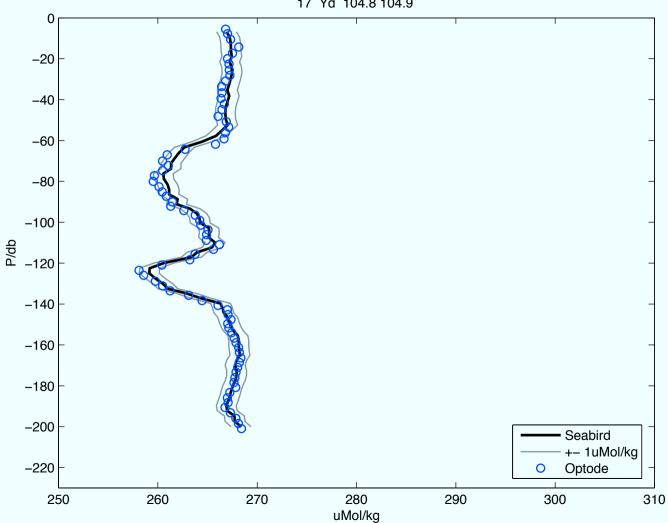
14 Yd 102.2 102.2



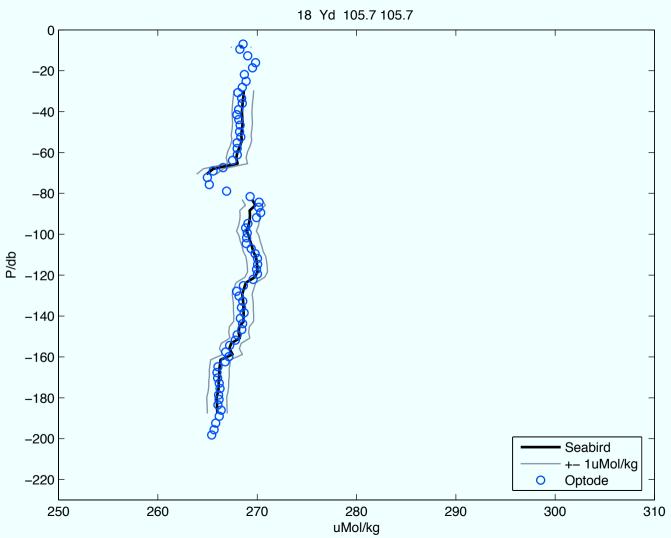
15 Yd 103.1 103.2

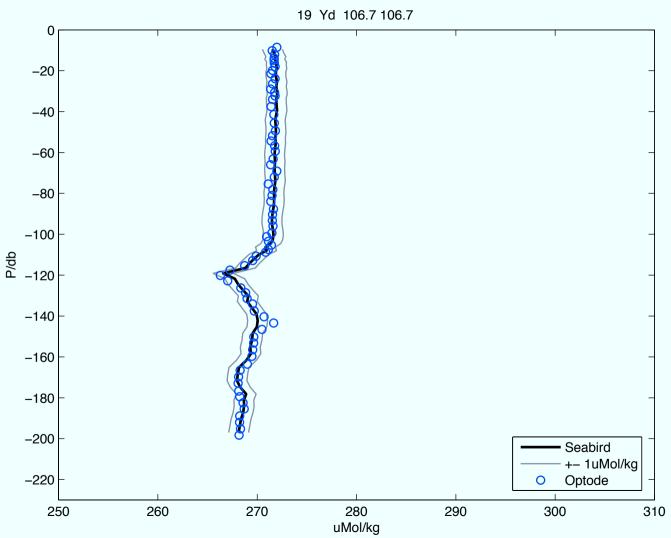


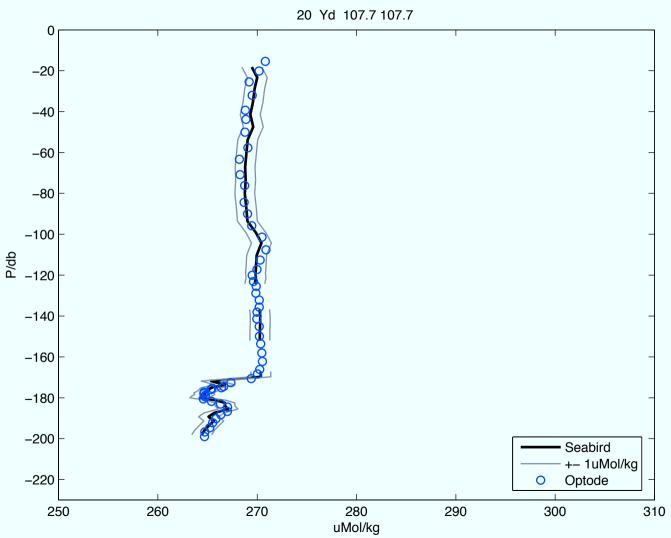


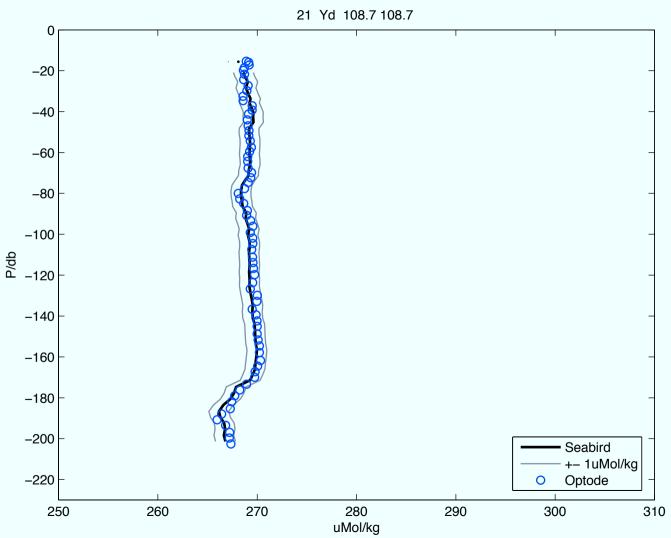


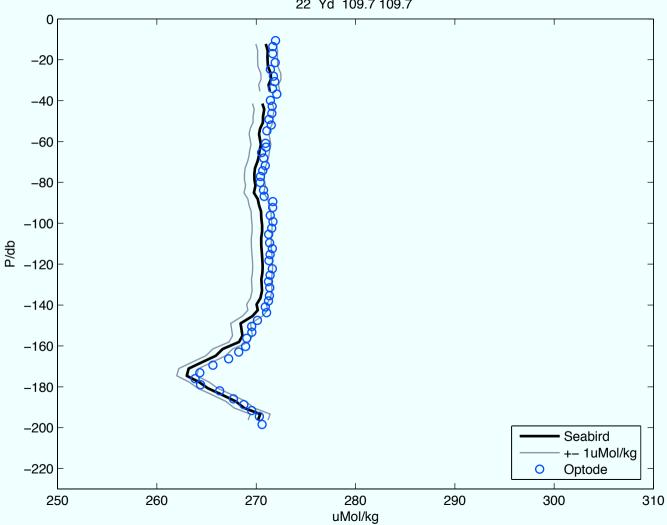
17 Yd 104.8 104.9



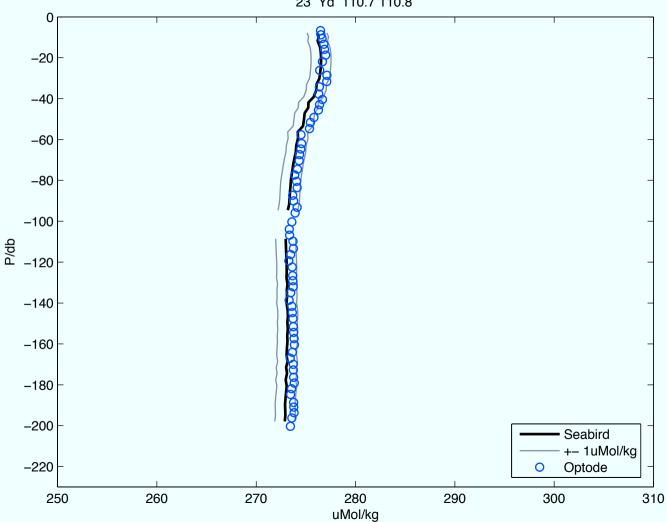






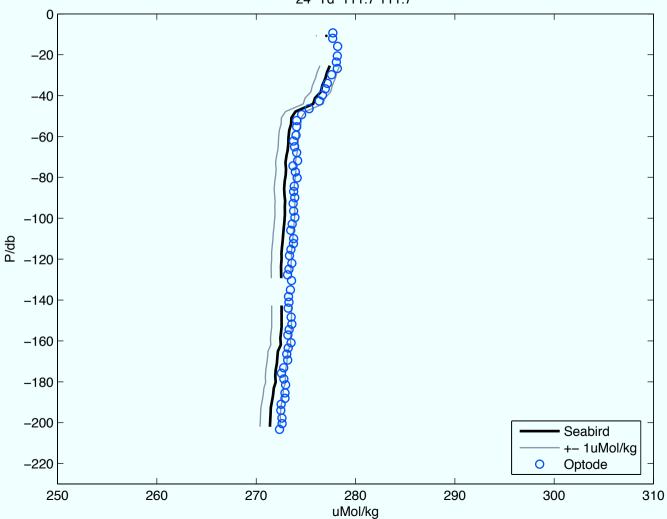


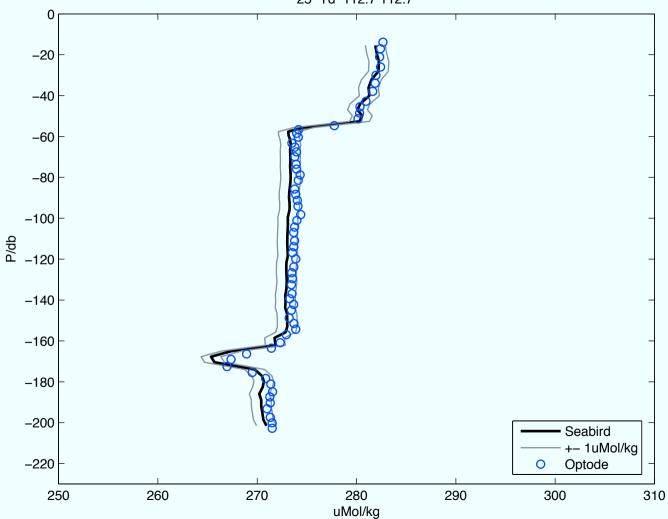
22 Yd 109.7 109.7



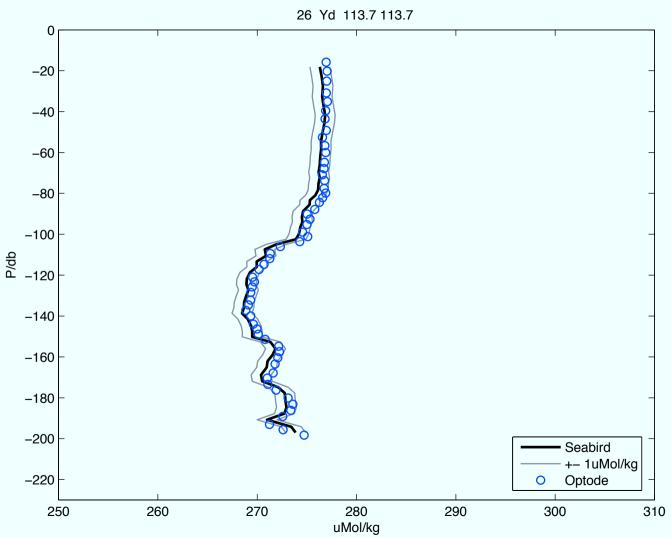
23 Yd 110.7 110.8

24 Yd 111.7 111.7

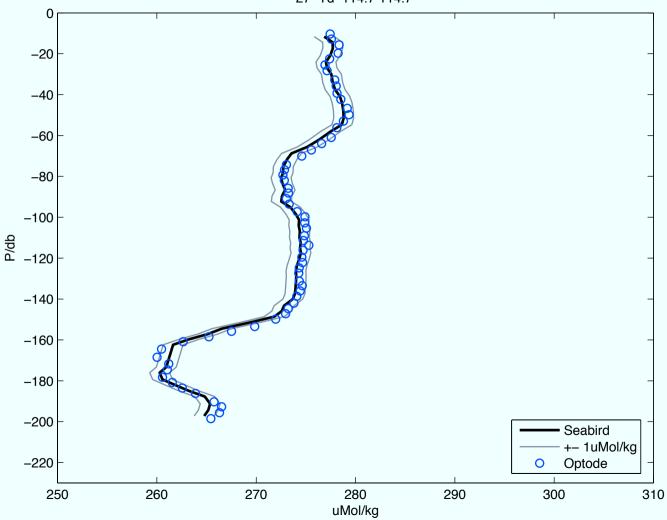


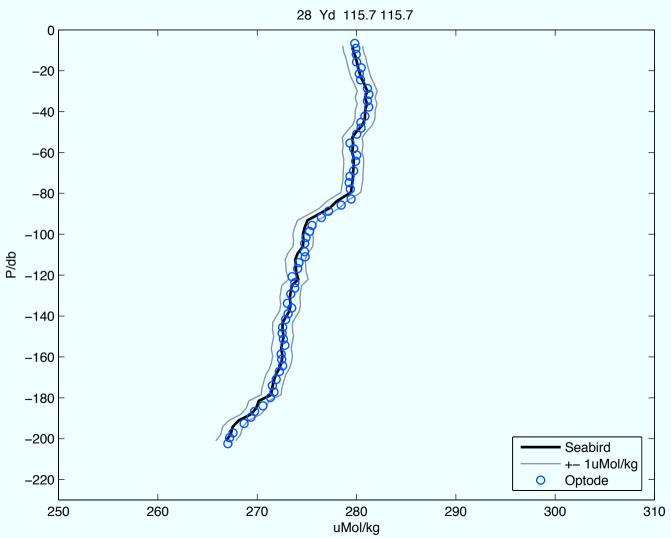


25 Yd 112.7 112.7

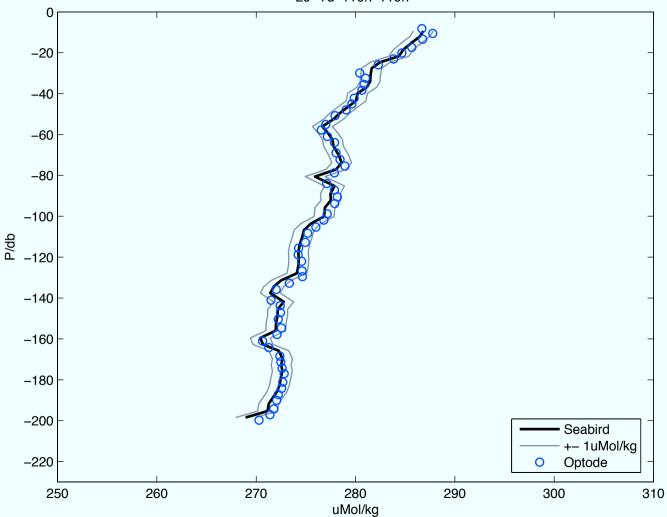


27 Yd 114.7 114.7

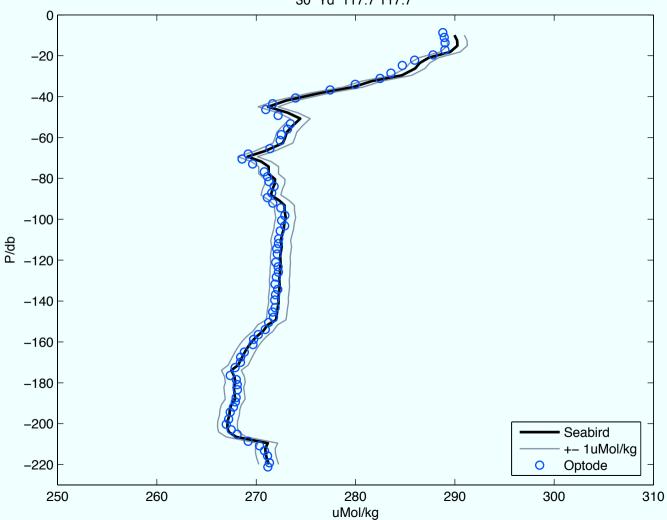




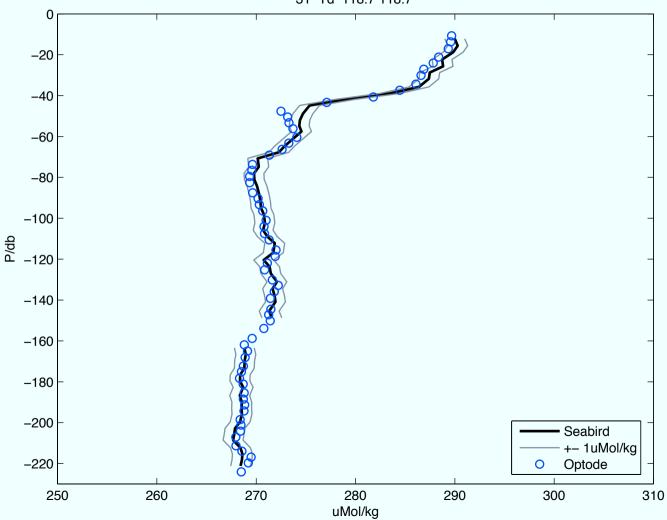
29 Yd 116.7 116.7



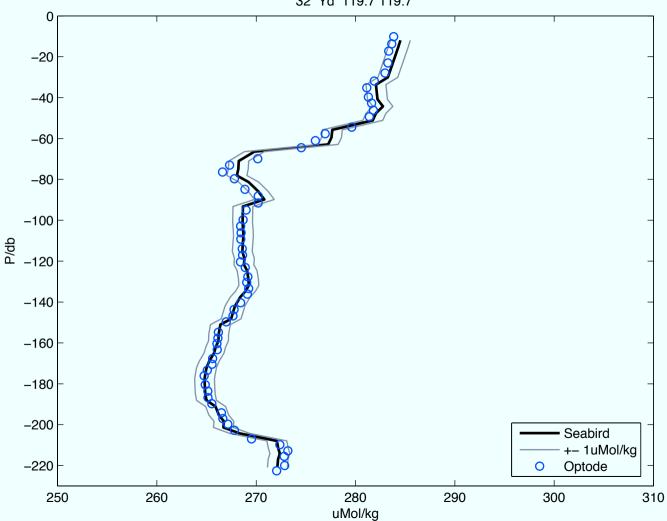
30 Yd 117.7 117.7



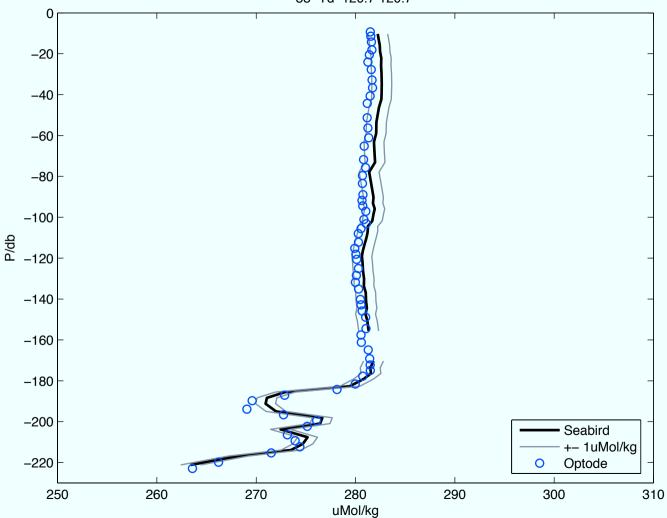




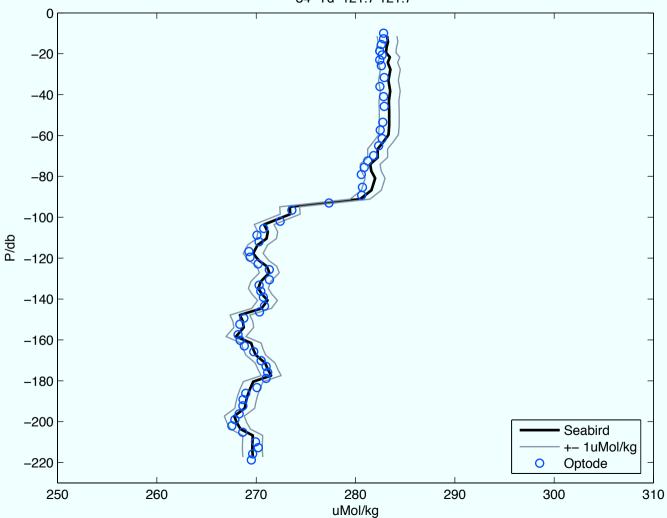
32 Yd 119.7 119.7



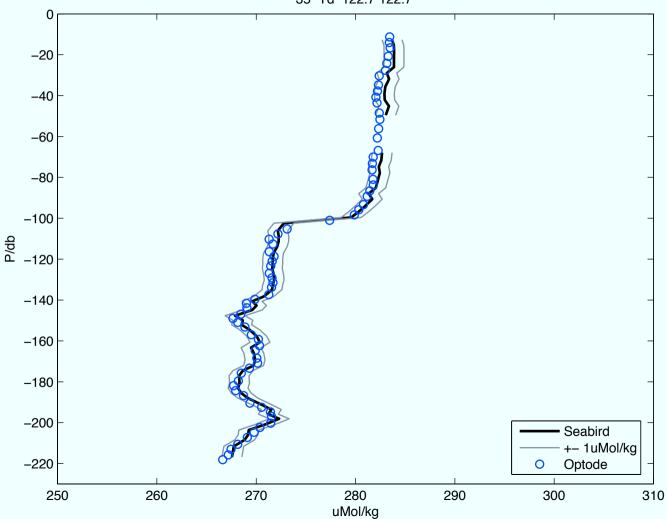
33 Yd 120.7 120.7



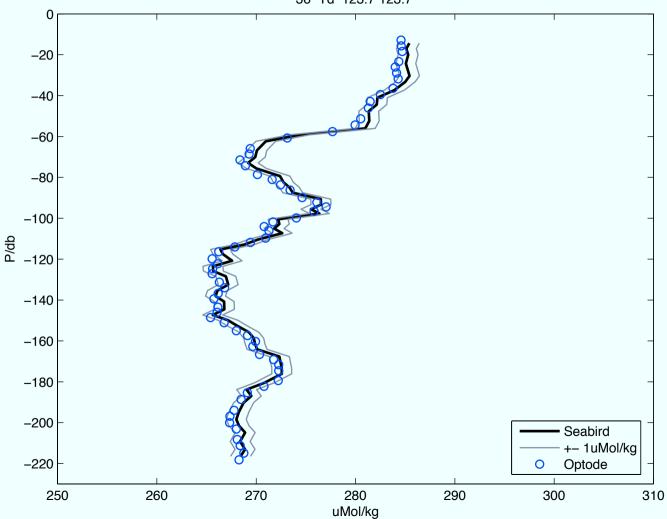
34 Yd 121.7 121.7



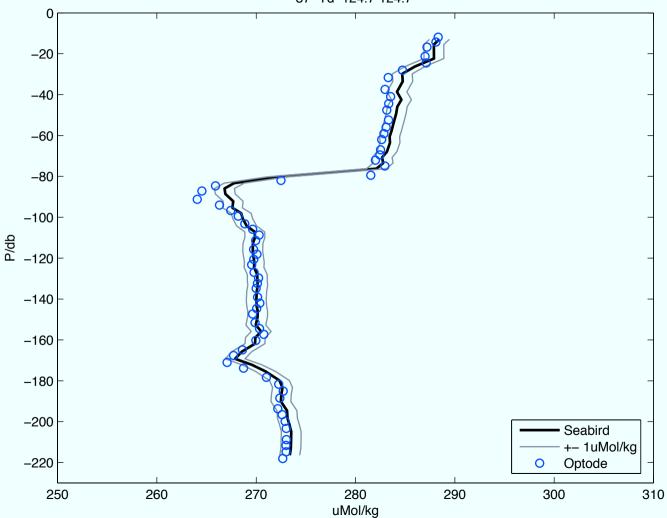
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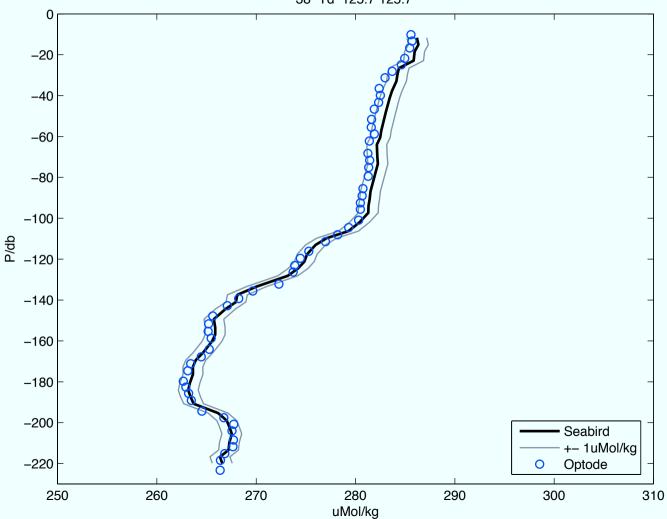
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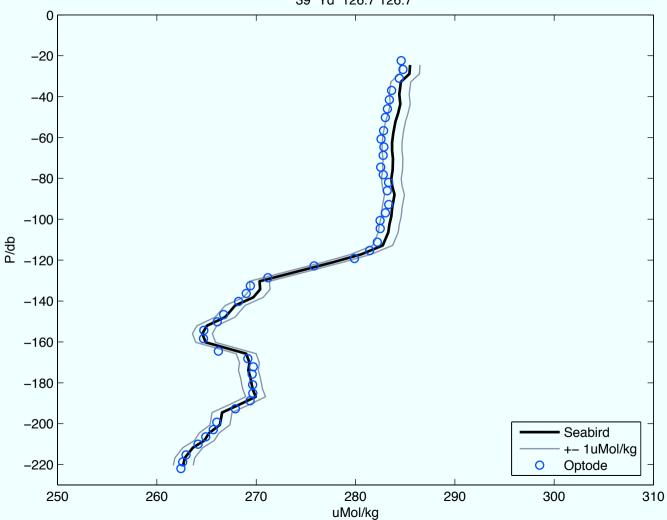


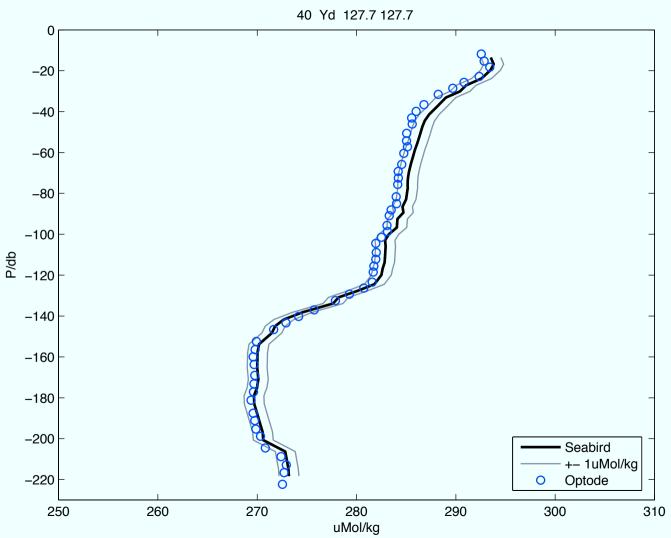


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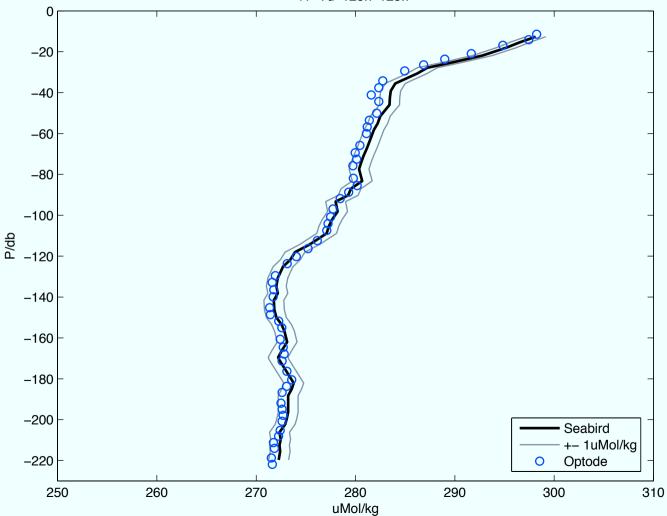


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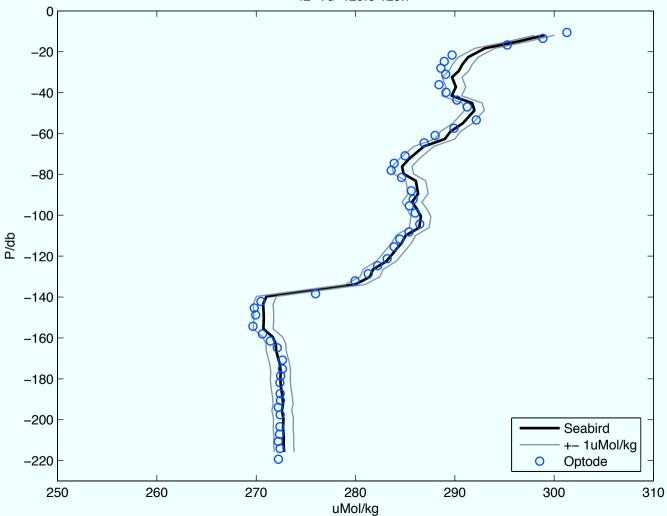


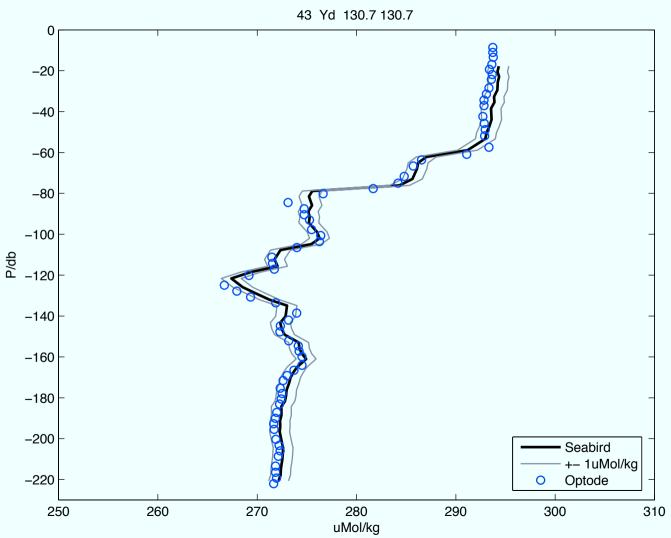




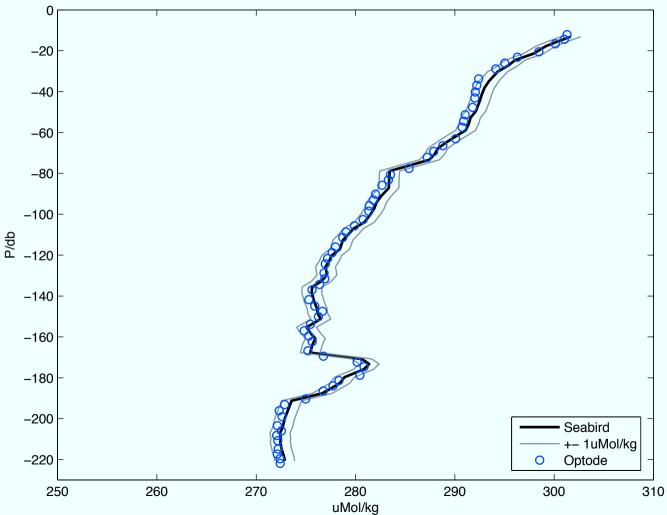




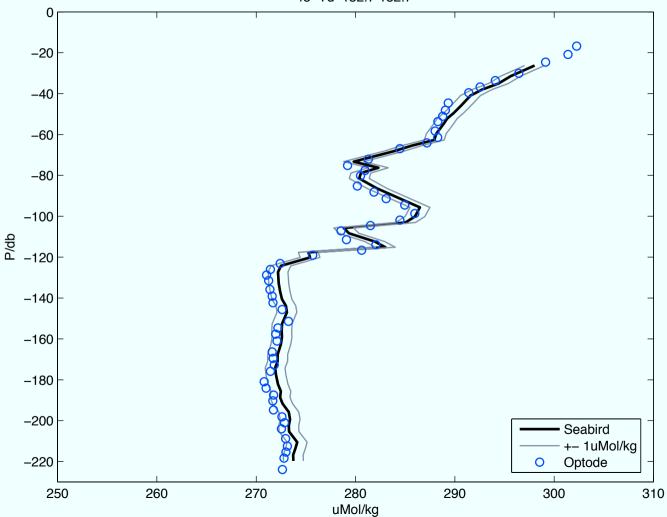




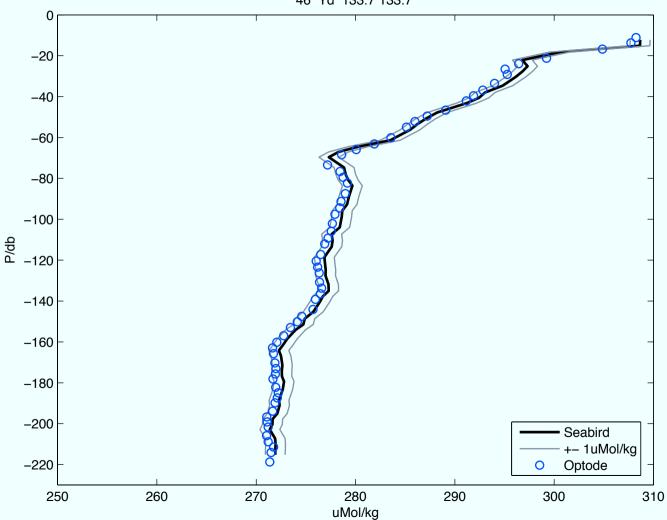




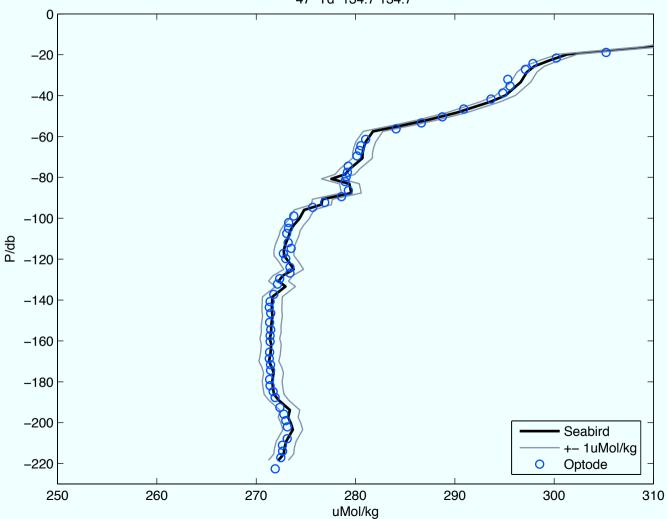




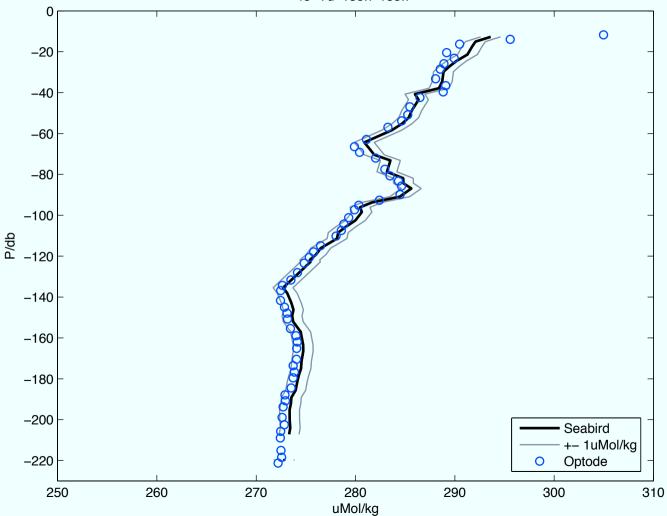
46 Yd 133.7 133.7



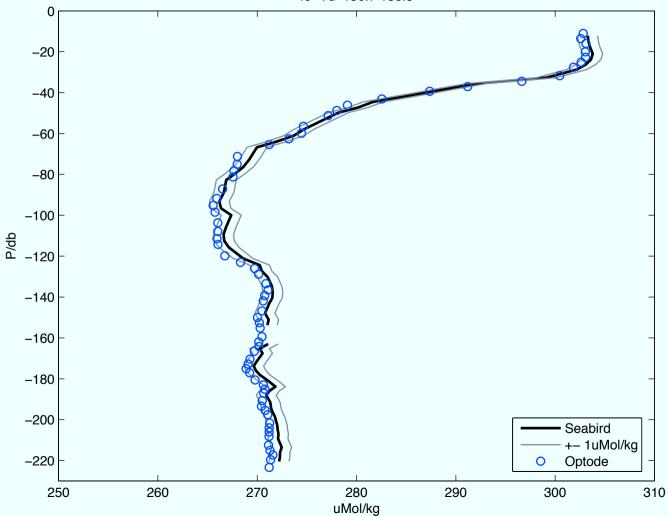




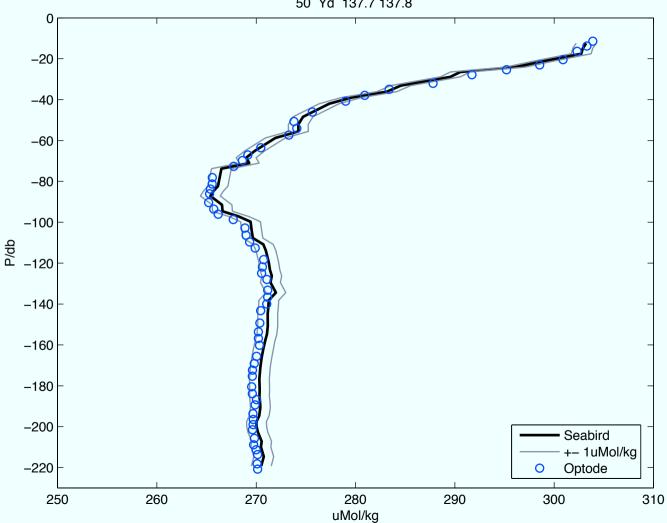




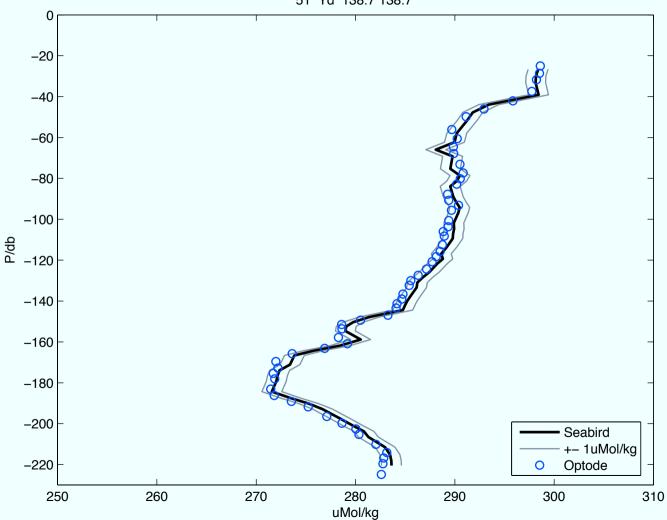
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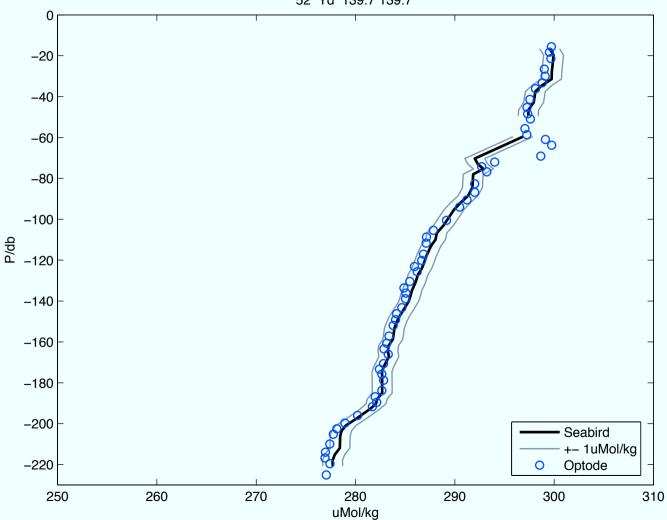
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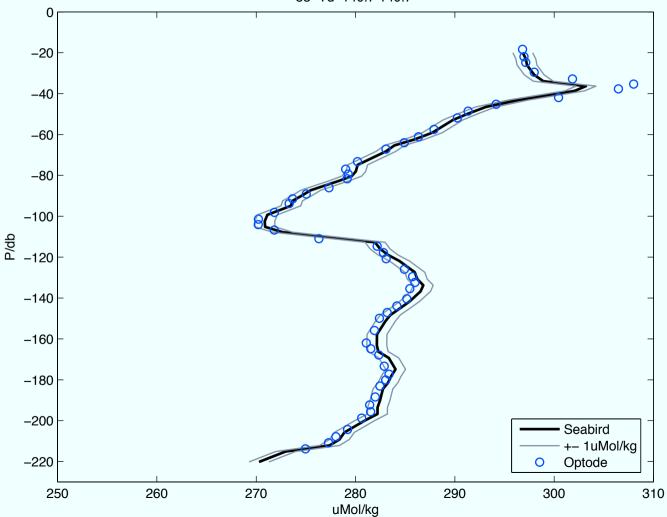
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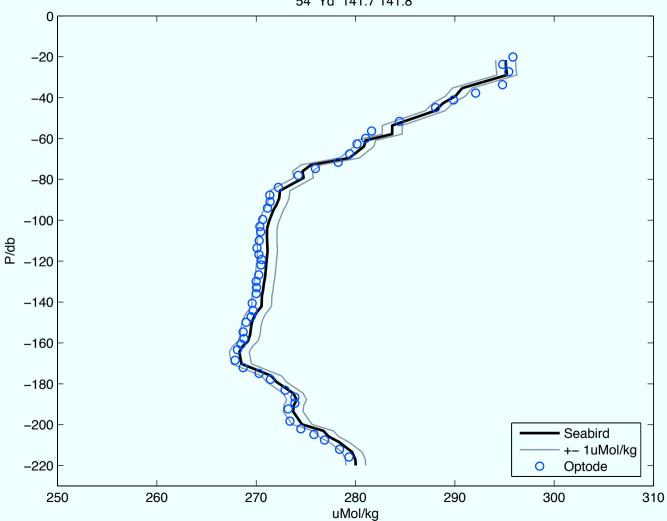
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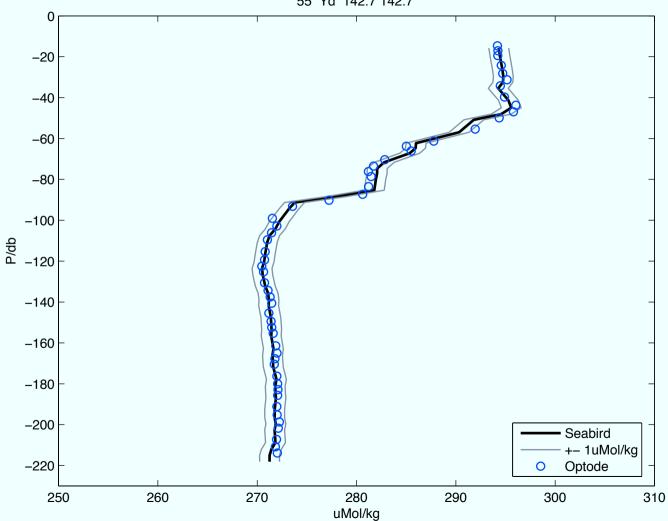






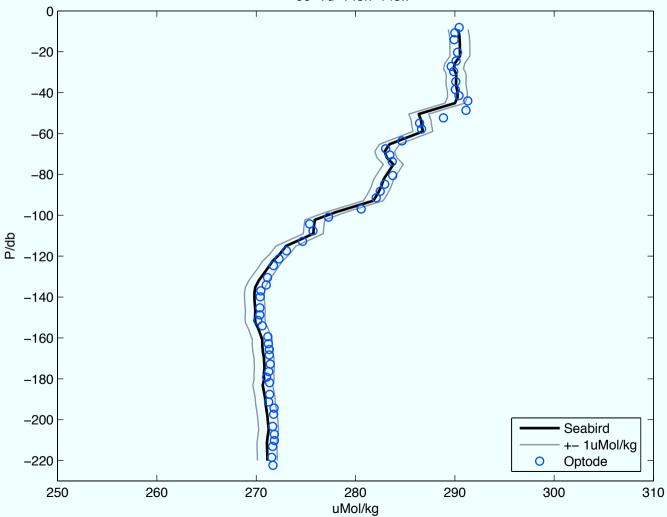




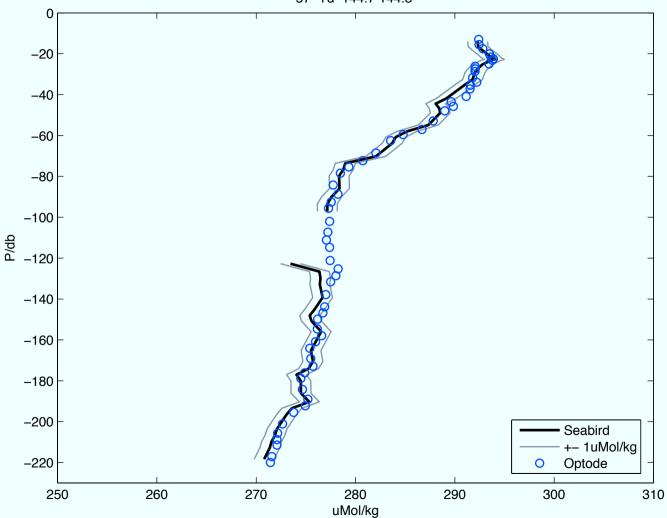


55 Yd 142.7 142.7

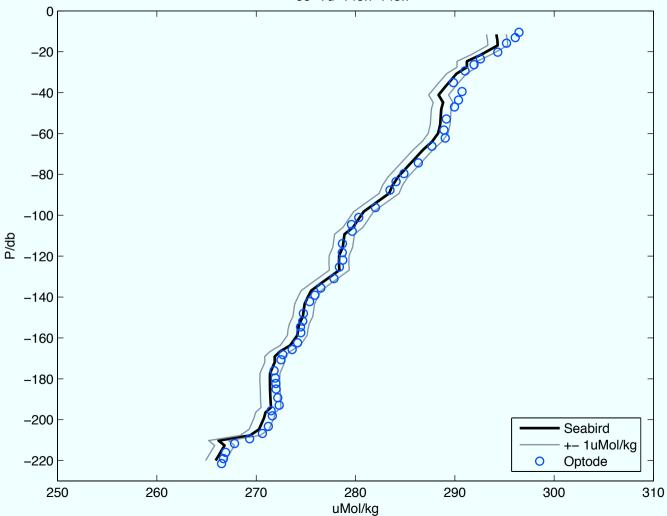






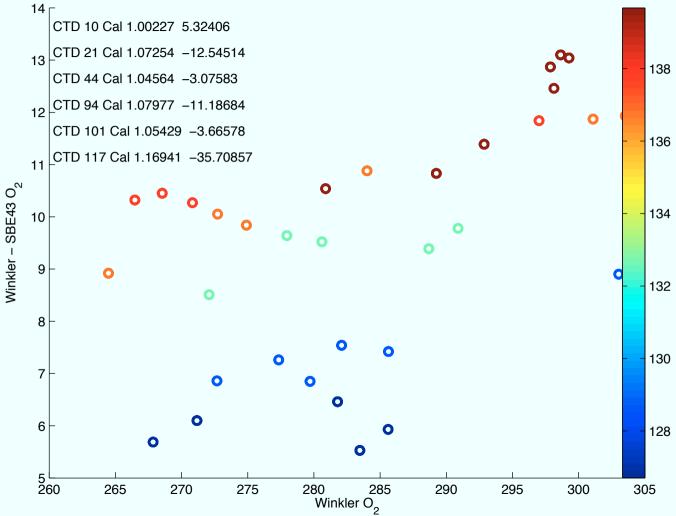


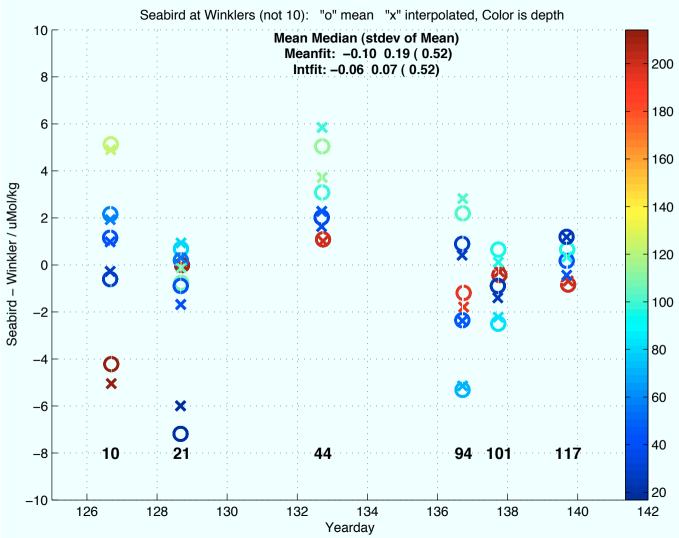


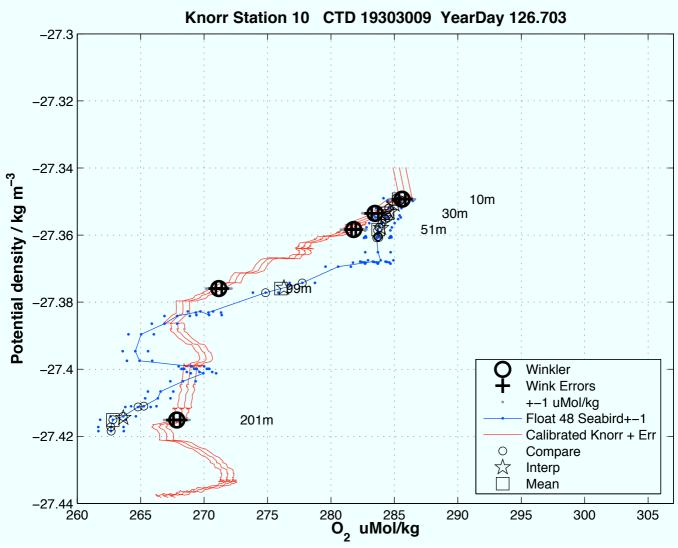


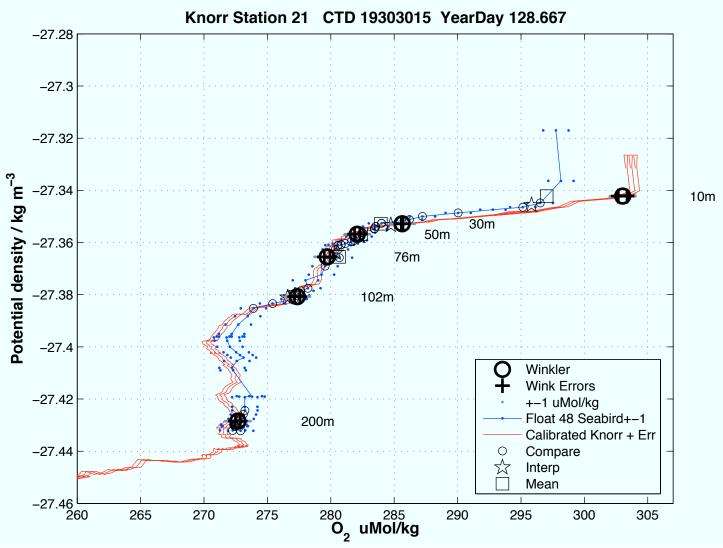
APPENDIX 2

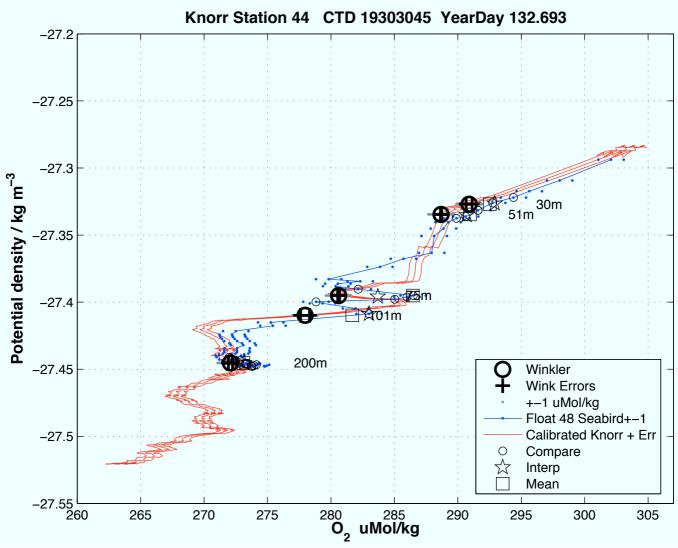
Calibration of Knorr CTD SBE-43 on Float Calibration Casts

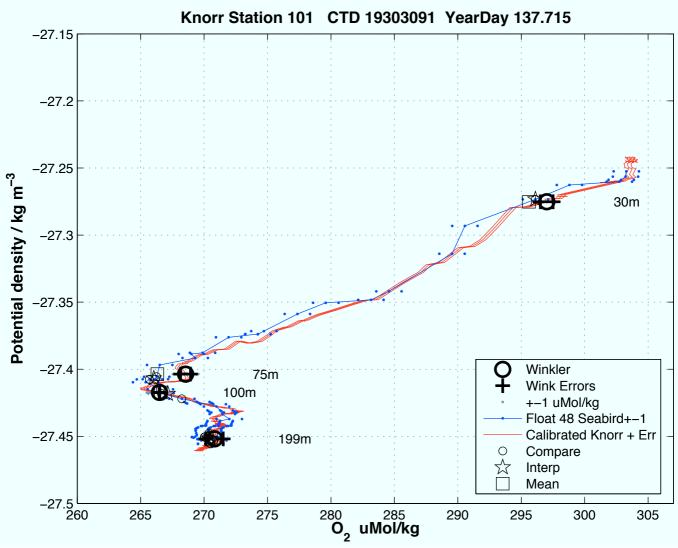


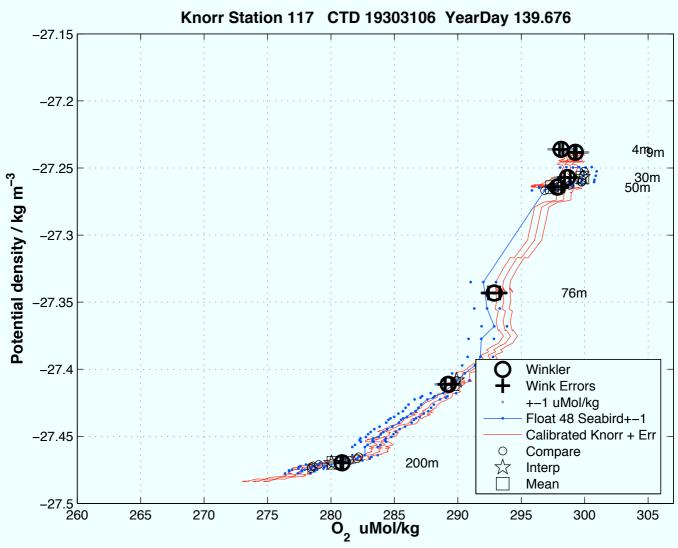


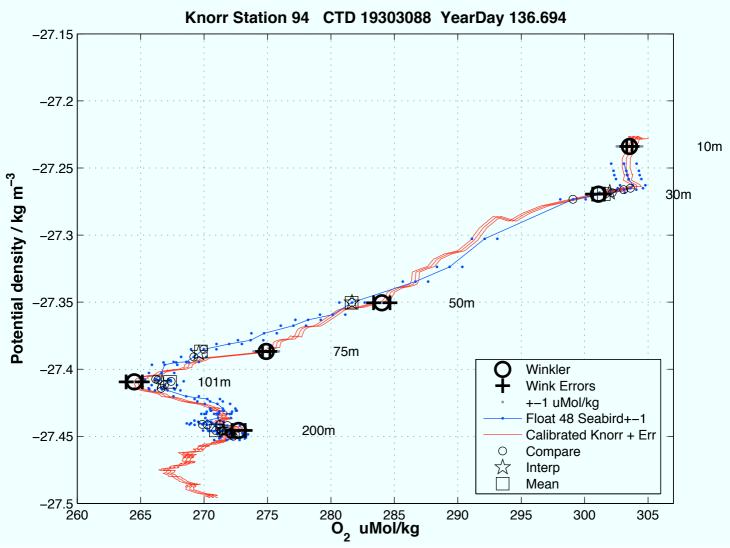












The 2008 North Atlantic Bloom Experiment Calibration Report #3 addendum Calibration of the Dissolved Oxygen Sensor on the *R/V Knorr* CTD with Winkler bottle samples Correction for *R/V Knorr* CTD

Ivona Cetinić University of Maine ivona.cetinic@maine.edu

Version 1.0, November 05, 2010.

ABSTRACT

The SBE43 factory calibrated output (μ mol kg⁻¹) and Winkler oxygen measurements were linearly correlated, but deviated from the 1-to-1 line (Fig. 1a). First, a linear correction was applied to SBE data (Fig. 2), followed by the time depended polynomial quadratic fit (Fig. 3). SBE43 measurements, corrected in this way, have an RMS deviation from the Winkler oxygen measurements of 3.199 µmol kg⁻¹. This correction is applicable to KN19303 *R/V Knorr* dataset only and has been applied to the data release v 5.0. The oxygen sensor on the R/V Bjarni Saemundsson was not calibrated with Winklers, and hence only the factory calibration was applied to that data. This report is an addendum to the existing Oxygen *Oxygen_Calibration-NAB08.pdf* and methodology behind Winkler oxygen measurements can be found in *Winkler_oxygen-NAB08.pdf*.

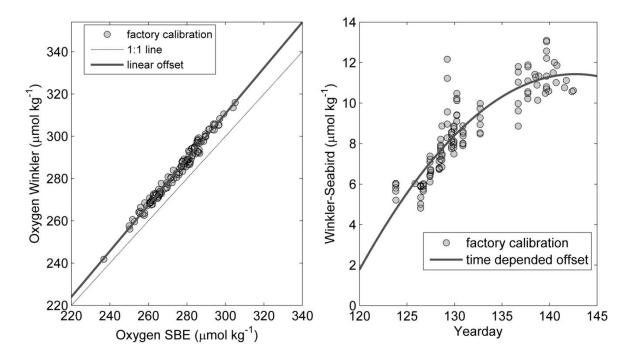
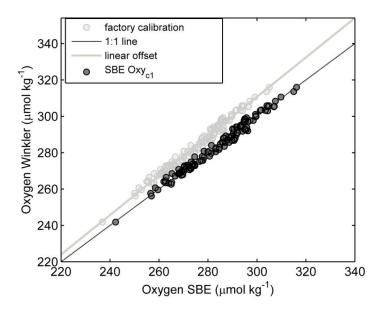


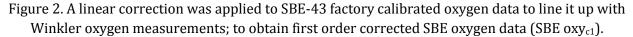
Figure 1. A) SBE dissolved oxygen with factory calibration and offset vs. Winkler dissolved oxygen. Light grey line is 1-to-1 relationship. B) Difference between Winkler oxygen and SBE dissolved oxygen with factory calibration as a function of time, with polynomial quadratic fit.

The SBE43 was calibrated immediately before the cruise. The factory calibration was applied to SBE43 oxygen sensor output, and after comparison to Winkler oxygen measurement two trends can be observed. First - a linear offset when compared to Winkler oxygen measurement, and the second - time depended trend (Figure 1a, gray dots). Second time depended trend is likely due to electrochemical drift (Figure 1b, gray dots; <u>http://www.seabird.com/application_notes/AN64-2.htm</u>).

Below explained correction will be applied to new (v5) release of Knorr CTD and bottle files, and it also applies to BCO-DMO released dataset.

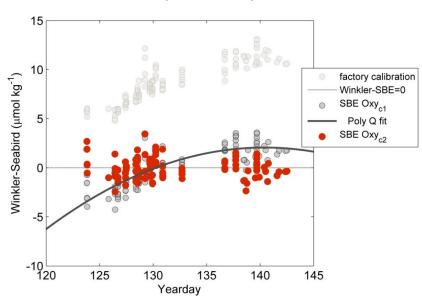


SBE oxy c1 = 1.0835±0.0127 * SBE oxy -14.3509±3.4988 (r2 = 0.9834)



Second correction

 $X = -0.01998 * (YD)^{2} + 5.61* (YD) - 391.7$ (r2 = 0.6784)



SBE oxy c2= SBE oxy c1 - X

Figure 3. Time depended (YD) quadratic polynomial correction was applied to Winkler corrected datatset (SBE oxy c1); which provided us with final dataset (SBE oxyc2).

FINAL RESULT:

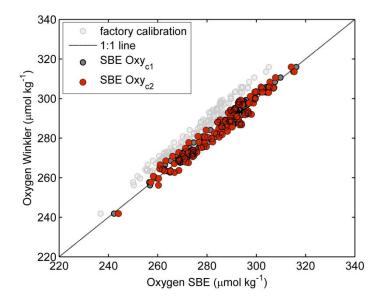


Figure 3. Comparison of the SBE measured dissolved oxygen and Winkler method measured dissolved oxygen for different calibration products; light gray dots - factory calibration only, dark gray dots - Winkler corrected data, red dots - final dataset, time and Winkler offset corrected.

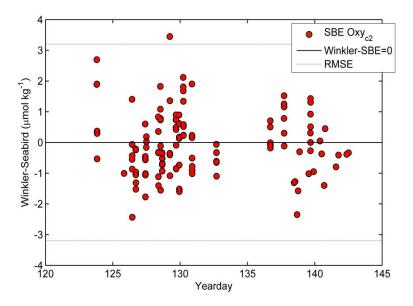


Figure 4. Final difference between Seabird (time and Winkler, c₂) calibrated and Winkler method measured dissolved oxygen as a function of time. RMSE (3.199 µmol kg⁻¹) is shown as dashed lines.