RRS *Discovery* cruise 365
11 May – 2 June 2011
CTD oxygen calibration

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Abstract

Only a limited number of dissolved oxygen samples were collected during RRS *Discovery* cruise 365. Correlation of these data with the Sea-Bird CTD dissolved oxygen sensor was poor. The relationship between the two was investigated and three different groups of data were found. However, the sample size of each group was very small reducing its statistical value. No reason could be found to prefer any one relationship over the others, they appear to be completely random. Since modern dissolved oxygen sensors can be quite stable, well-behaved and precise, it was concluded that calibrating the sensor data risked introducing greater error than was already present.

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Introduction

During RRS *Discovery* cruise 365 triplicate dissolved oxygen samples were collected from up to four selected depths on 19 CTD casts taken throughout the cruise (Read et al, 2011). The total number of samples collected and analysed was 150, giving 50 independent samples for calibration of the CTD dissolved oxygen sensor.

Comparison with the CTD oxygen sensor showed a large amount of scatter making it difficult to define a correction to the CTD sensor. Here the data are considered in more detail with possible problems presented. It is concluded that the oxygen sample data are inadequate to calibrate the CTD oxygen sensor. Reasons for this are explained and a better procedure is recommended.

Dissolved oxygen samples

Water column dissolved oxygen was determined from selected CTD samples collected throughout the cruise to calibrate the CTD dissolved oxygen sensor. Samples were drawn in triplicate from up to four selected depths on 19 CTD casts taken throughout the cruise. A total of one hundred and fifty samples were collected and analysed.

The Winkler chemistry methodology of Carrit and Carpenter (1966) was used to fix and titrate the sample. A *Copenhagen Radiometer* auto-titrator was used for the titrations and the end point was determined spectrophotometrically. (Read et al, 2011). A fuller account of the method used is given in Sherwin et al (2009).

CTD oxygen sensor

A SeaBird 43 dissolved oxygen sensor was mounted as an auxiliary sensor on the SeaBird SBE911+ CTD. Configuration of the sensor, serial number 43-1882 (V0) is given in Table 1. A total of 55 CTD profiles were worked during the three week cruise. Maximum depths reached were less than 3000 m and a large number of profiles were worked in shallower water, including the Scottish Shelf, where depths were about 30-50 m.

Table 1. Oxygen sensor configuration

A/D voltage 0, Oxygen, SBE 43		C :	-2.41260e-006
Serial number :	43-1882	E :	3.60000e-002
Calibrated on :	10-Jul-2010	Tau20 :	1.82000e+000
Equation :	Sea-Bird	D1 :	1.92634e-004
Soc :	4.96700e-001	D2 :	-4.64803e-002
Offset :	-5.00600e-001	H1 :	-3.30000e-002
A :	-3.52060e-003	H2 :	5.00000e+003
B :	1.57910e-004	H3:	1.45000e+003

CTD data were processed in two steps. Initial processing was performed with the SeaBird software, SeaSoft. Data were then transferred to pstar for further work (Read et al, 2011).

In SeaSoft the data were read from the raw (hex) CTD data file and converted to engineering units using DatCNV. Oyxgen data were shifted by +5 seconds using

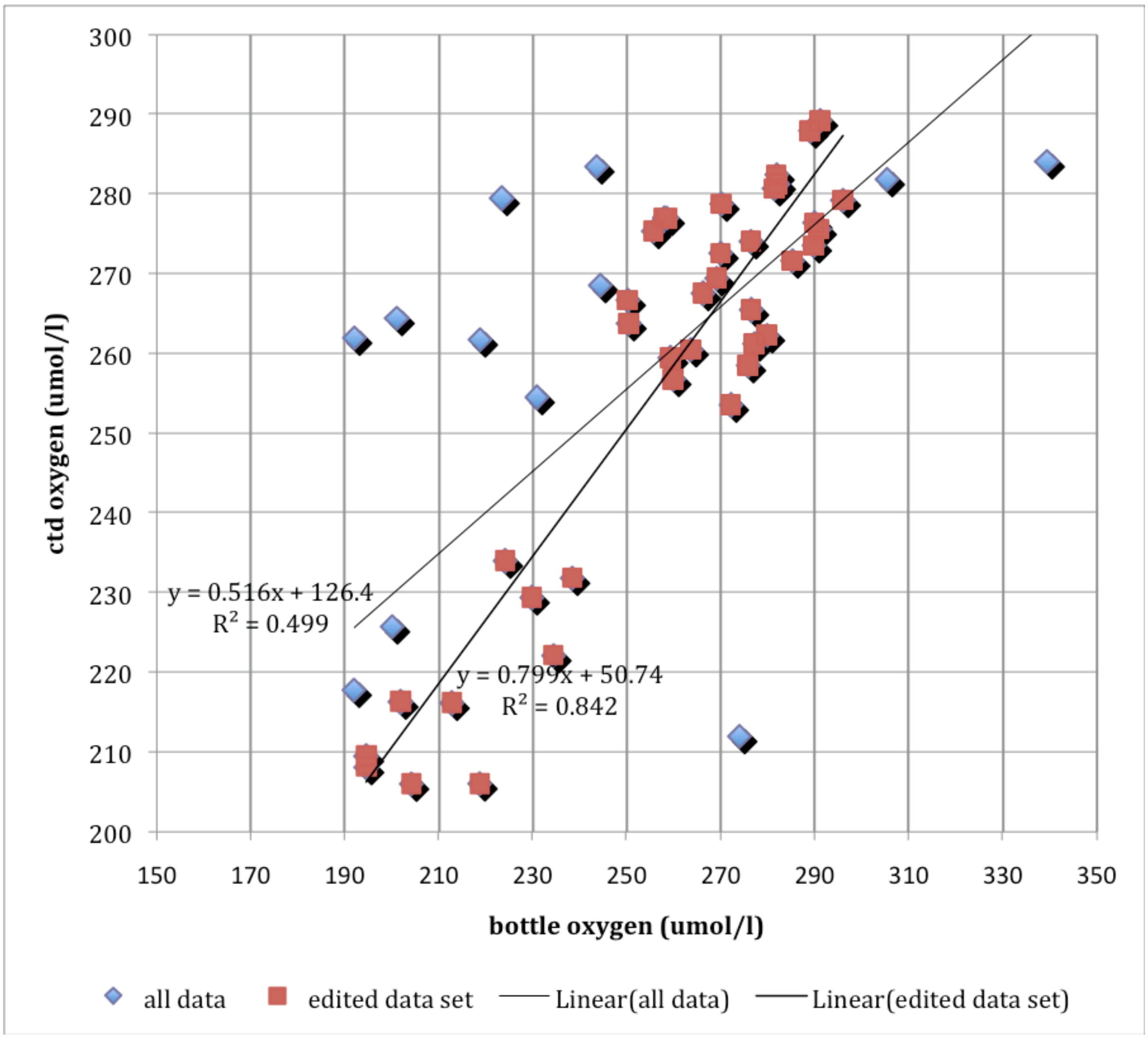
AlignCTD to compensate for hysteresis and lags in the sensor response time. Variables oxygen voltage, oxygen concentration and oxygen saturation were included in the output. Spot scans at the time each Niskin bottle was fired were saved in a separate file (ros). Profile data were further processed, with spikes deleted using WildEdit, where points were removed when outside 2 standard deviations on a first pass and 10 standard deviations on a second pass over a scan range of 500 data points. The profile data were output to an ascii file (cnv) for transfer to pstar binary format. Data were stored at 24 hertz, but a secondary file of ten second averages was also generated.

The bottle firing times were read into pstar and merged with the ten second average file to give a 10-second mean value for each bottle sample. The average of the triplicate oxygen samples was merged. Note that individual oxygen values were edited on standard deviation of the average of the three samples. The resulting file contained 10-second mean CTD values for each bottle fired and average oxygen concentration for each Niskin bottle sampled.

Results

Bottle oxygen and CTD oxygen concentrations are compared in **Figure 1**.

Figure 1. Bottle oxygen vs CTD oxygen



All 50 data points are shown in Figure 1 and reveal a lot of scatter in the data. A regression (equation 1) gives a low correlation coefficient, the gradient is low (half unity) and the offset high, because the calculation is influenced by the outliers.

1. Y = 0.516X + 126.4 r2 = 0.499 n = 50

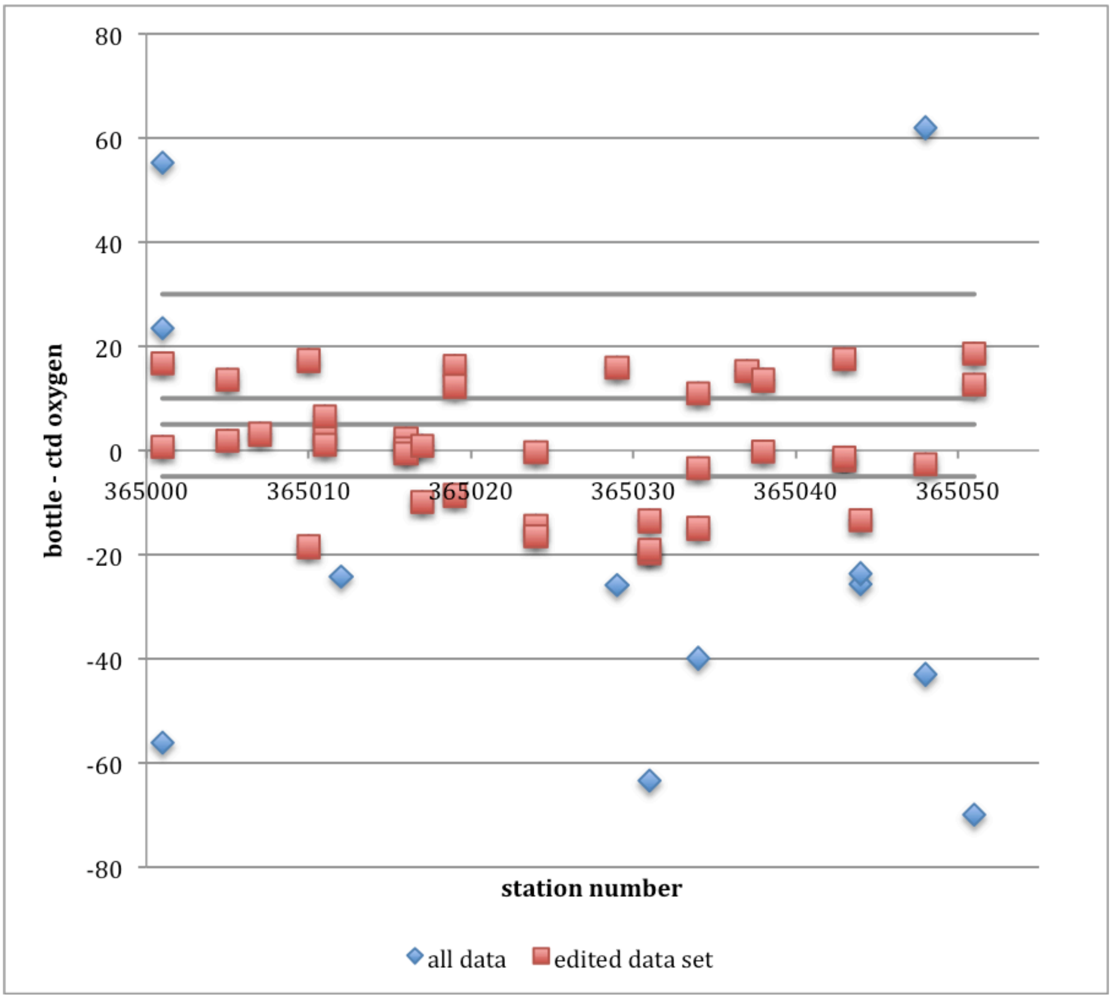
We define the oxygen residual as the difference between bottle oxygen and ctd oxygen. This is a measure of the relationship between the two data sets and we use the residual to identify good and bad data. Excluding the values having the largest residual (or limiting the residual to ±20) leaves 38 good values giving the relationship of equation 2,

2. Y = 0.799X + 50.74 r2 = 0.842 n = 38

The correlation coefficient is improved to more than 0.8, while the gradient is closer to one and the offset is halved.

However, it can now be seen that there are two lines of points within the data. This is illustrated by a plot of the residuals against station number (Figure 2) where station number is a proxy for time. The two lines revealed in Figure 1 can be defined as those values centred around ±5 (eqn 1) and those values lying between 10 – 30 (eqn 2). The remaining points make a third, scattered, group of values less than -5 . The groups appear as roughly straight lines over time.

Figure 2. Bottle – ctd oxygen residuals by station number



Regression of the three groups separately gives (Figure 3)

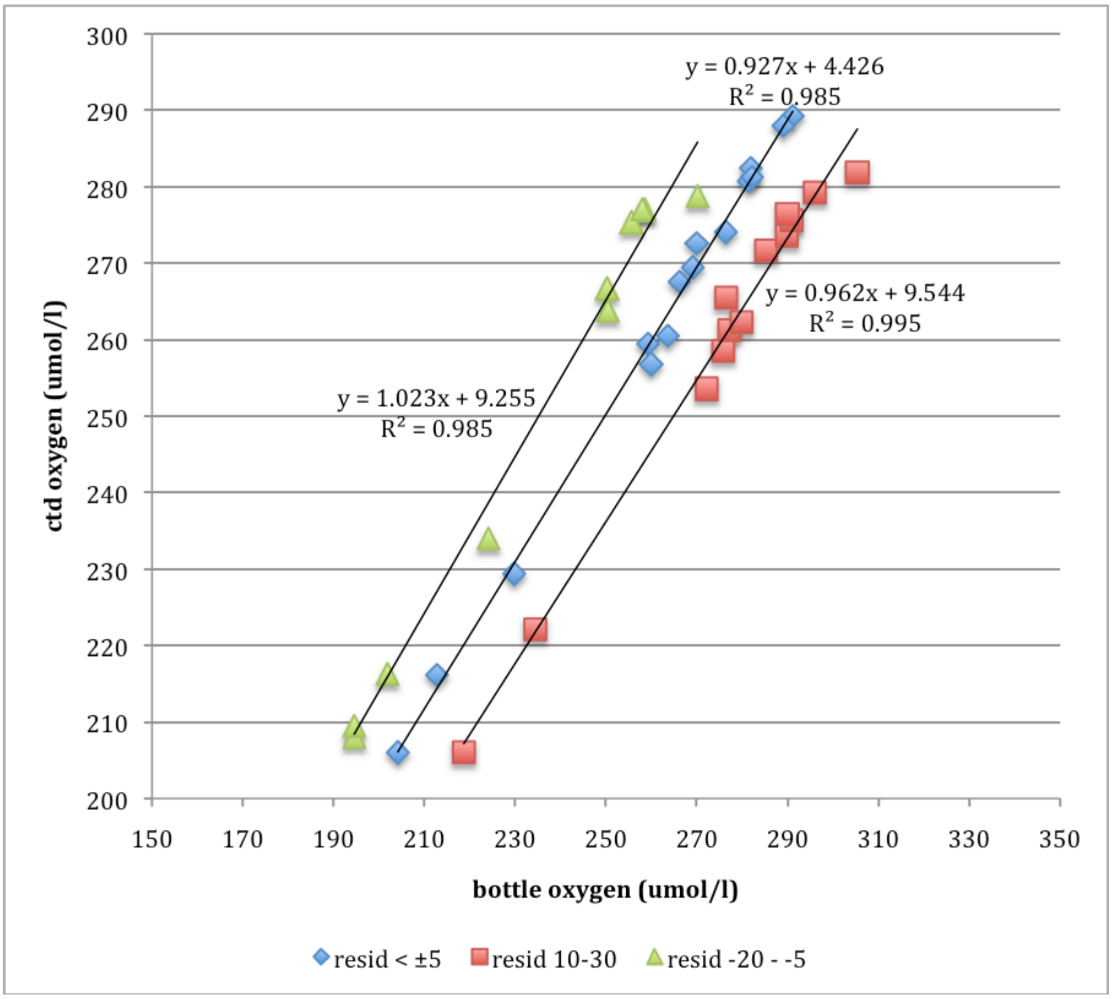
3. Y = 0.962X + 9.544 r2 = 0.995 n = 15 for residual <±5

4. Y = 0.927X + 4.426 r2 = 0.985 n = 13 for residual between 10-15

5. Y = 1.023X + 9.255 r2 = 0.985 n = 10 for residual between -20 - 05

Each of the three groups has a much better correlation coefficient (>0.9) than the correlation of the edited data set. The gradients are all close to 1 and the offset is greatly reduced. Any one equation would appear to be an improvement on the un-edited data set. The argument against using them is that the samples are so small and as N decreases towards 2, the correlation coefficient improves towards one as does the gradient and the offset tends towards zero.

Figure 3. Regression of bottle vs CTD oxygen



Why are there three lines and why should any one be preferred over the others?

The measurement of dissolved oxygen is influenced by both environmental and technical factors. Possible technical issues include temperature, as it affects the instrumentation, Niskin bottle e.g. whether the bottle has a good seal, or sampler and analyst. Environmental influences that affect the behaviour of the membrane in the sensor, hence the measurement of dissolved oxygen, are primarily pressure, temperature and salinity. To investigate possible relationships with any of these factors bottle oxygen was plotted against pressure (Figure 4), temperature (Figure 5), Niskin bottle number (Figure 6) and station number

(Figure 7) as a proxy for time. Salinity is not shown as the effect is very much smaller than temperature, the effect of which it mimics. No data are available on samplers and analysts.

Figure 4. Bottle oxygen against pressure grouped by residual offset

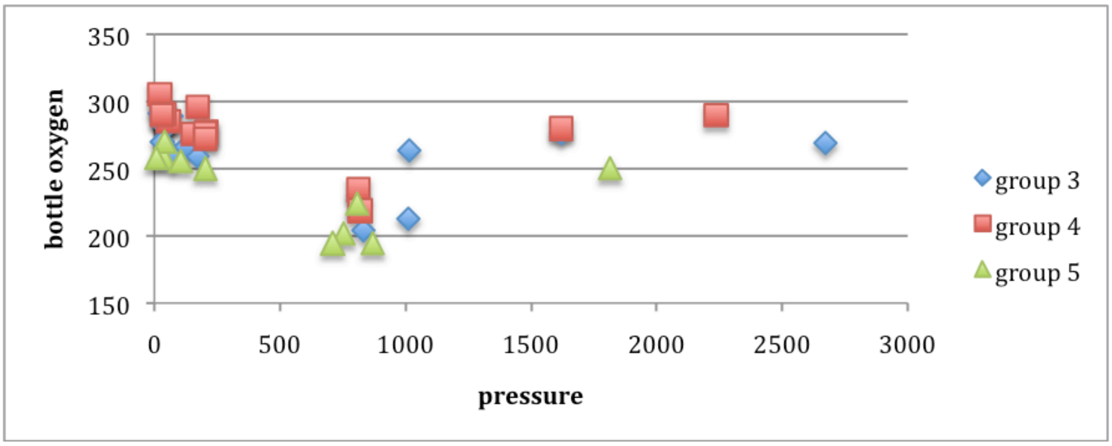


Figure 5. Bottle oxygen against temperature grouped by residual offset

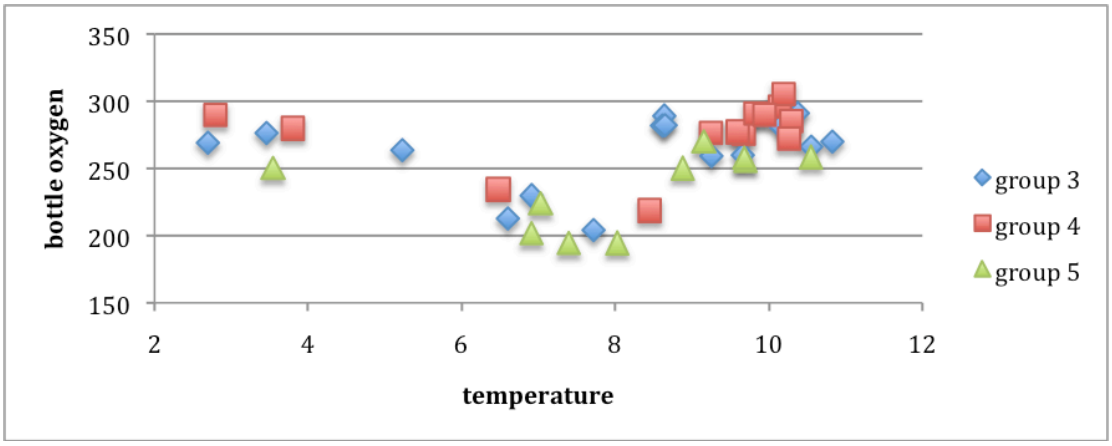


Figure 6. Bottle oxygen against Niskin bottle number grouped by residual offset

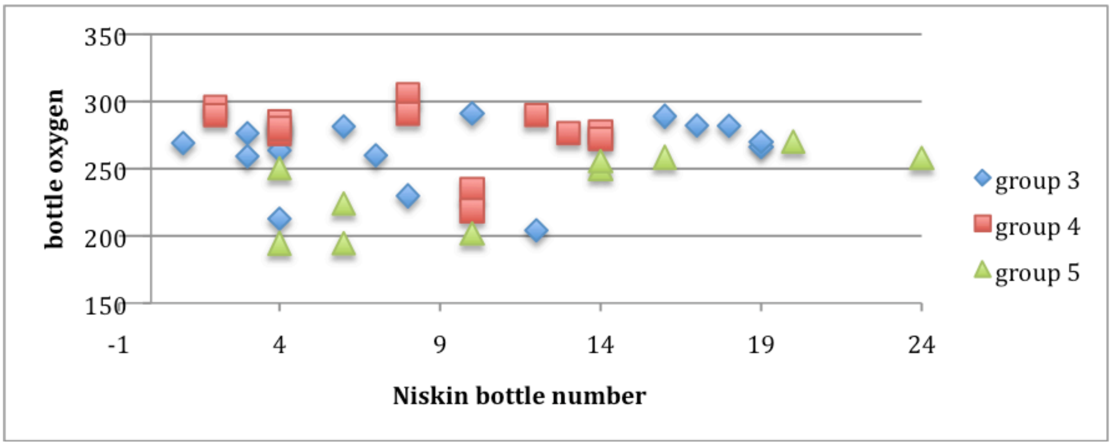
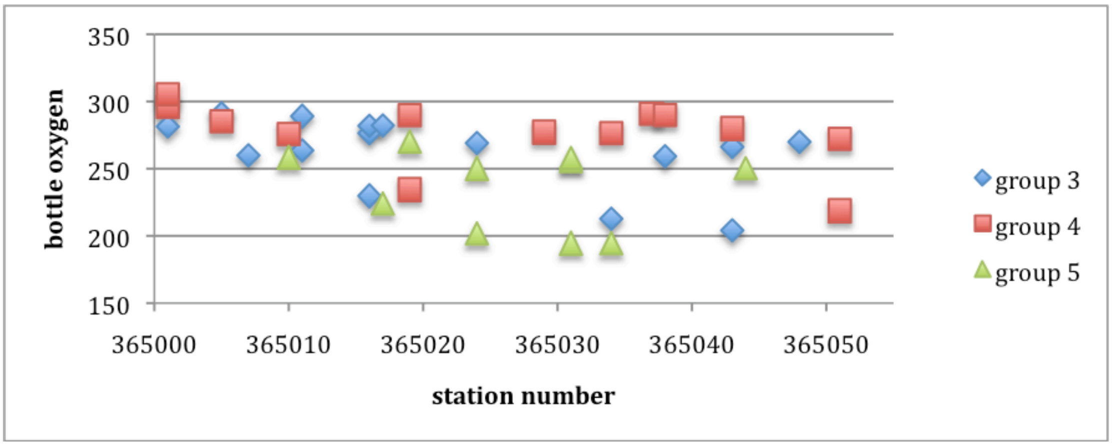


Figure 7. Bottle oxygen against station number grouped by residual offset



Figures 4-7 show that samples from all three groups of data appear across all pressures, temperatures, Niskin bottle numbers and station numbers. Therefore the groups do not appear to be linked to any one of these factors and it can be concluded that the different groupings are random.

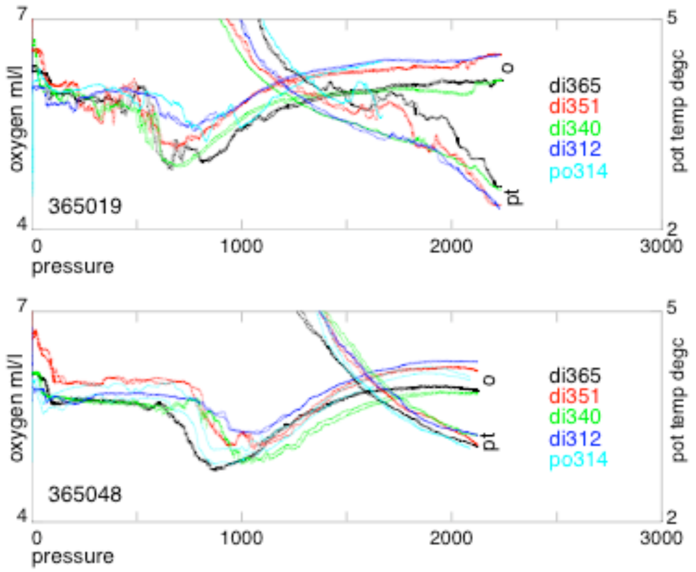
Since the CTD oxygen sensor was highly unlikely to be changing on such a random basis, the cause of the groupings appears to lie with the bottle samples.

It has been noted in the past that individuals may achieve very different precisions using apparently identical methods. These samples were analysed by one chemist, but the samples were drawn from the Niskin bottles by three different people, one of whom was an experienced sea-goer and sampler but the other two were both inexperienced students. It is not known who collected which sample. Previous experience has shown individuals to vary hugely in their ability to achieve precise and consistent oxygen measurements (Read, unpublished data; Allen, pers comm.). Drawing oxygen samples is not difficult but requires meticulous attention to detail. It is possible that the scatter in the samples results from the inexperience or imprecise practise of novice samplers, but it seems unlikely that three individuals should produce a unique relationship with a dissolved oxygen sensor. However, it is one fact that might impact on the calibration yet it is not possible to investigate further.

Comparison with previous data sets

The RRS *Discovery* cruise 365 data set was collected as part of the Extended Ellett Line and many of the stations were repeats of previous occupations. High quality data has been collected over 35 years. Therefore it is possible to compare the current data set with other data from exactly the same place. Since dissolved oxygen is an indicator of water mass properties, comparison can be made with temperature to check how much variability there is in the water masses observed, where the temperature sensor is calibrated in the laboratory to high precision and accuracy.

Figure 8. Dissolved oxygen profiles from four Extended Ellett Line cruises. Black – Discovery cruise 365 (2011), red – Discovery cruise 351 (2010), green – Discovery cruise 340 (2009), blue – Discovery 312 (2006), turquoise – Poseidon 314 (2004).



Sadly this proves unhelpful. The year to year variability as revealed by temperature is significant and the scale of variability is large enough to mask any possible problems in the calibration of dissolved oxygen. Figure 8 shows two examples of five years of data from the same station. Other stations showed similar results.

Conclusions

We have three possibilities.

1. Calibrate the CTD oxygen sensor using the edited data set (equation 1)
2. Calibrate the sensor using one of the three different groupings of data
3. Leave the sensor uncalibrated.

We have no reason to prefer any one of the three groupings over the others, and have little confidence in them because of the small sample size.

Some dissolved oxygen sensors are very precise in their measurements (e.g. RRS *James Cook* cruise 66, unpublished data) and need little correction. Conversely, some oxygen sensors need quite significant corrections (eg. RV *Poseidon* cruise 314, Read et al 2006).

However, options 1 and 2 risk introducing greater error into the sensor output than might be there at present. Therefore, the conclusion reached is not to attempt to calibrate the RRS *Discovery* 365 CTD dissolved oxygen sensor with the available sample data. CTD dissolved oxygen data should be flagged as ‘suspect’.

Recommendations

The gas permeable Teflon membranes of dissolved oxygen sensors are affected by the temperature, salinity and pressure of the environment in which the membrane is submerged (Owens & Millard, 1985). To correct for these differing affects a third order polynomial calibration is needed unless the effects are otherwise compensated for.

Pressure changes the permeability characteristics of the membrane. The changes have long time constants and depend on the sensor's time-pressure history. The slow processes result in hysteresis in long, deep casts and Sea-Bird recommend that a hysteresis correction is recommended for profiles deeper than 1000 m (Sea-Bird, Application Note 64-3).

The Sea-Bird SBE 43 sensor contains a thermistor to compensate for temperature effects (Sea-Bird Application Note 64).

Sensor drift results from fouling, which can be minimised by rinsing the sensor (Sea-Bird Application Note 64-2). This is usually done routinely at the end of each CTD.

Sea-Bird Electronics find that the internal corrections to the SBE 43 mean that the output is linear (Sea-Bird Application Note 64-2).

Although the hysteresis correction is made routinely in the NOC standard processing path and temperature effects are compensated internally, it is good practice to draw sufficient independent samples to check that the instrument is performing as expected. For example, experience has shown that a poorly maintained sensor does not always behave correctly. The data collected on the Extended Ellett Line in 2004 identified offsets with depth and drift over time in the Sea-Bird 43 oxygen sensor (Read, 2006). Data collected on the Extended Ellett Line in 2006 also showed a gradual drift with time (Allen & Stinchcombe, 2007). To identify such problems and to achieve a calibration means obtaining good sample coverage over a range of depths (especially the greatest depths reached) and temperatures.

Best practice for dissolved oxygen calibration was laid out for the World Ocean Circulation Experiment (WOCE) by Culberson (1991) and it is recommended that this be followed whenever dissolved oxygen sensors are used, to avoid the problems described here.

References

Allen, J.T., Stinchcombe, M.C. et al. 2007. RRS *Discovery* Cruise 312, 11-31 Oct 2006. The extended Ellett Line 2006. National Oceanography Centre Southampton Cruise Report, No 15, 146pp.

Carrit, D.E., Carpenter, J.H., 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining oxygen in seawater. A NASCO Report. Journal of Marine Research, 24, 286-318.

Culberson, C.H., 1991. In 'The WOCE Operations Manual (WHP Operations and Methods)', WHPO 91/1, WOCE Report No 68/91, Woods Hole.

Owens, W.B., Millard Jr, R.C., 1985. A new algorithm for CTD oxygen calibrations. Journal of Physical Oceanography, 15, 621-631.

Read, J., 2006. RV *Poseidon* cruise 314, 11 – 23 July 2004, CTD sensor calibration. National Oceanography Centre internal report (unpublished document), 16pp.

Read, J.F. et al., 2011. RRS *Discovery* cruise 365, 11 May-02 Jun 2011. The Extended Ellett Line 2011. National Oceanography Centre Cruise Report No 6, 90pp.

Sea-Bird Electronics Application Note No 64. SBE 43 Dissolved Oxygen Sensor – Background Information, Deployment Recommendations, and Cleaning and Storage. July 2012.

Sea-Bird Electronics Application Note No 64-2. SBE 43 Dissolved Oxygen Sensor Calibration and Data Corrections. June 2012

Sea-Bird Electronics Application Note No 64-3. SBE 43 Dissolved Oxygen (DO) Sensor – Hysteresis Corrections. February 2010.

Sherwin, T., Aldridge, D., Allen, J., Amin, S., Attard, K., Beaton, J., Brand, T., Barnard, C., Calderwood, J., Dumont, E., Hebden, M., Ivanov, V., Macey, A., Marsay, C., McLachlan, R., McRae, J., Mogg, A., Mohammed, K., Porter, M., Read, J., Rerolle, V., Richier, S., Short, J., Steigenberger, S., Wager, N., 2009. RRS *Discovery* cruise D340a, Reykjavik to Dunstaffnage via Rockall and the Wyville Thomson Ridge, 10 June to 25 June 2009. Scottish Association for Marine Science, Internal Report No 264, 196pp.