DOTSS Voyage 2001, Nutrient data reprocessing.

Rebecca Cowley, Susan Wijffels, December, 2008.

This is an abridged version of the original report which contains more detail on the correction methods investigated. For the full version, contact Rebecca.Cowley@csiro.au.

Introduction;

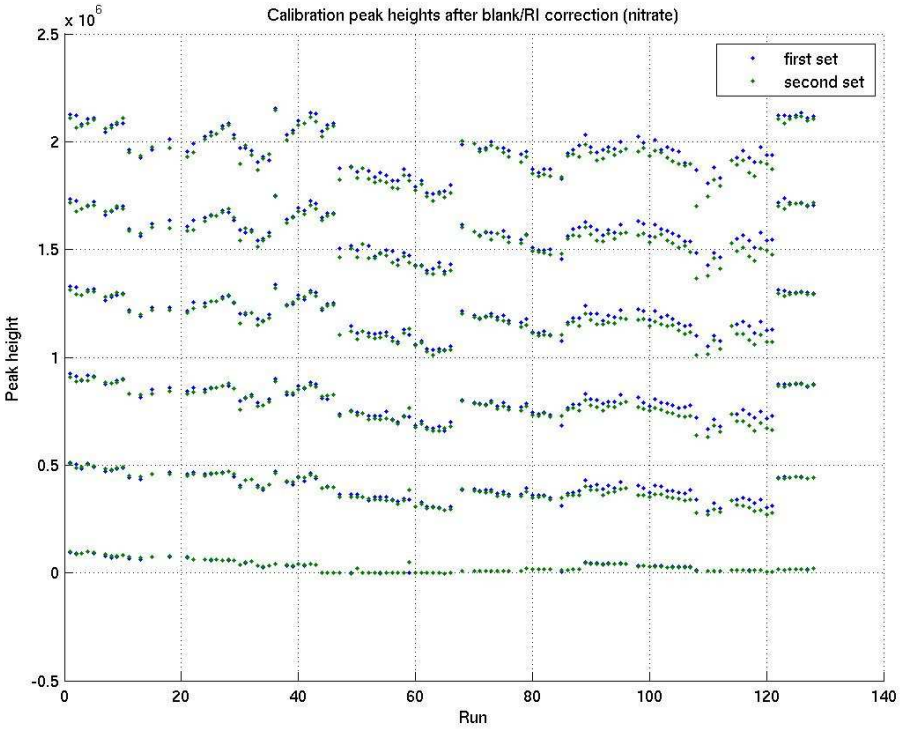
Data was collected in the Southern Pacific Ocean along P15S during 2001. The nutrient data from the voyage was known to have large errors associated with it, particularly with nitrate and phosphate. The data has been reviewed and re-processed, comparing it to the DISCO 1996 voyage along the same section. This report discusses the reprocessing method and results. All final results are reported in umol/kg. Nitrate concentrations refer to nitrate+nitrite.

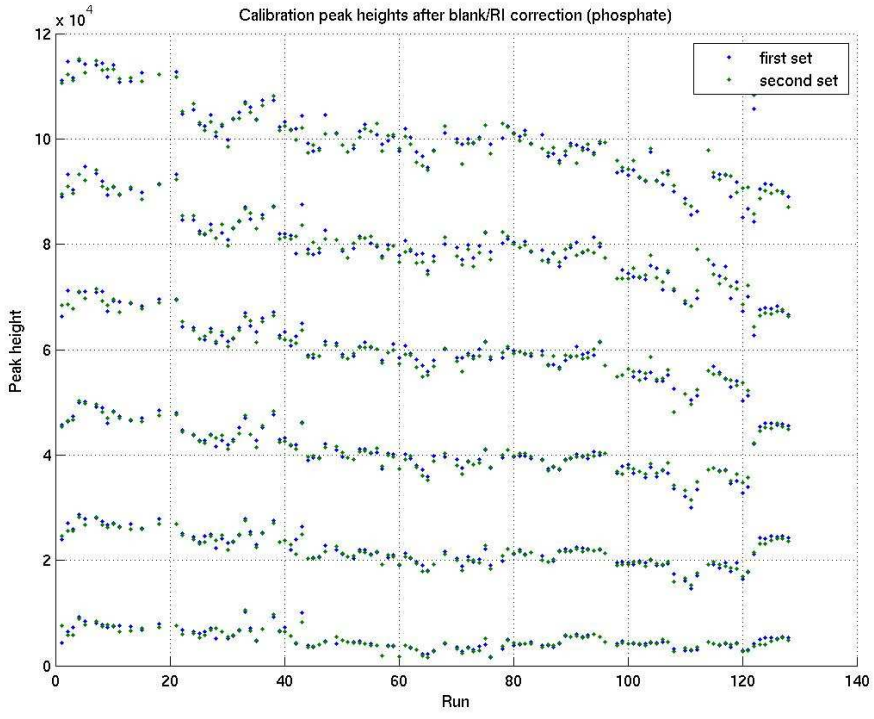
Procedure:

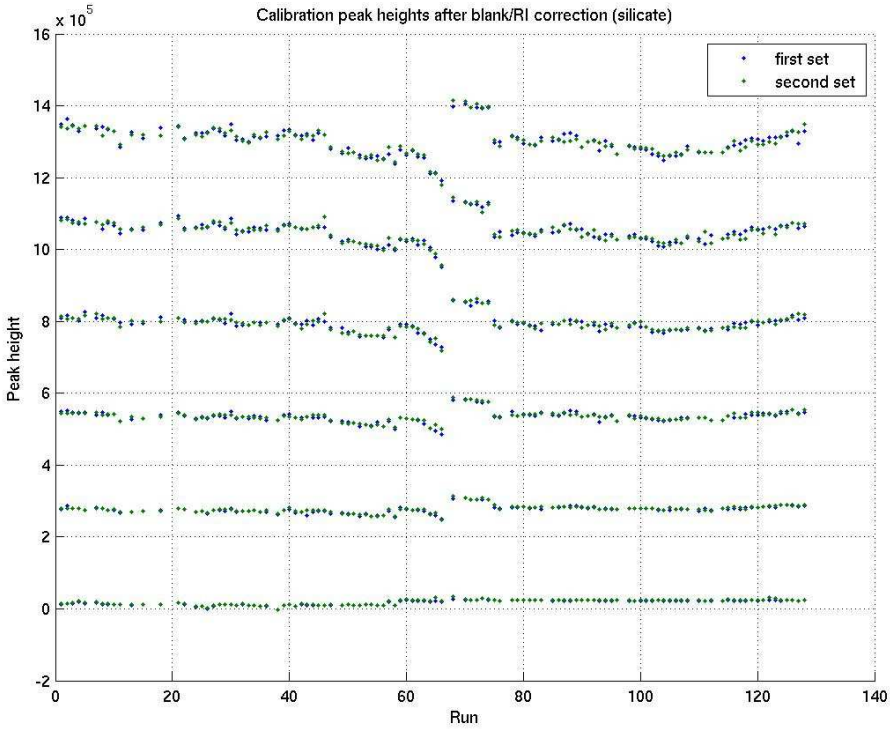
1. **Re-calculate concentrations:** From about run 40 to near the end of the voyage, it was clear there was an issue with the Alpkem in both the nitrate and phosphate channels. It was discovered at the end of the voyage that there was a growth in both flow cells. This resulted in depressed peak heights (see figures below – 'first set/second set' refers to the first and second set of calibrants in each run).

   The re-calibration method uses the f values for each level of calibrant, and the sample results were calculated based on the f values from the next-highest calibrant.

2. **Final plots to flag outliers:** The final results were plotted against ctd pressure and theta to identify outliers. The outliers were flagged as 'bad' (with a 4 according to WOCE standards). Any results where pressure was missing were flagged with a 4 and any where oxygen and salinity were missing were flagged with a 3 (questionable).


Calibration peak heights after blank/RI correction (nitrate)
x 10^6
first set
second set
Peak height
Run
2.5
2
1.5
1
0.5
0
-0.5
0
20
40
60
80
100
120
140

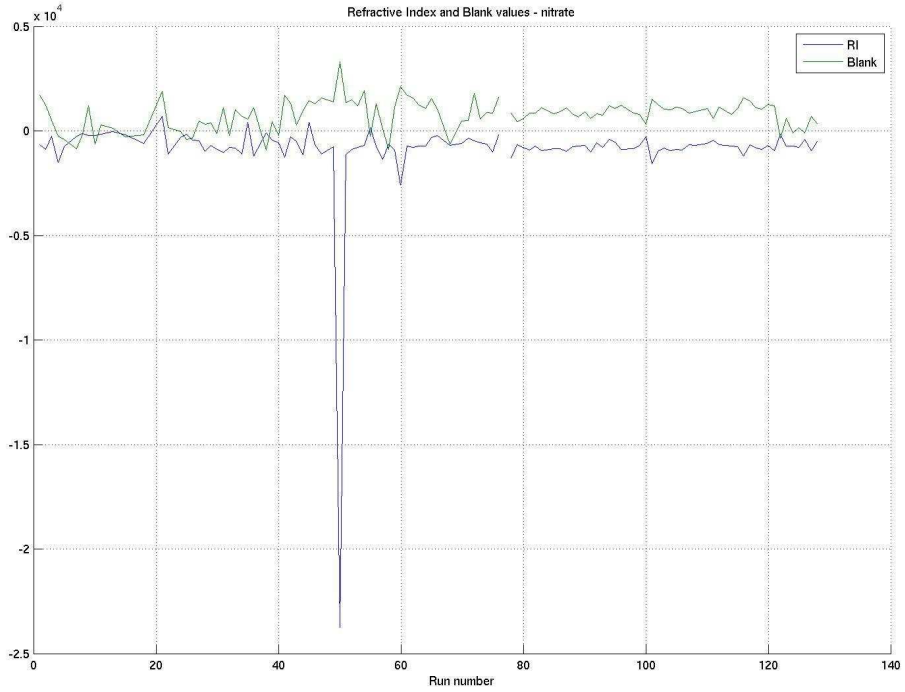

Calibration peak heights after blank/RI correction (phosphate)
x 10^4
first set
second set
Peak height
Run
12
10
8
6
4
2
0
0
20
40
60
80
100
120
140


Calibration peak heights after blank/RI correction (silicate)
x 10^5
Peak height
Run
first set
second set
16
14
12
10
8
6
4
2
0
-2
0
20
40
60
80
100
120
140

Corrections to Nitrate/nitrite data

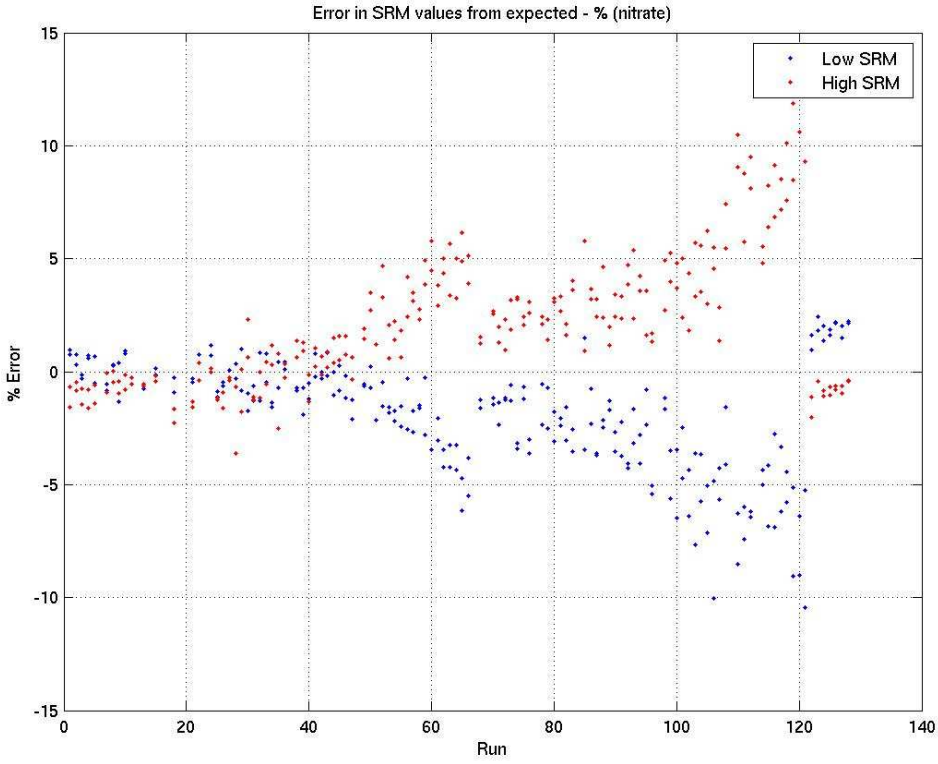
1. **Use an average refractive index and blank value.** In place of the actual refractive index and blank values for each run, an average value from all the runs was calculated and used in the peak height correction for each run. This made some improvement in the precision of the results between runs.

Refractive Index and blank values for each run.

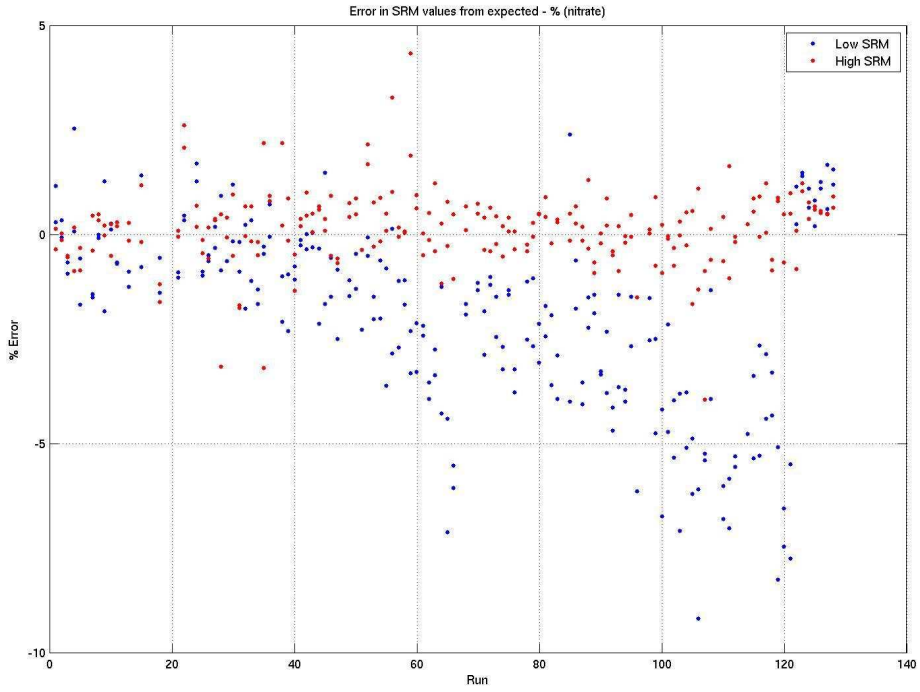


2. **Recalculation of data with sensitivity factors from the next highest calibrant.** Closer evaluation of the WOCE method (looking at actual OSU runs) showed that OSU only utilised one standard when calculating the sensitivity factors. This makes sense when the system is completely linear and the sample concentrations are close to the calibrant concentration used. For this data, the next highest calibrant from the sample concentration was used to calculate the concentration.

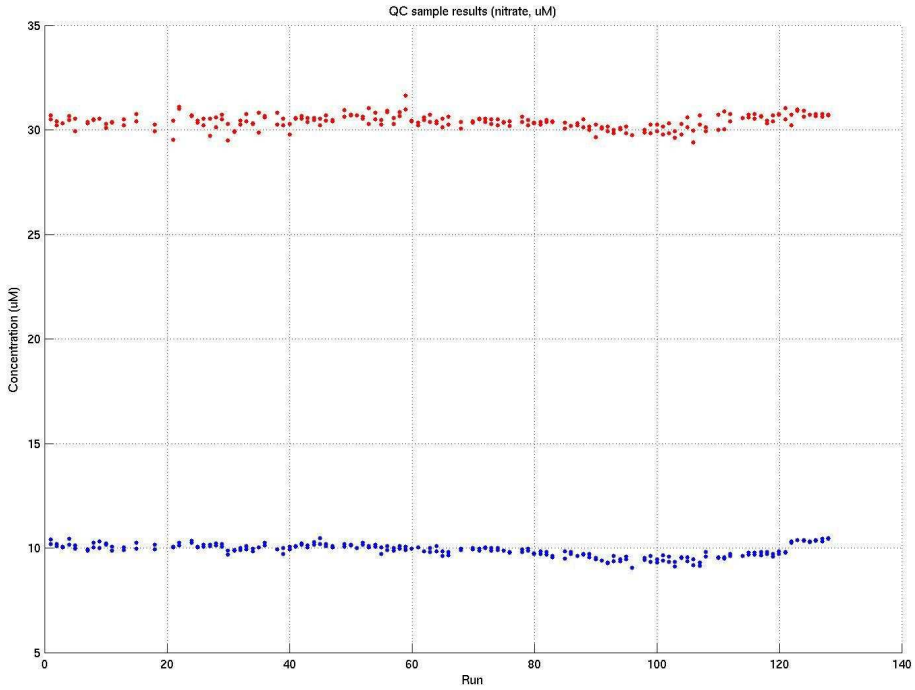
SRM results from the original calibrations.



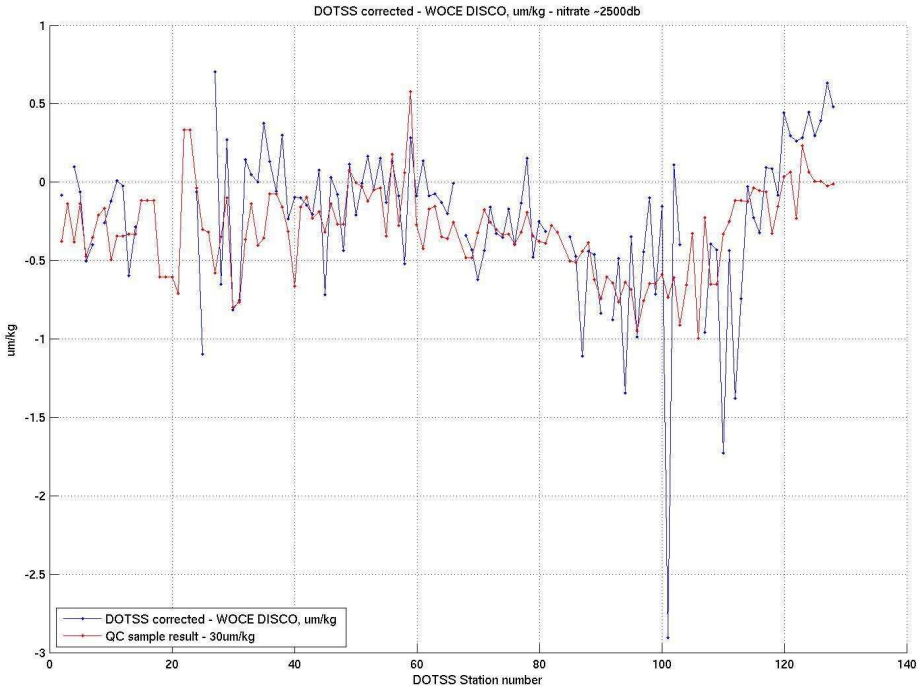
SRM results after inclusion of average RI and blank values, then calibration with the next highest calibrant.



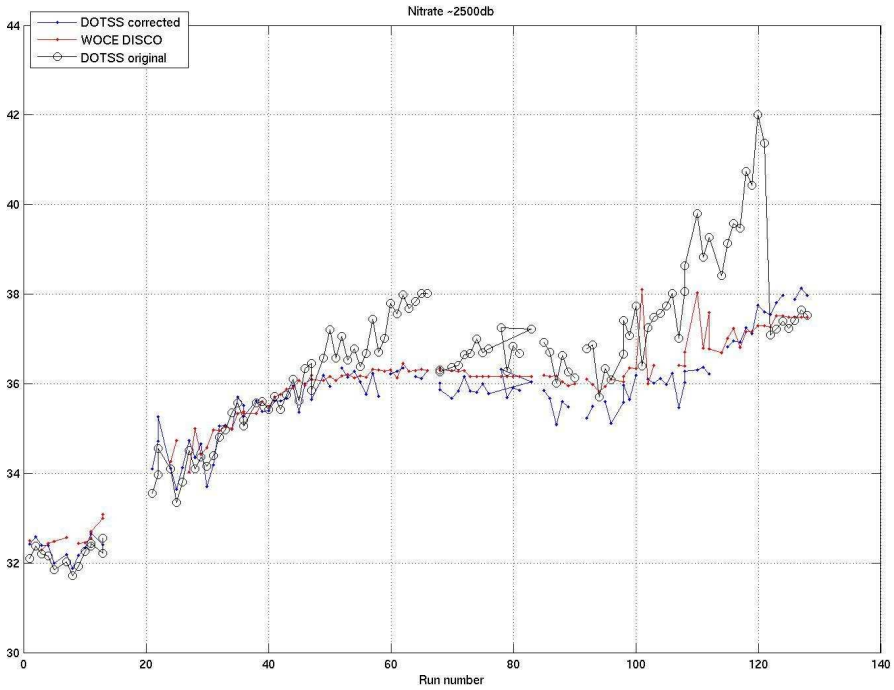
QC sample results



QC sample results and DOTSS-WOCE results:



Comparison with WOCE data and original DOTSS data at 2500db after inclusion of average RI and blank values, then calibration with the next highest calibrant.



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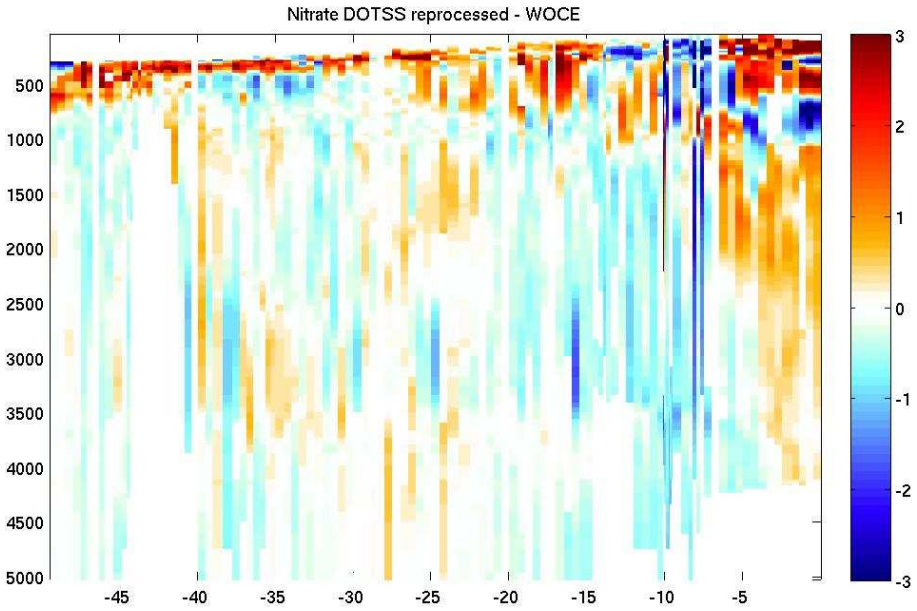
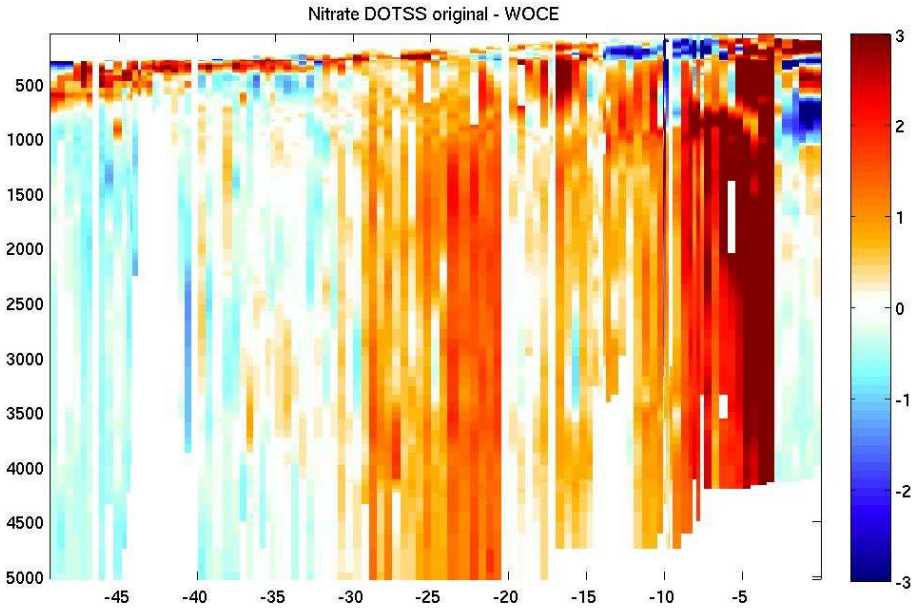
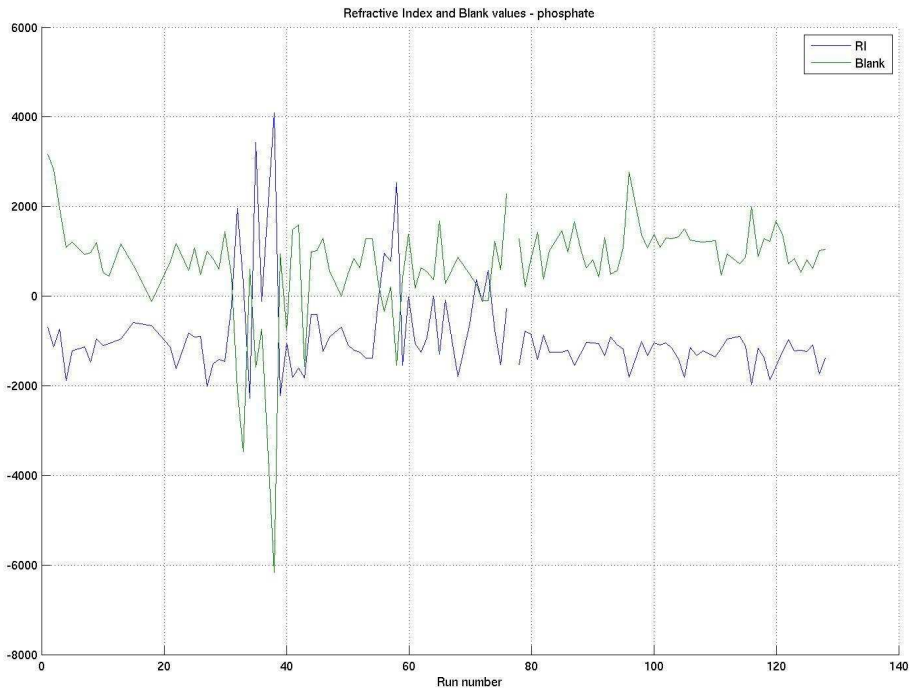




Corrections to Phosphate data

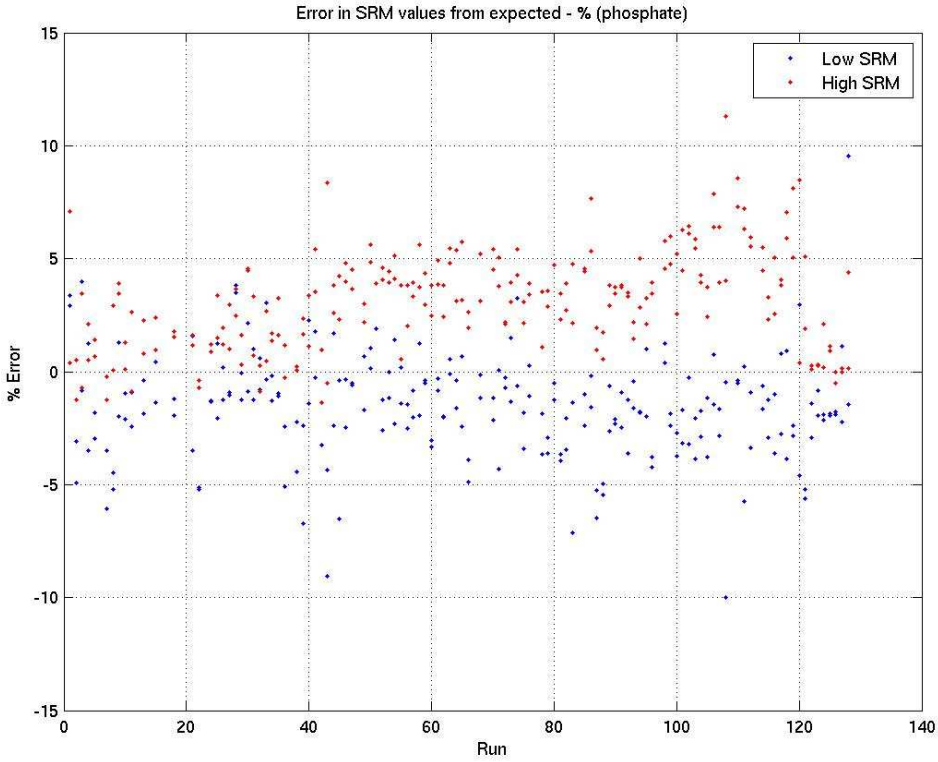
1. **Mean RI and blank values subtracted from peak heights:** The mean RI and blank values for all runs was subtracted from the peak heights during the calculations, rather than the individual run's values.

Refractive Index and blank values for each run.

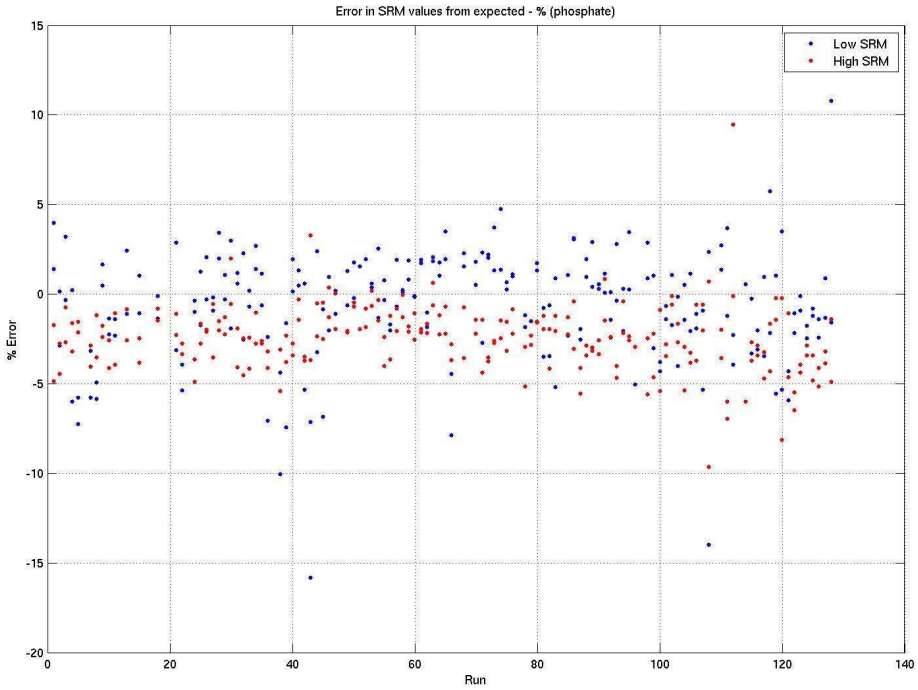


2. **Recalculation of data with sensitivity factors from the next highest calibrant.** Closer evaluation of the WOCE method (looking at actual OSU runs) showed that OSU only utilised one standard when calculating the sensitivity factors. This makes sense when the system is completely linear and the sample concentrations are close to the calibrant concentration used. For this data, the next highest calibrant from the sample concentration was used to calculate the concentration.

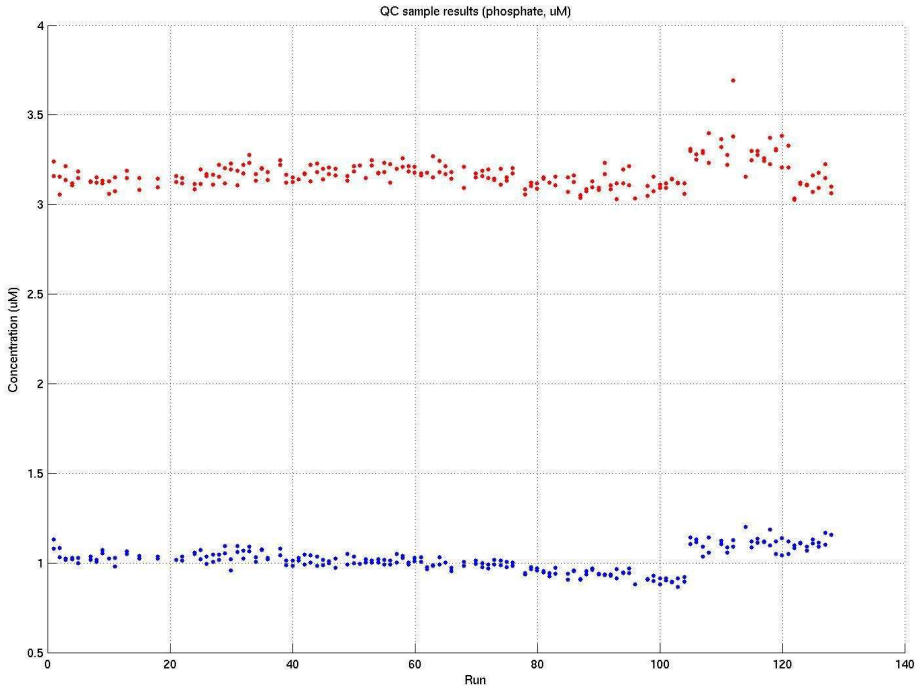
SRM results from the original calibrations.



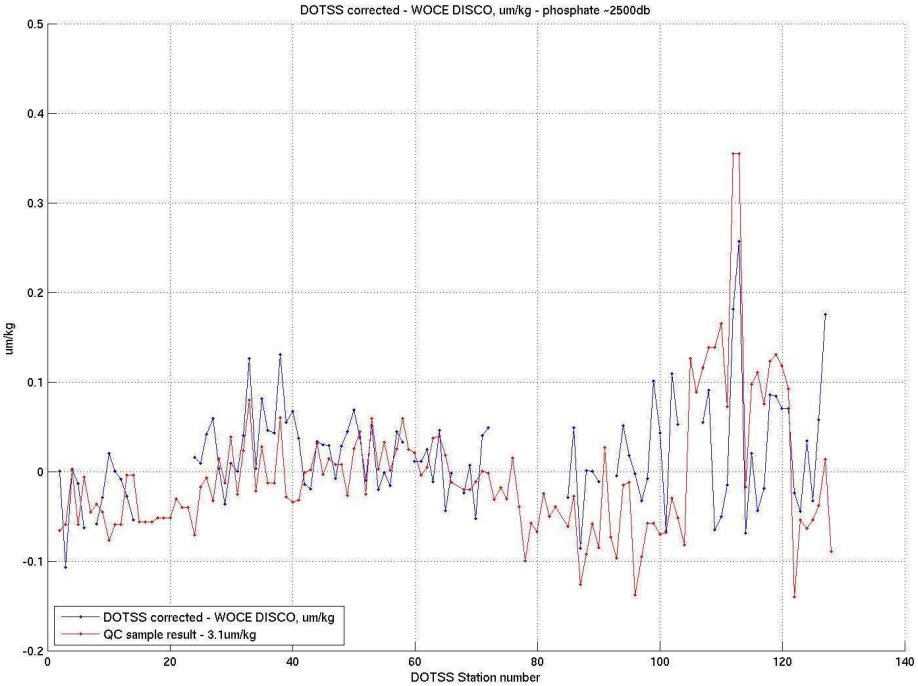
SRM results after inclusion of average RI and blank values, then calibration with the next highest calibrant.



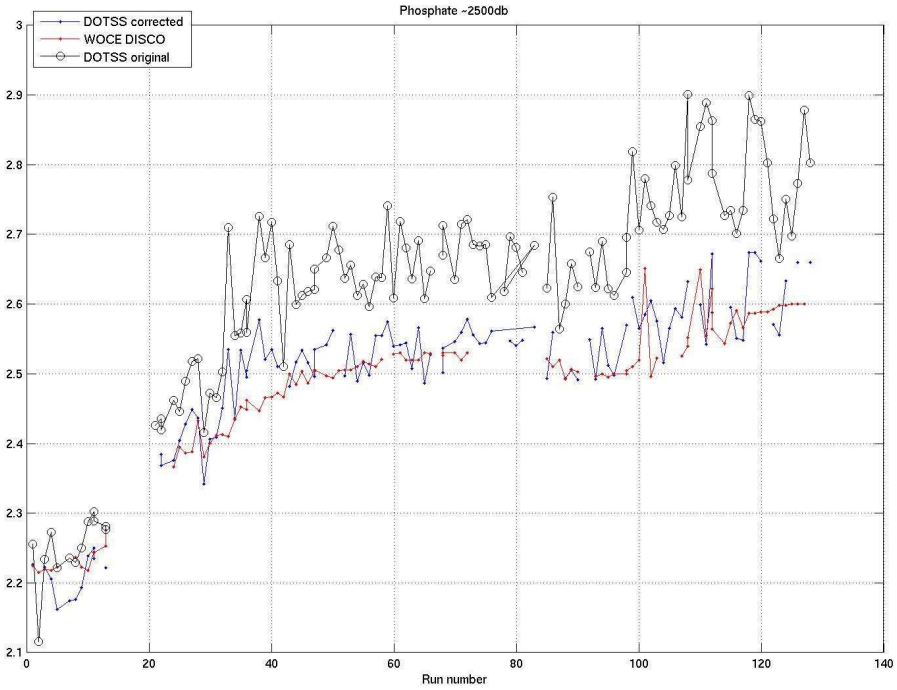
QC sample results:



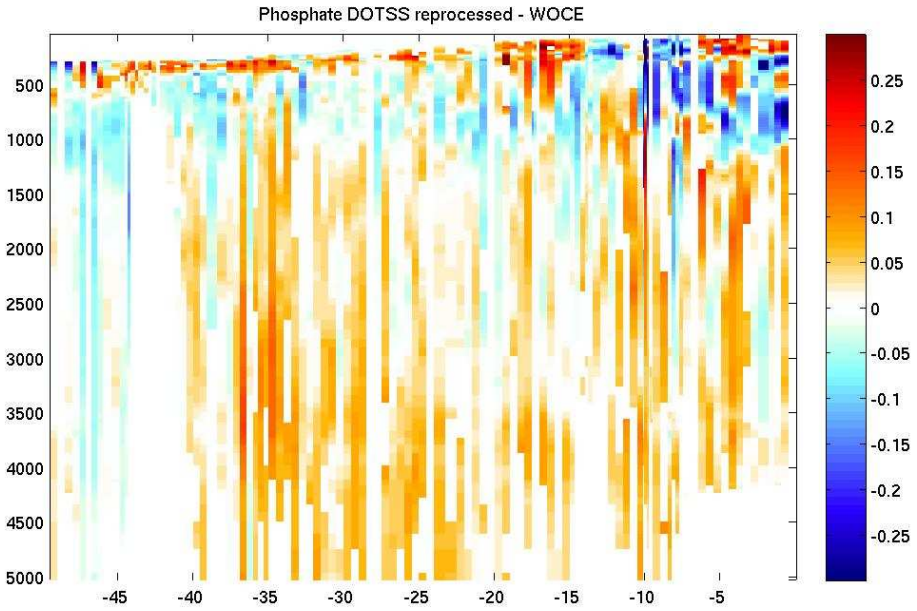
QC sample results and DOTSS-WOCE results:

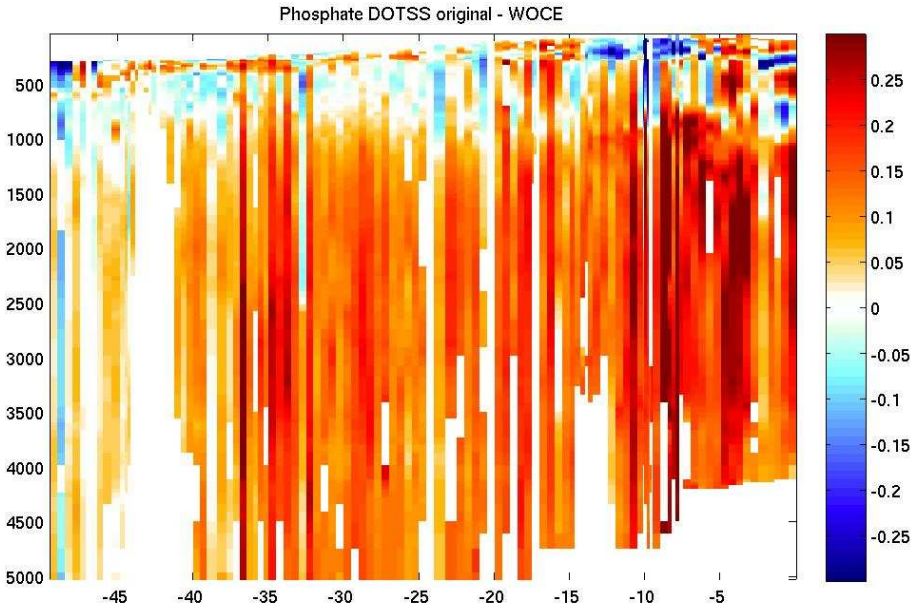


Comparison with WOCE data and original DOTSS data at 2500db after inclusion of average RI and blank values, then calibration with the next highest calibrant.



Comparison with WOCE data and original DOTSS data after inclusion of average RI and blank values, then calibration with the next highest calibrant.

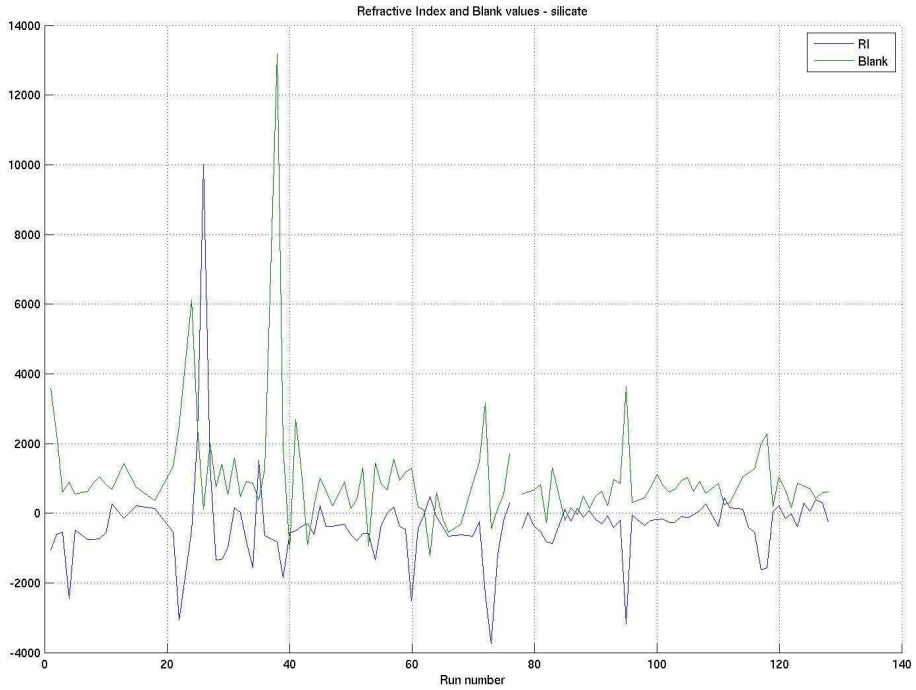




Corrections to Silicate data

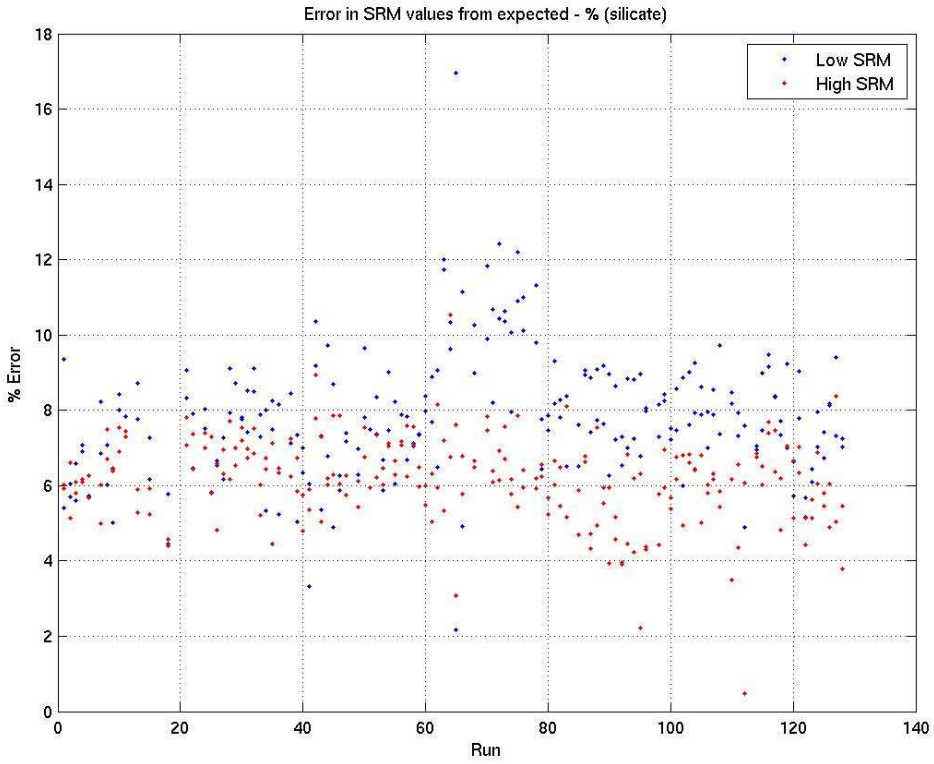
1. **Mean RI and blank values subtracted from peak heights:** The mean RI and blank values for all runs was subtracted from the peak heights during the calculations, rather than the individual run's values.

Refractive Index and blank values for each run.

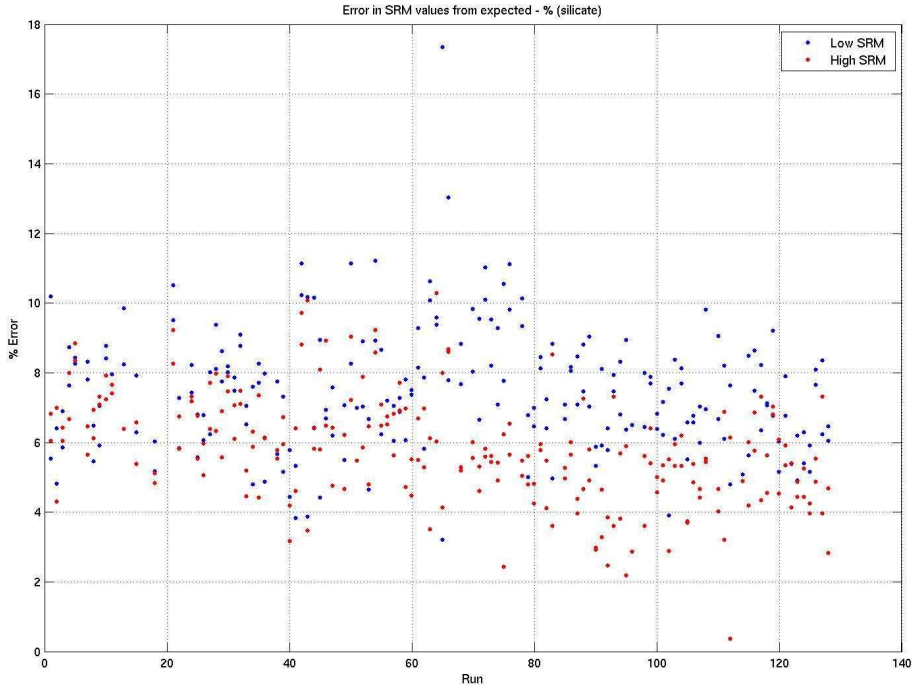


3. **Recalculation of data with sensitivity factors from the closest calibrant.** Closer evaluation of the WOCE method (looking at actual OSU runs) showed that OSU only utilised one standard when calculating the sensitivity factors. This makes sense when the system is completely linear and the sample concentrations are close to the calibrant concentration used. For this data, the next highest calibrant from the sample concentration was used to calculate the concentration.

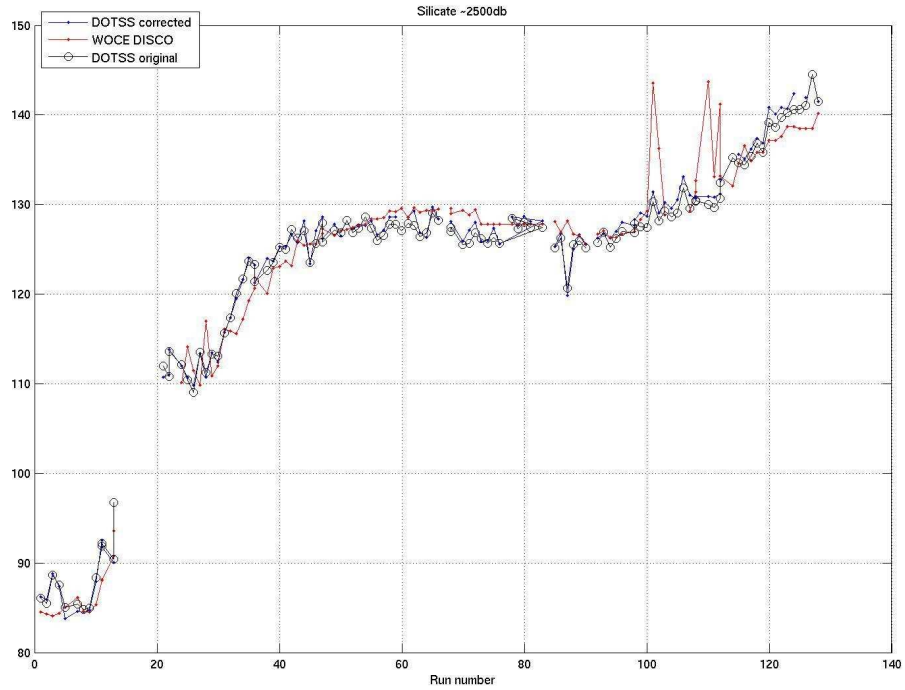
Original SRM results.



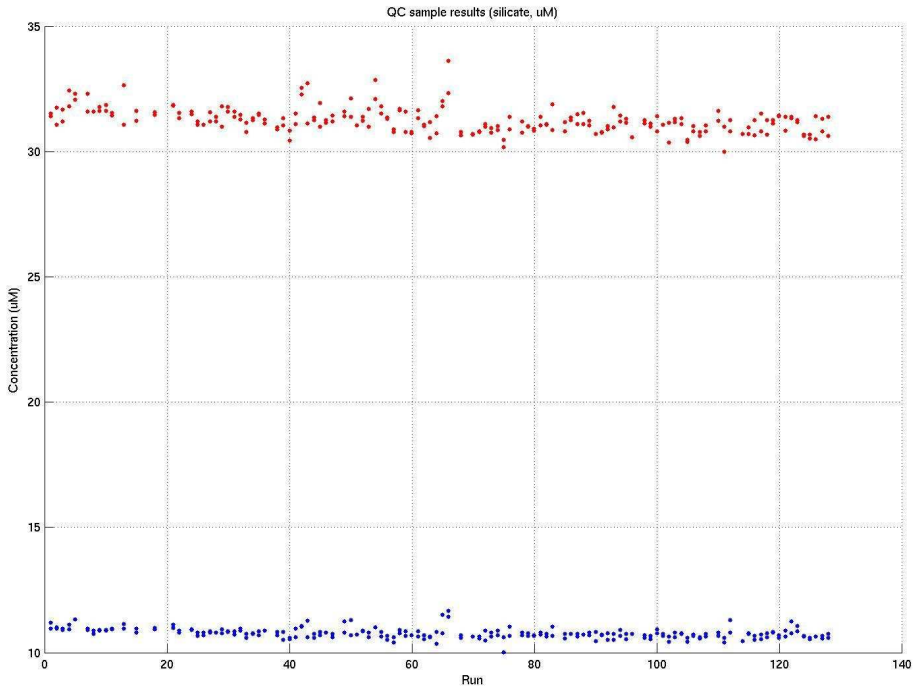
SRM results after inclusion of average RI and blank values, then calibration with the closest calibrant.



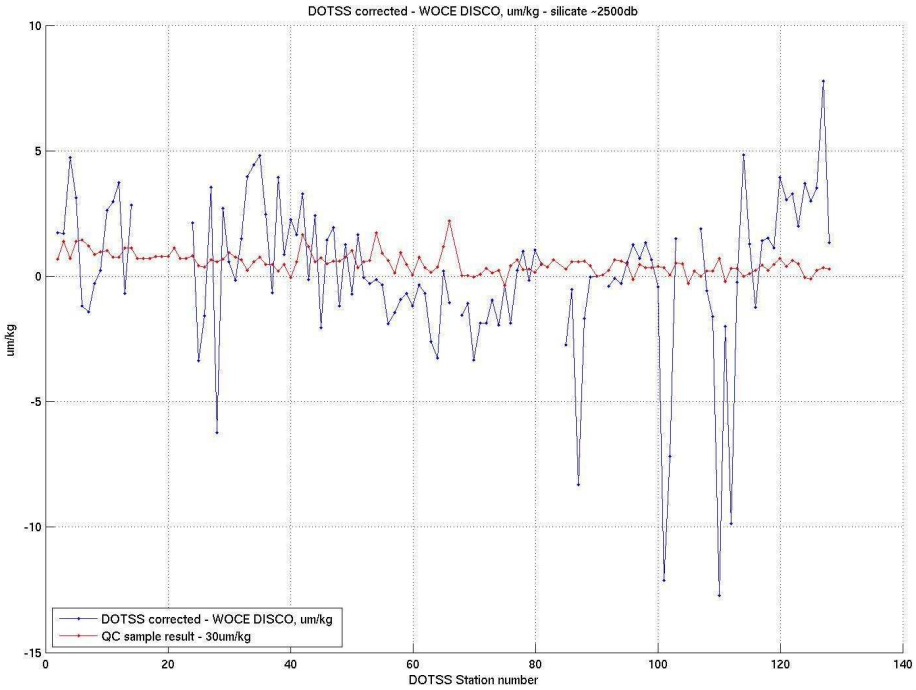
Comparison with WOCE data and original DOTSS data at 2500db after inclusion of average RI and blank values, then calibration with the closest calibrant.



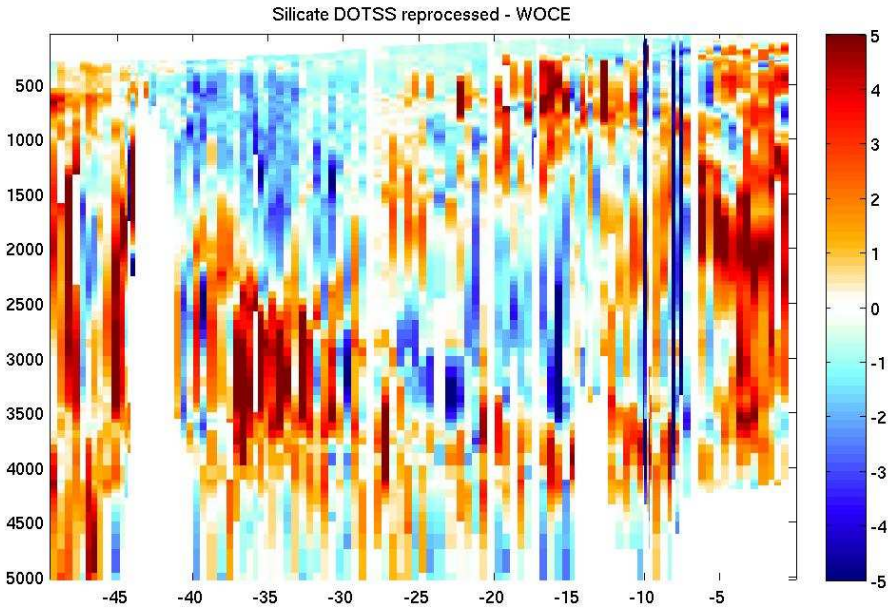
QC sample results:

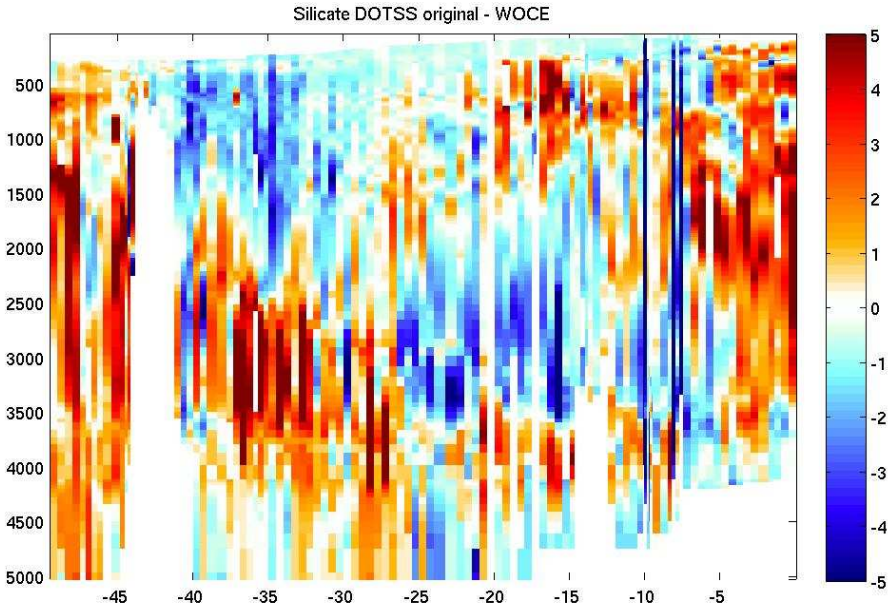


QC sample results and DOTSS-WOCE results:



Comparison with WOCE data and original DOTSS data after inclusion of average RI and blank values, then calibration with the closest calibrant.





Conclusions

The data from this voyage is very noisy. The analysis for nitrate and phosphate was flawed, and the results difficult to repair. The bias in the nitrate and phosphate results was very much improved by calibration of the results using the *f* value of the next-highest calibrant, and the noise between runs was improved by using a mean refractive index and reagent blank value.
Sensitivity (f-value) is calculated as

$$f = \frac{C_a}{(A_c - A_z)}$$

Where C_a is the calibrant concentration, A_c is the absorbance of the calibrant and A_z is the absorbance of the matrix (or zero calibrant). To calculate the concentration of a sample, the peak height is multiplied by its regressed f value.

The source of the bias in the results may be attributed to one or all of the following:

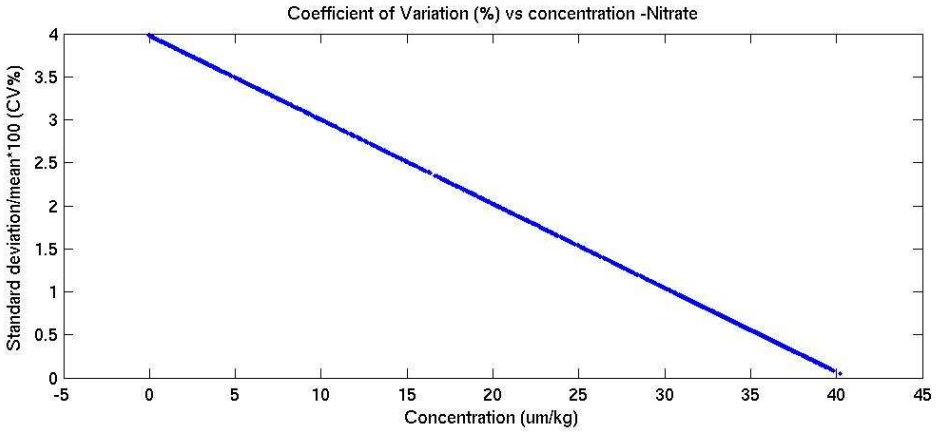
- Poor performance of the instrument at the time of analysis was not addressed immediately, and this is the main source of the bias. In particular, not cleaning the system regularly seems to be the main problem.
- Post-run analysis – positioning of the baseline markers during post-run analysis could result in an offset.
- Errors during calibrant make-up.

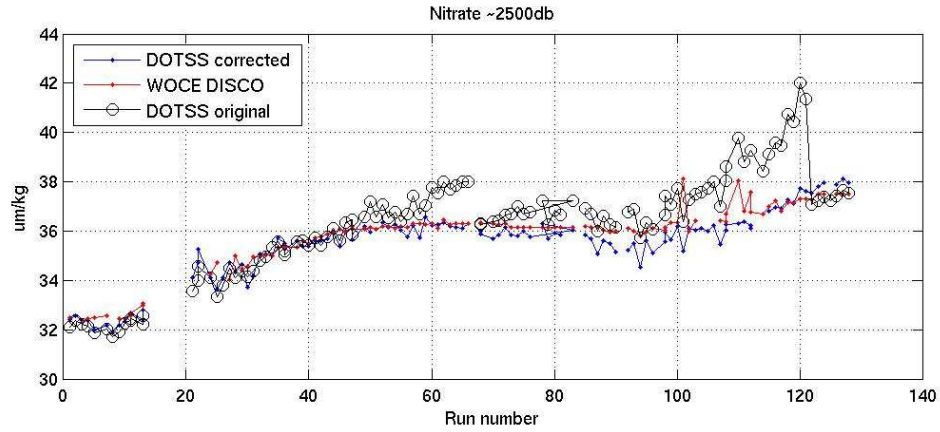
The source of the inter-run noise may be attributed to one or all of the following:

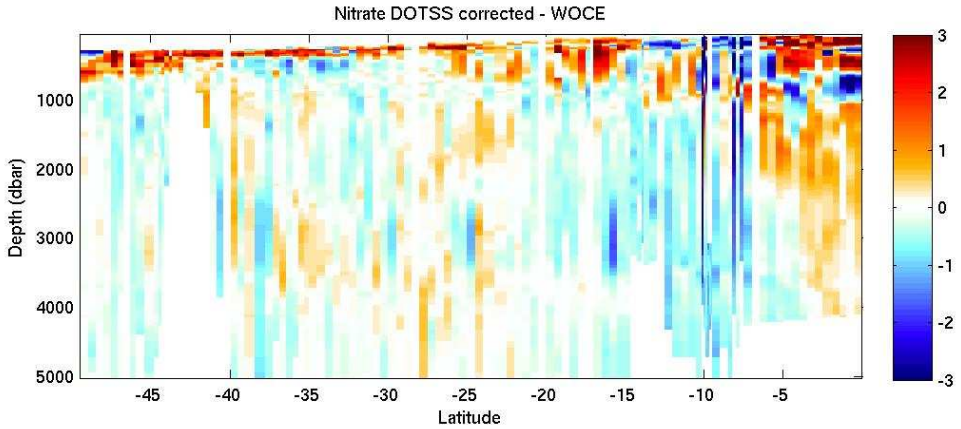
- Instrumental noise – the Alpkem system was notoriously noisy.
- Errors during calibrant make-up.
- Contamination of samples during sampling/analysis.

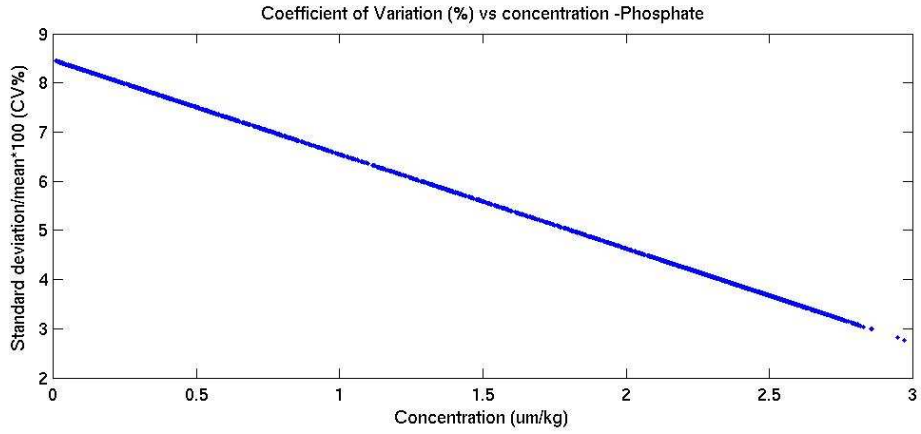
Estimation of error in the results

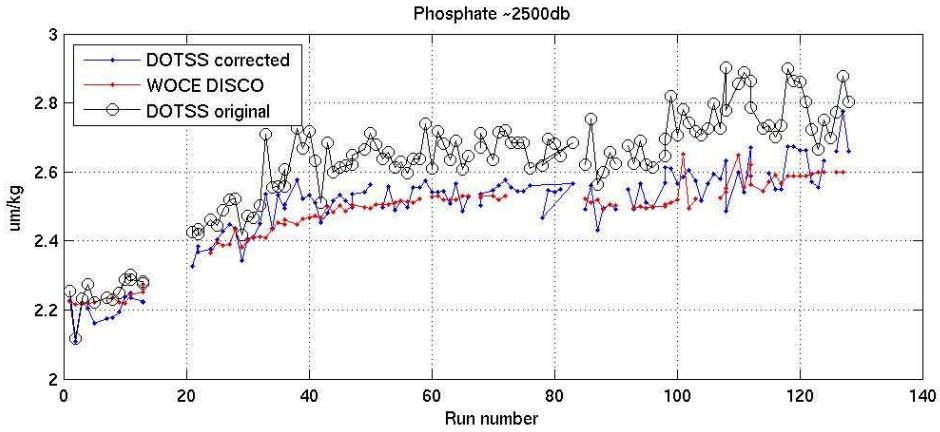
Using the final method of calibration, the coefficient of variation in the results was calculated (based on a pooled standard deviation of the QC samples that were run through the entire voyage). Below are the coefficient of variation results for the final results.
The average coefficient of variation for the results is:
Nitrate/Nitrite: 1.64%
Silicate: 1.35%
Phosphate: 5.3%

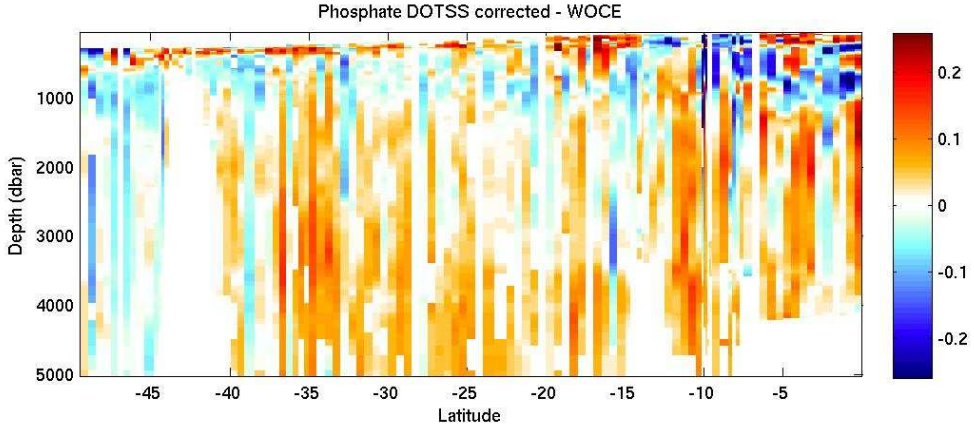

Coefficient of Variation (%) vs concentration -Nitrate
Standard deviation/mean*100 (CV%)
Concentration (um/kg)

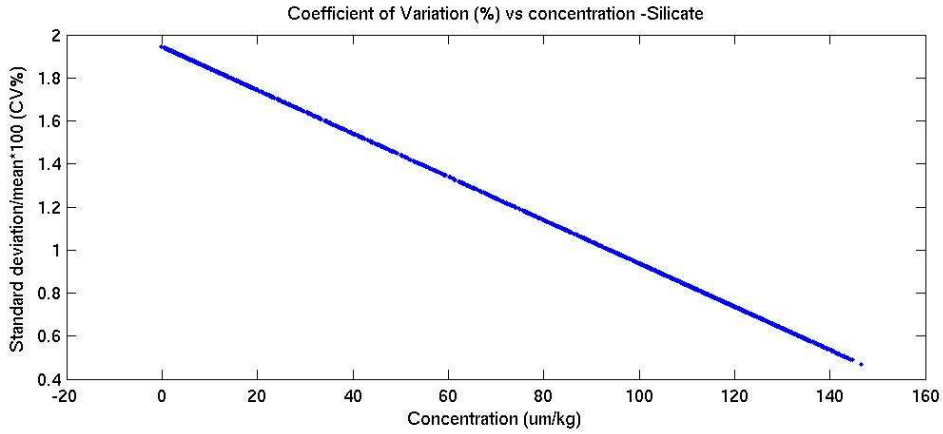

Nitrate ~2500db
DOTSS corrected
WOCE DISCO
DOTSS original
um/kg
Run number

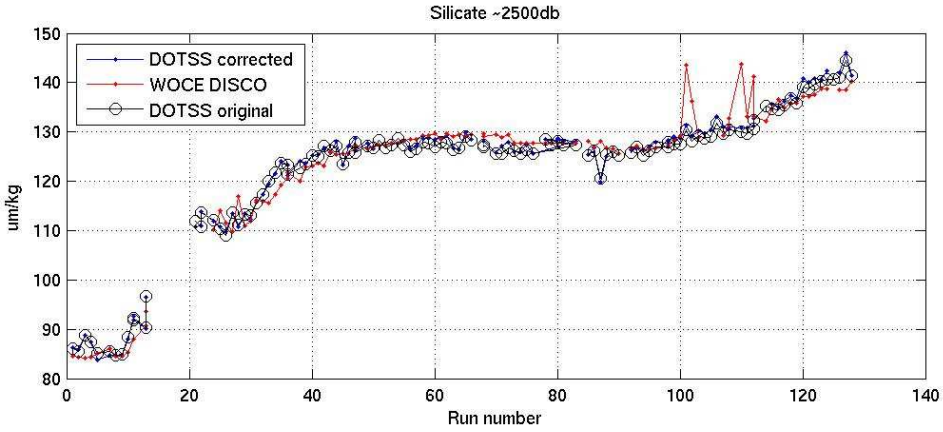

Nitrate DOTSS corrected - WOCE
Depth (dbar)
Latitude

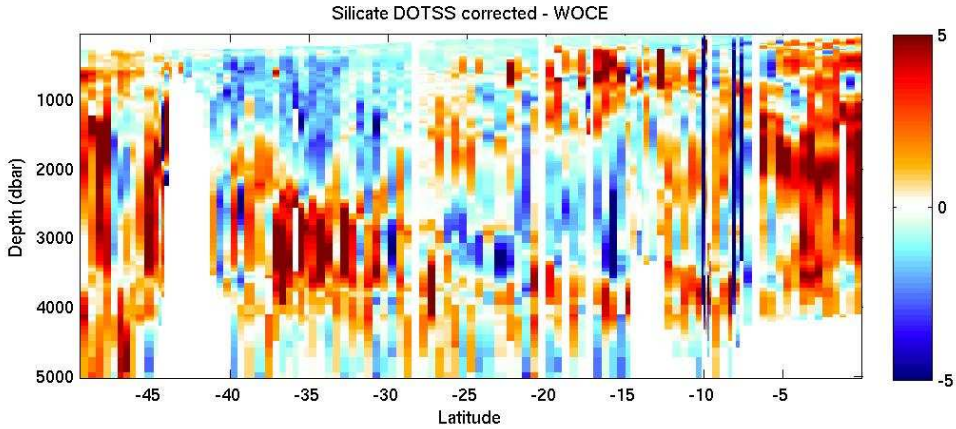

Coefficient of Variation (%) vs concentration -Phosphate
Standard deviation/mean*100 (CV%)
Concentration (um/kg)
9
8
7
6
5
4
3
2
0
0.5
1
1.5
2
2.5
3


Phosphate ~2500db
DOTSS corrected
WOCE DISCO
DOTSS original
um/kg
Run number
3
2.8
2.6
2.4
2.2
2
0
20
40
60
80
100
120
140


Phosphate DOTSS corrected - WOCE
Depth (dbar)
Latitude
1000
2000
3000
4000
5000
-45
-40
-35
-30
-25
-20
-15
-10
-5
0.2
0.1
0
-0.1
-0.2


Coefficient of Variation (%) vs concentration -Silicate
Standard deviation/mean*100 (CV%)
Concentration (um/kg)


Silicate ~2500db
DOTSS corrected
WOCE DISCO
DOTSS original
um/kg
Run number


Silicate DOTSS corrected - WOCE
Depth (dbar)
Latitude

References

WOCE Operations Manual, Volume 3. WHP Office Report WHPO 91-1. WOCE Report No. 68/91. November 1994, Revision 1.

CSIRO Hydrochemistry Operations Manual (1999). Cowley, R., Critchley, G., Eriksen, R., Latham, V., Plascke, R., Rayner, M., Terhell, D