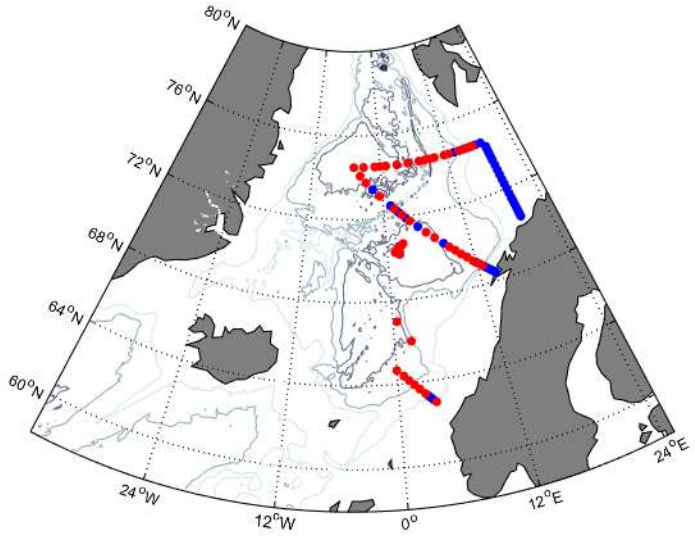
CARBON DATA ON JOHAN HJORT JH2019205 – 58JH20190515

Report written by Siv K. Lauvset (NORCE Norwegian Research Centre, siv.lauvset@norceresearch.no)

December 9, 2021



The map shows all stations on the cruise. Marked in red are those with carbon chemistry.

DIC and pH were analyzed on leg 1, AT and pH were analyzed on leg 2. All carbon samples were taken in 250mL glass bottles following SOP (Dickson et al., 2007).

Samples (full water column) were taken at stations 498-502, 547-556 and analyzed in the lab after the cruise. In addition, surface samples (shallowest niskin) were taken at stations 575-592 and analyzed in the lab after the cruise. Samples taken for later analysis were taken in 500mL glass bottles, poisoned with 1 drop $HgCl_2$, and stored dark. All samples were analyzed within 2 months of the end of the cruise.

See metadata for details on analytical methods and instruments used.

DIC, PI onboard: Steve Jones and Tor de Lange, post-processing: Siv K. Lauvset

Measured onboard during the first leg (stations 488-505, DIC measured only on stations 488, 492-502, 504).

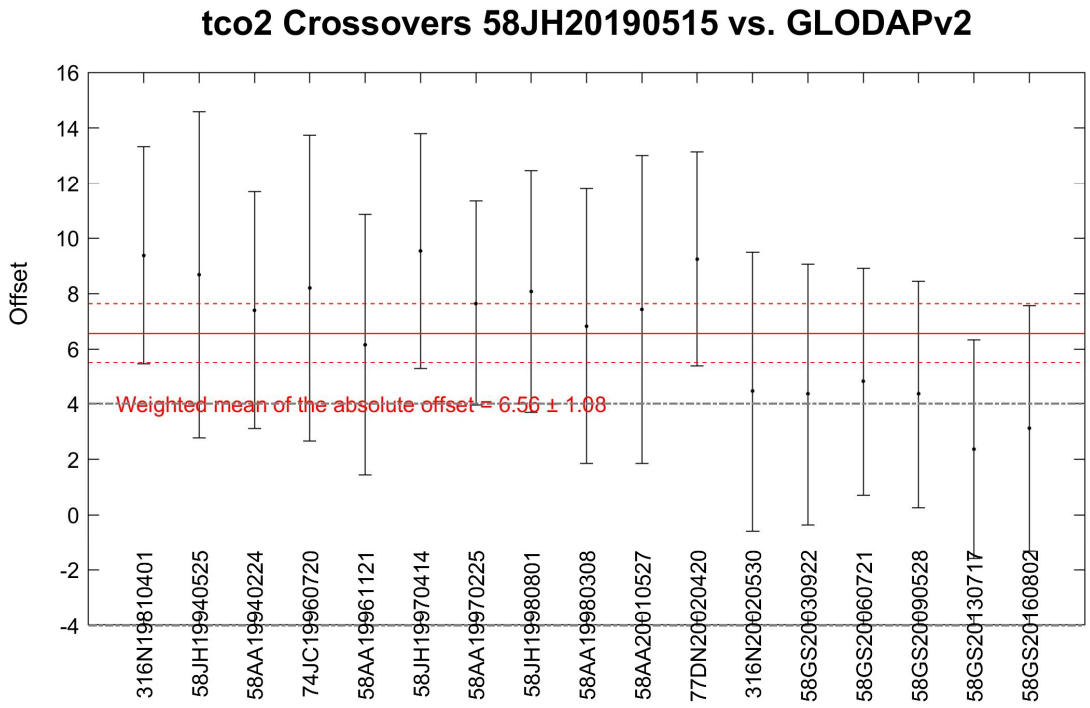
We experienced quite a lot of problems with the instrument. Especially linked to large drift in CRM values over a cell life (~100 mmol kg^{1}). Unknown reasons, but possible contamination and possible bad batch of KI.

For cells where the standard deviation of all CRM runs exceed 10 µmol kg^{-1} all data are flagged WOCE 4 (bad). This threshold is chosen rather arbitrarily based on my judgement that this much spread in CRM runs means the data generally are bad.

On the first leg lab analyzes were made on samples from stations 498-502. For stations 498-500 we also have good data measured onboard. The two analyzes compare well but not excellently. Ship-based analyzes are generally higher than the lab-based analyzes. Mean difference (± one standard deviation) is 4.39±4.16 µmol kg^{-1}.

For the second leg (stations 506-592) no DIC was measured onboard, so the data in the file are samples analyzed in the lab (by Kristin Jackson-Misje) after the cruise. These are all flagged WOCE 2 (good). No detailed analysis has yet been done on the lab analyzed data so it is possible, though unlikely, some data will be flagged at a later stage. Below 1500m these data compare very well with GLODAPv2.2019.

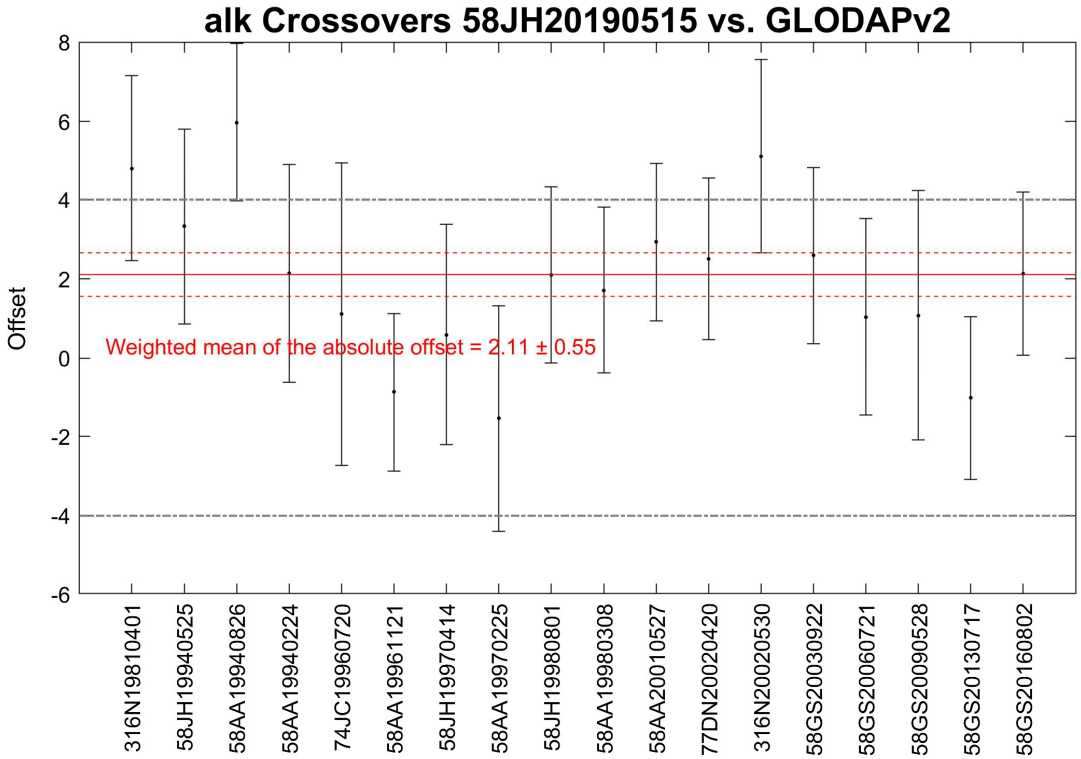
Uncertainty in DIC data are estimated to ±1.5 µmol kg^{-1}, based on the standard deviation of CRM-analyses.



AT, PI onboard: Steve Jones and Tor de Lange, post-processing: Siv K. Lauvset

Measured onboard on the second leg (stations 506-592, AT only measured on stations 516-517,519-521,523,525-530,532,534,536,538,541,543,545-558,560-561,563,565,567,569)

Overall good data. Below 1500m these data compare very well with GLODAPv2.2019



The lab-based analyzes are always 10-15 mmol kg^{-1} higher than the ship-based analyzes where we have both. The reason is suspected to be evaporation prior to analysis in the lab. Measurements of DIC and pH were done on the same bottle before the AT analysis, and all analyzes were made during the warmest period of summer 2019 when temperatures in Bergen were close to or above 30°C. The lab is not air-conditioned.

None of the lab-based AT analyzes, except the surface samples along Fugløya-Bjørnøya (stations 575-592), are included in the data file. The surface samples are included, but all flagged questionable.

Uncertainty in the AT data are estimated to ±2.5 μmol kg^{-1}, based on the standard deviation of CRM-analyses.

Spectrophotometric pH, PI onboard: Siv K. Lauvset and Nick Roden, post-processing: Siv K. Lauvset

Measured on both legs of the cruise.

For stations 488,492-497,499-505,516-517,519-523,525,527-530,532 pH was measured with a temperature controlled cell. For all other stations there was no temperature control on the cell. For the latter stations the temperature at the beginning of analysis (input-T) and at the end of analysis (output-T) were recorded. The data were corrected in post-processing to 25°C from the output-T. Only pH @ 25°C is included in the data file, as well as the output-T.

On stations 519-532 there were problems with the cell. The reasons are unknown, but could be some form of contamination. On these stations the blank runs indicated high absorbance in the 487.6 wavelength (where the m-cresol purple dye absorbs). All data from these stations are flagged WOCE 4.

On the first leg the average (± standard deviation) of all good CRM runs (excluding the ones on stations 519-532) was 7.8835±0.0076. On the second leg the average (± standard deviation) of all good CRM runs (recalculated to 25°C) was 7.8781±0.0042. We have not corrected our pH measurements to the CRM pH value since this is a calculated, not certified, value. Instead we consider the standard deviation of the CRM runs a measure of uncertainty in our pH measurements. TRIS was measured during the cruise, but has not been used to correct the data.

We have not corrected for the addition of dye. Onboard and in the lab double dye analyses were run, but (by coincidence or poor planning) the range of pH over which these double dye analyses are made is very narrow (~0.1 pH units). Analyses made in the lab in late November 2019 (~6 months after the cruise ended) indicate that the correction should be on the order of -0.0039 on average. Given that the dye degrades quite quickly we have not used these results to correct the cruise data for dye addition, but include it as an uncertainty in our measured pH.

Total pH uncertainty – ±0.0085 – is estimated as the squared sum of squares of the standard deviation of CRM runs (0.0076) and the estimated influence of added dye (0.0039).

The pH data measured onboard compares well with those from 77DN20020420. Below 1500m they are nearly identical. Given the anthropogenic change, and the area of comparison (Greenland Sea), this suggests that the 2019 data are slightly too high.

pH measured on samples brought back to the lab compares well with that measured onboard. The differences range from -0.025 to 0.025 pH units, with a median of zero. The pH data measured in the lab post-cruise are 0.005 pH units higher than the data from 77DN20020420 below 1500m. This makes sense since DIC was measured before pH on these bottles and it is likely that some carbon was lost to air-sea exchange in that process.

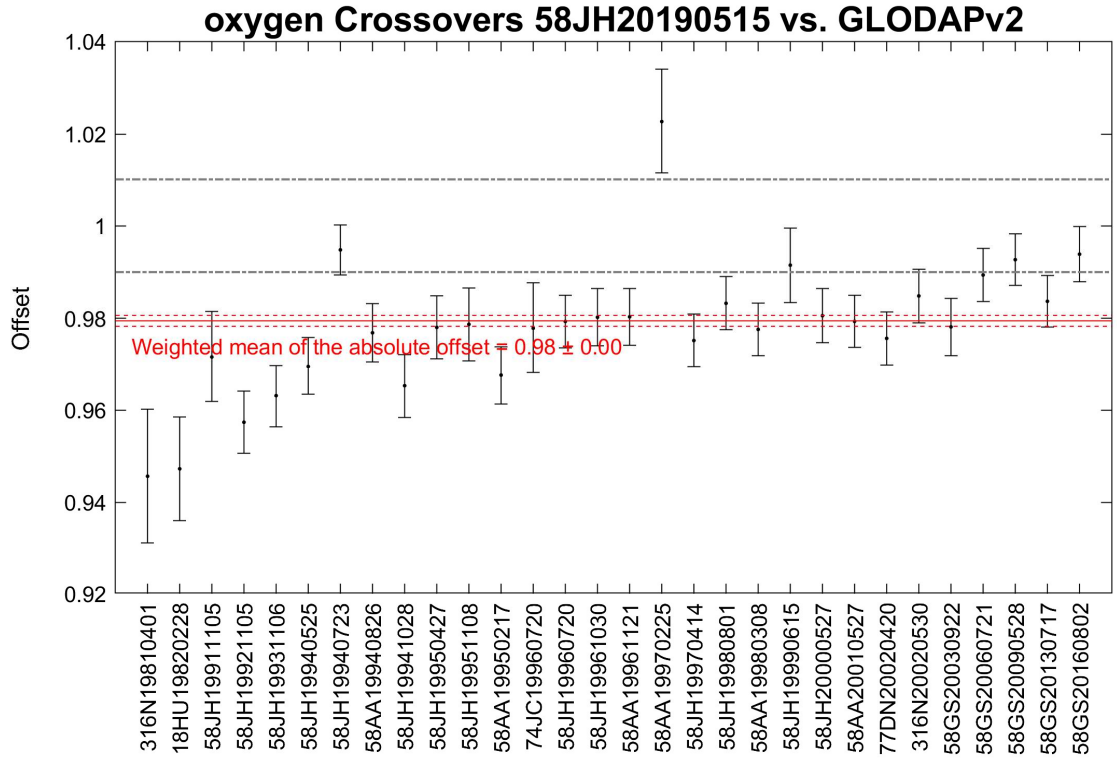
OTHER RELEVANT DATA ON JOHAN HJORT JH2019205 – 58JH20190515

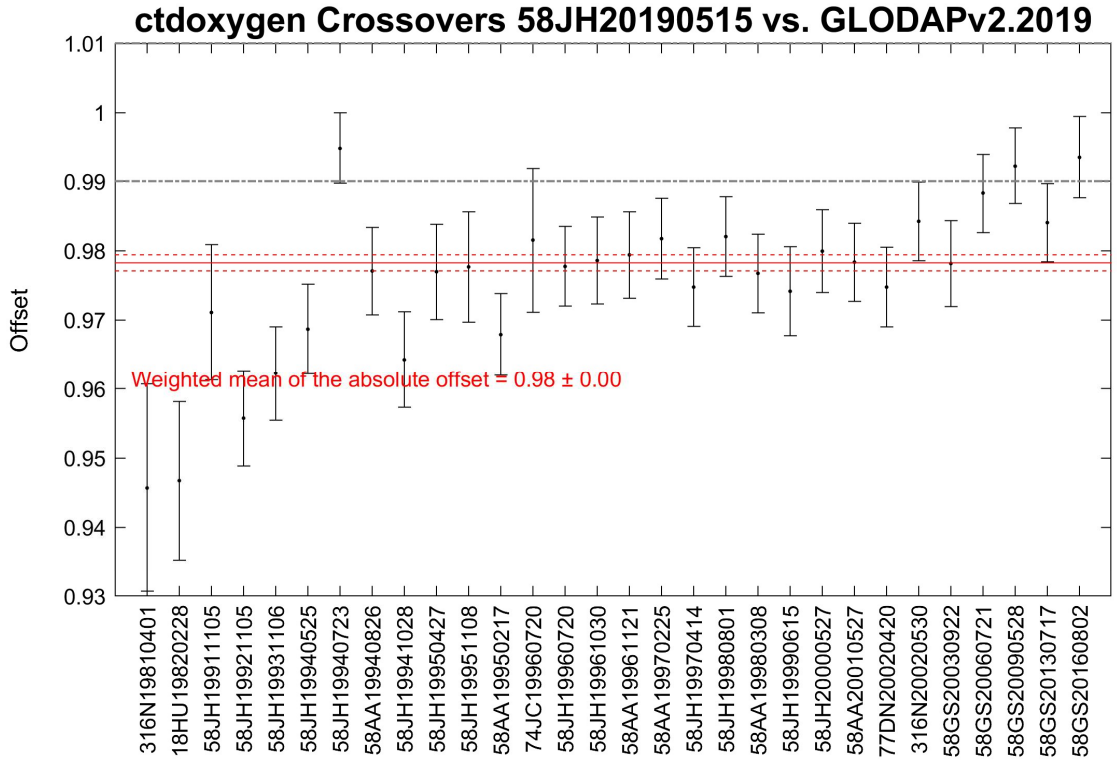
Oxygen, PI onboard and post-processing (bottle samples): Kristin Jackson-Misje

CTD-data: Are Olsen

Winkler oxygen in ml/l was converted to mmol/kg using the factor 44.661 and seawater density (calculated with CTD salinity). Winkler oxygen data have no bias compared to GLODAPv2.2019. The 2019 data fit into the known trend.

On one station all niskins were closed at the same depth, and one sample for each niskin was taken for Winkler analysis. At two of the Argo stations (501-502, and 547-548) two niskins were closed at each depth. All niskins were sampled for oxygen. Using the standard deviation of these replicate samples, the uncertainty in the Winkler oxygen data is estimated to ±0.3 μmol kg^{-1}.





Oxygen were measured on the CTD and in bottle samples using winkler titration onboard. Not all stations and bottle sampling depths had winkler titrations. Figure 6 illustrates winkler oxygen sample coverage vs CTD data coverage.

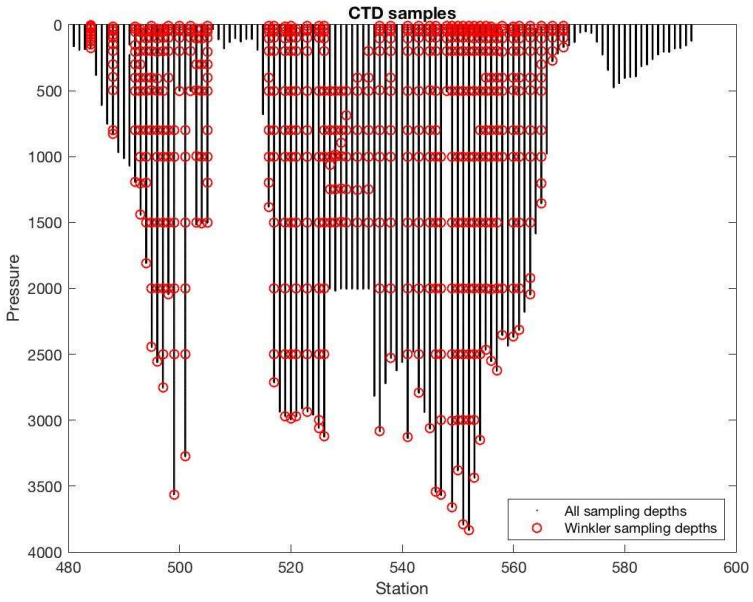


Figure 6: Winkler sampling stations and depths on top of CTD stations and depths.

CTD oxygen data corrections were based on the CTD downcast files to avoid potential issues with hysteresis. These were reported as ml/L. For the winkler oxygen, density at θ and in situ salinity were used for the per liter to per kg conversion according to recommended operating procedures.

Figures 7 and 8 show differences between uncorrected CTD oxygen at bottle sampling depths and winkler oxygen, vs pressure and station. These offsets show a clear pressure dependency and also an overall slight increase with station number.

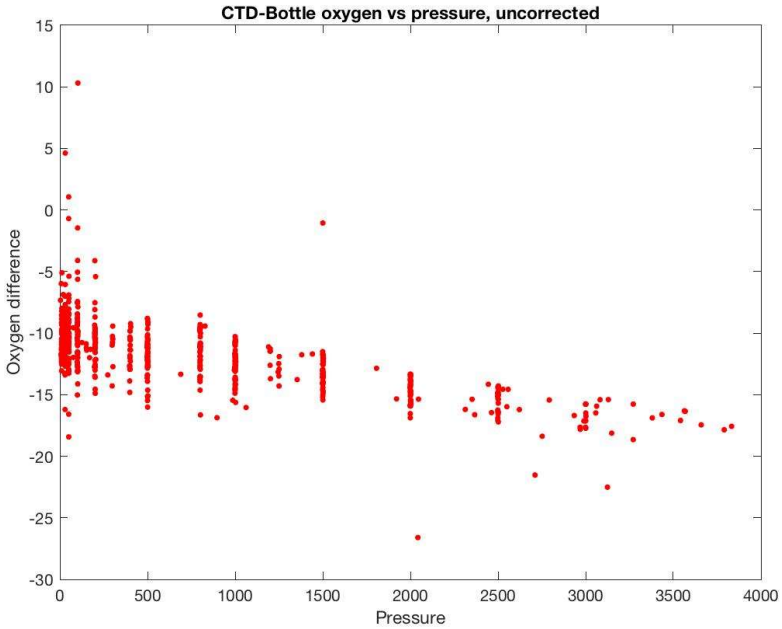


Figure 7: Offsets between CTD and Winkler oxygen vs pressure

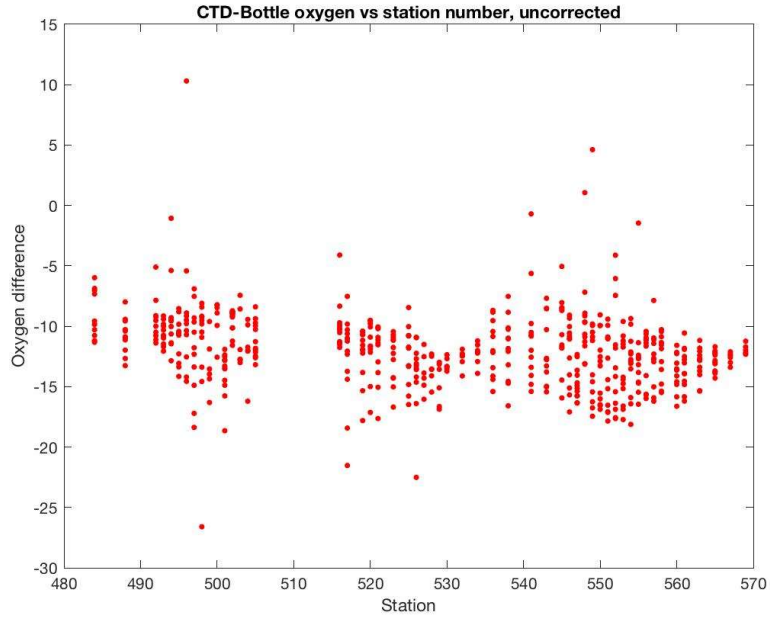


Figure 8: Offsets between CTD and Winkler oxygen vs station

CTD oxygen was corrected by fitting the Seabird calibration equation to the data

$$O_2 = S_{oc} \cdot \left(V + V_{off} + \tau_{20} \cdot e^{(D_1 \cdot p + D_2 \cdot (T-20))} \cdot dV/dt\right)$$
$$\cdot O_{sat} \cdot (1 + A \cdot T + B \cdot T^2 + C \cdot T^3) \cdot e^{[(E \cdot p)/(273.15+T)]}$$

where the coefficients S_{oc}, V_{off}, τ_{20} and E were optimised. Several groupings of stations were tried during the fitting procedure. In the end, it was decided to fit the equation on a per-station basis as for the other options the difference between corrected CTD and winkler data showed station dependencies, indicating the presence of drift over the cruise, as can also be seen in Fig 8. Figures 9 and 10 show differences between corrected CTD and winkler oxygen vs pressure and station. It also shows the values marked as outliers during the optimisation (2.8 standard deviation). Note that instead of using actual dV/dt values, I set this to 4 x 10^{-4}, which is approximately the mean of actual dV/dt values. Using real dV/dt lead to very noisy downcast CTD Oxygen profiles in the end, while using a constant value made them much smoother. Using a constant value did not otherwise affect the correction, in fact it made the fit between winkler and corrected CTD values slightly better (rmse 0.5 vs 0.6 when using real dV/dt.)

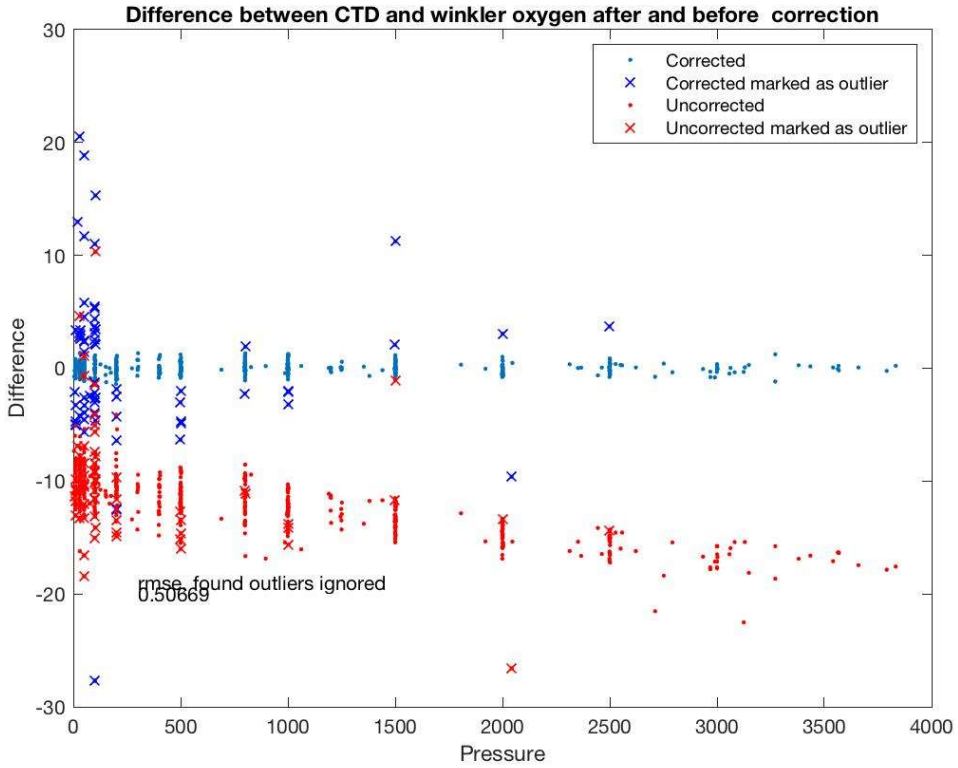


Figure 9: Difference between uncorrected/corrected CTD oxygen and winkler data , vs pressure.

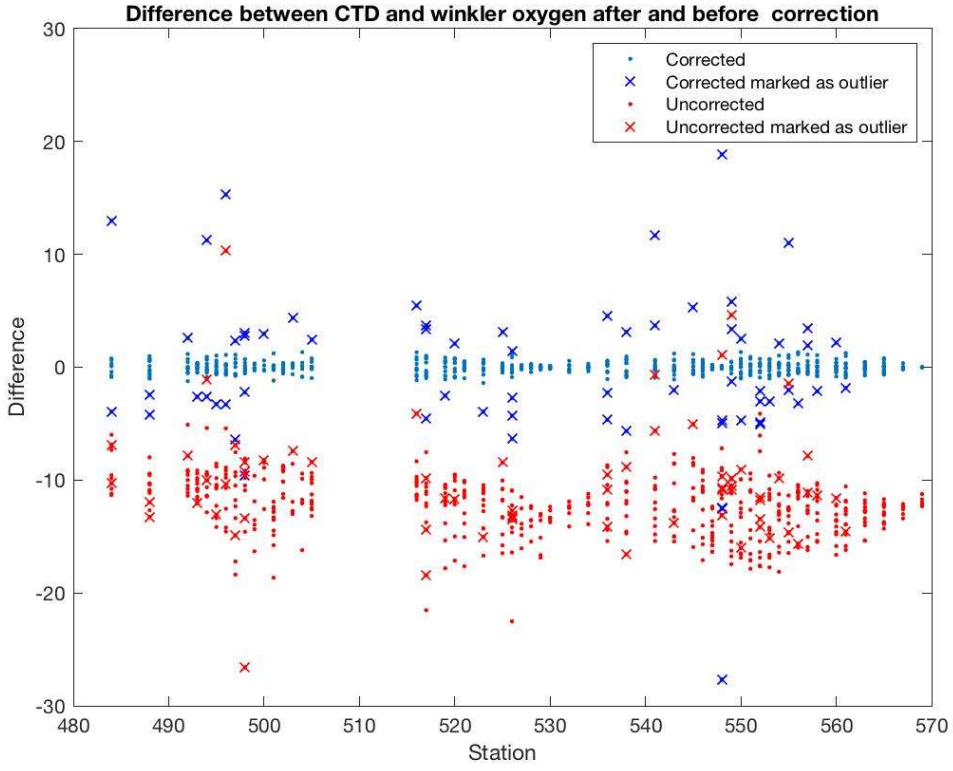


Figure 10: Difference between uncorrected/corrected CTD oxygen and winkler data, vs pressure.

For the stations without any winkler measurements the coefficients were determined using nearest neighbor interpolation of the coefficients from the surrounding stations, in a simple sequential order. We believe the coverage of winkler data are sufficient for such a procedure. Figure 11 shows magnitude of all corrections applied, beneath differences between uncorrected CTD and winkler data, showing that the magnitude of corrections are reasonable for all stations

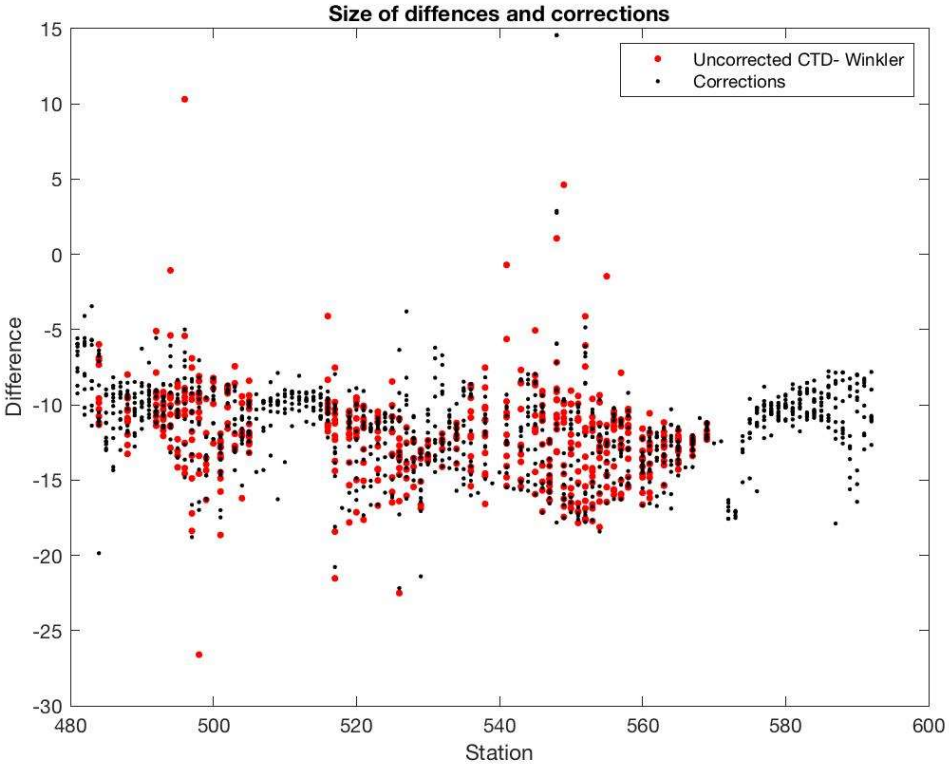


Figure 11: Difference between uncorrected CTD oxygen and winkler, (red) and size of applied corrections for all stations (in black)

Salinity, PI: Kristin Jackson-Misje (bottle samples), Are Olsen (CTD data)

Samples were taken at four depths on all stations where the carbon parameters are measured. These have been analyzed in the lab, and appear to be offset slightly high compared to GLODAPv2.2019.

The CTD salinity data were corrected fall 2021. Only CTD salinity in the bottle files were corrected as IMR had run their own corrections for the downcast files. There is a very slight depth dependent difference in these corrected salinities (<0.003 at depth), likely because IMR used a constant conductivity offset for their corrections while we used a conductivity and pressure dependent polynomial, as described below.

Figure 1 and 2 shows difference in conductivities derived from the measurements on the Portasal conducted by UiB and those in the CTD bottle files, versus pressure and station number. There is a large offset for station 488-498 and much smaller offset for station 498 and beyond. We have strong reasons to believe that the UiB conductivity data for the first group of stations are in error: Bottle salinities from IMR showed no such large offset for the first group of stations, and the UiB bottle salinities are a bit lower than expected for the region. These data are ignored for the corrections, and have been flagged WOCE 3.

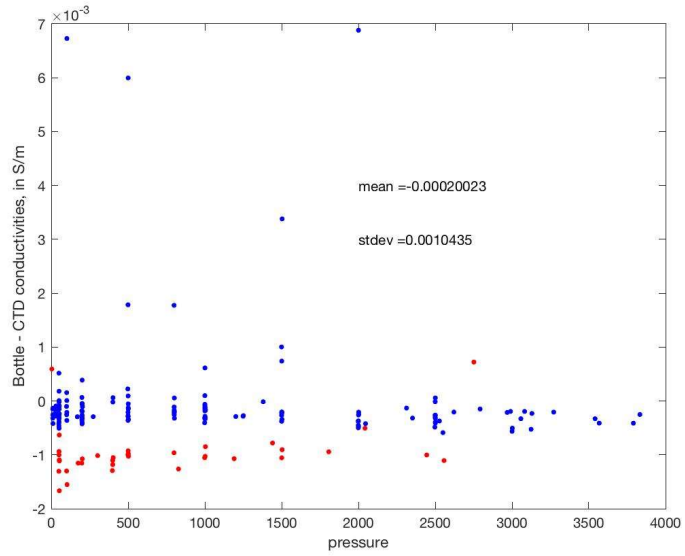


Figure 1: Difference in CTD and bottle conductivity vs pressure. Red points are for stations 488-498.

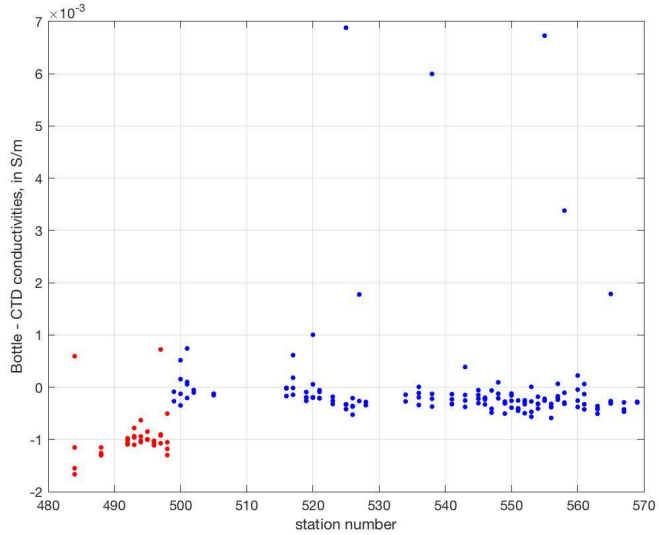


Figure 2: Difference in CTD and bottle conductivity vs station number. Red points are for stations 488-498.

The following equation following GO SHIP recommended procedures, was fit to to the measurements from stations 499 onwards:

$$C_{cor}=C + cp2P^2 + cp1P + c2C^2 + c1C+c0 \qquad (1)$$

Here, the coefficients to be optimised are cp2, cp1, c2, c1 and c0. P is pressure and C is conductivity. For the optimisation, conductivity as calculated from UiB bottle salinities were used for C_{cor}, while P is CTD pressure and C is uncorrected CTD conductivity. The optimisation was conducted iteratively, removing outliers greater than 2.8 standard deviations at each step until no more outliers remained. Determined coefficients are given in Table 1

Table 1: Coefficients for Eq. (1) as determined using data for stations 499 onwards. Coefficients were determined for conductivity in S/m at insitu temperature and pressure.

Coefficient	**Value**

cp2	1.094e-11
cp1	1.112e-09
c2	5.352e-4
c1	3.284e-3
c0	4.802e-3

Once coefficients had been derived, Eq. (1) was used to determine corrected conductivity and subsequently salinity for all stations. Figures 3 and 4 show differences between bottle and corrected and uncorrected conductivities vs pressure and station. Figure 5 shows salinity offsets vs station. Apart from the large offsets for stations 488-498, not systematic offsets in the corrected data are evident. This was also the case vs pressure and other parameters.

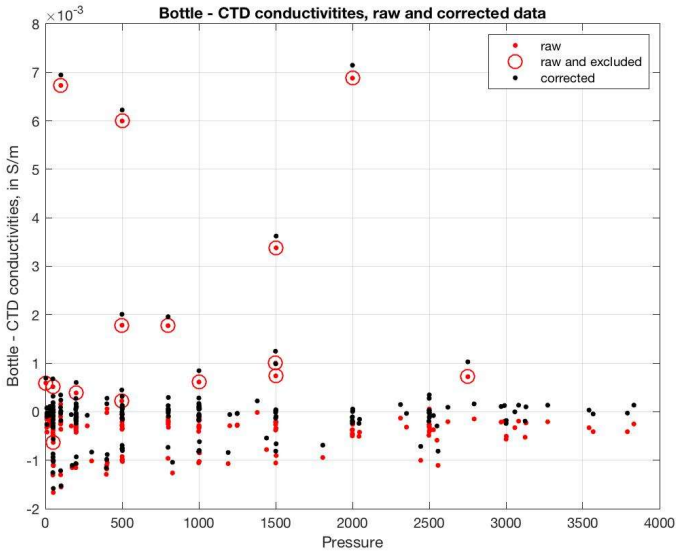


Figure 3: Difference in uncorrected/corrected CTD and bottle conductivity vs pressure. Red points are for stations 488-498. Note, for these we believe the bottle conductivity are in error, as explained in the text, so an offset remains after correction. Circles highlights data that were excluded as outliers during the curve fitting.

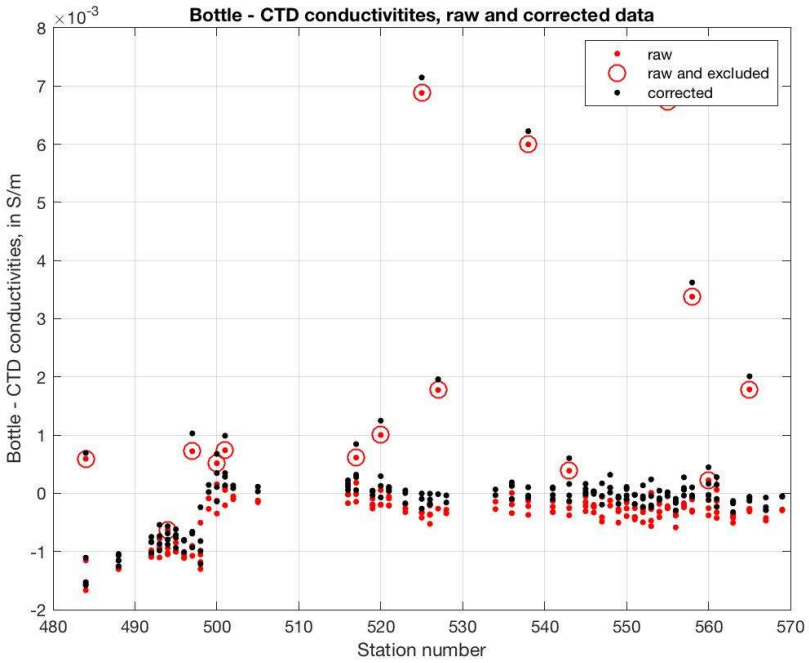


Figure 4: Difference in uncorrected/corrected CTD and bottle conductivity vs station number. Red points are for stations 488-498. Note, for these we believe the bottle conductivity are in error, as explained in the text, so an offset remains after correction. Circles highlights data that were excluded as outliers during the curve fitting.

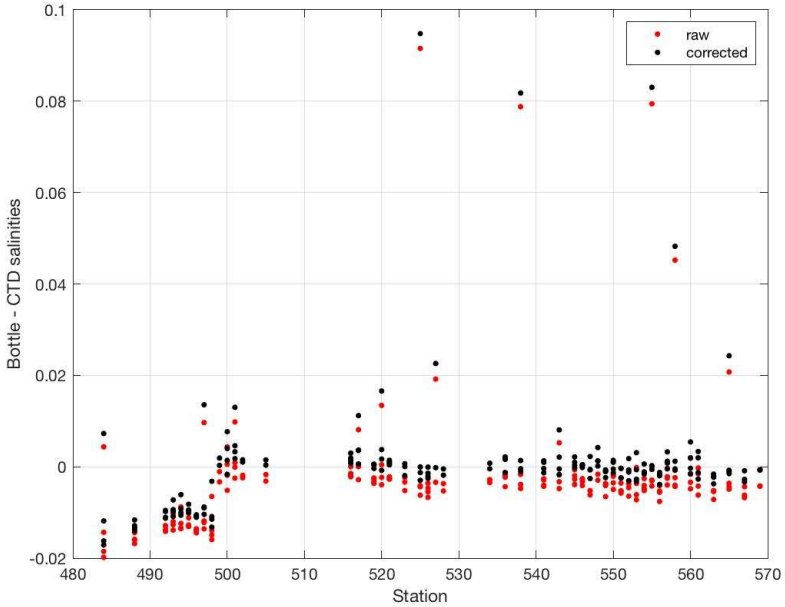
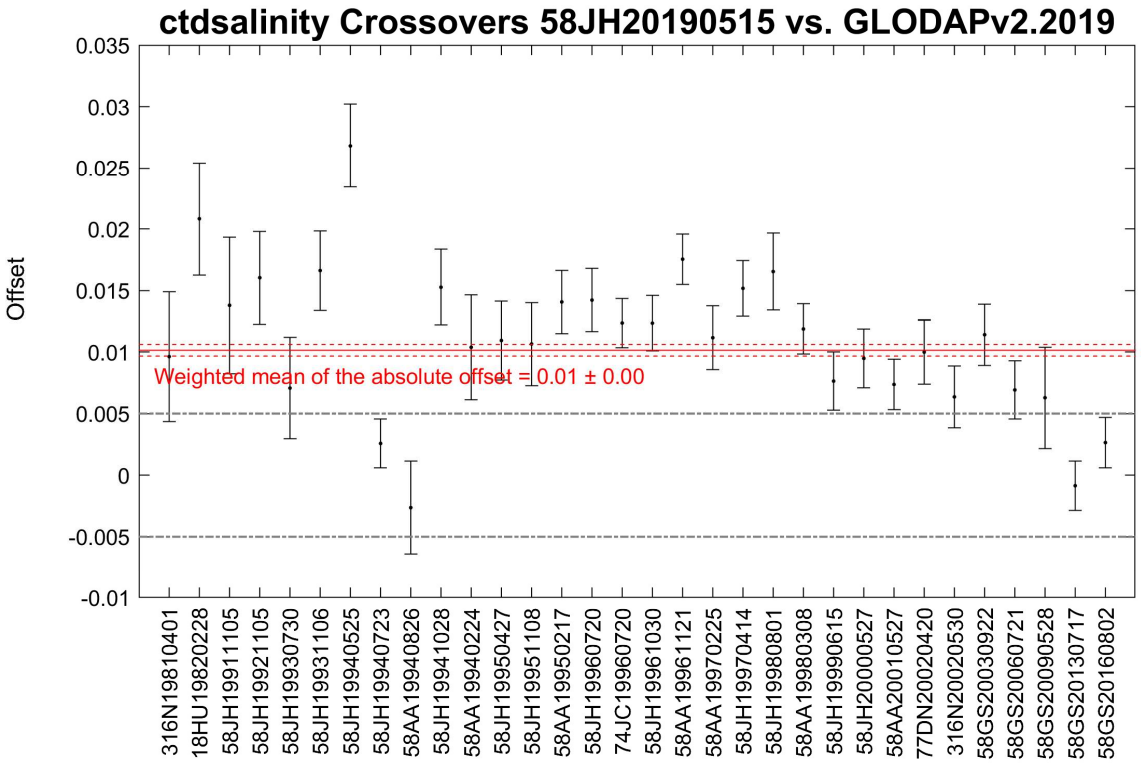
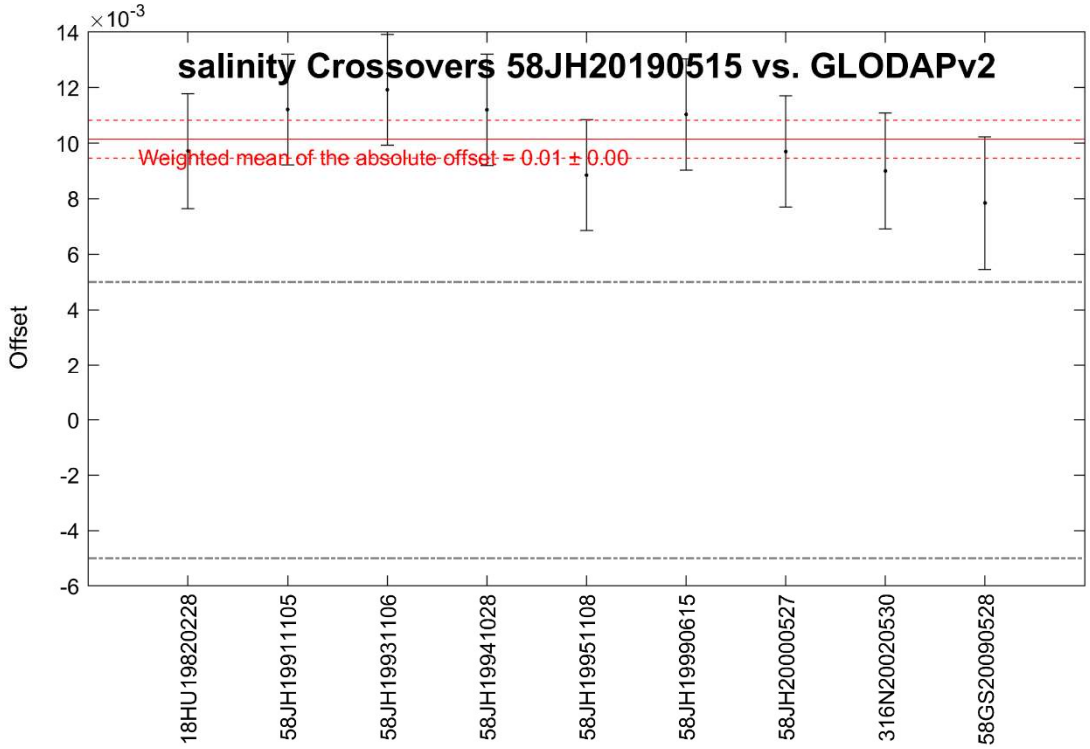


Figure 5: Difference in uncorreced/corrected CTD and bottle salinity vs station number. Red points are for stations 488-498. Note, for these we believe the bottle conductivity are in error, as explained in the text, so an offset remains after correction. No outliers have been highlighted in this figure.





Nutrients, PI onboard: Monika ? (sampling), analysis and post-processing: Linda Fonnes Lunde

Nutrient samples were taken by people from the Institute of Marine Research (IMR) onboard, and subsequently analyzed in their lab by Linda Fonnes Lunde. Units were converted from µmol/L to µmol/kg using density calculated from CTD salinity (since bottle salinities are not available on all bottles, and also appear biased).

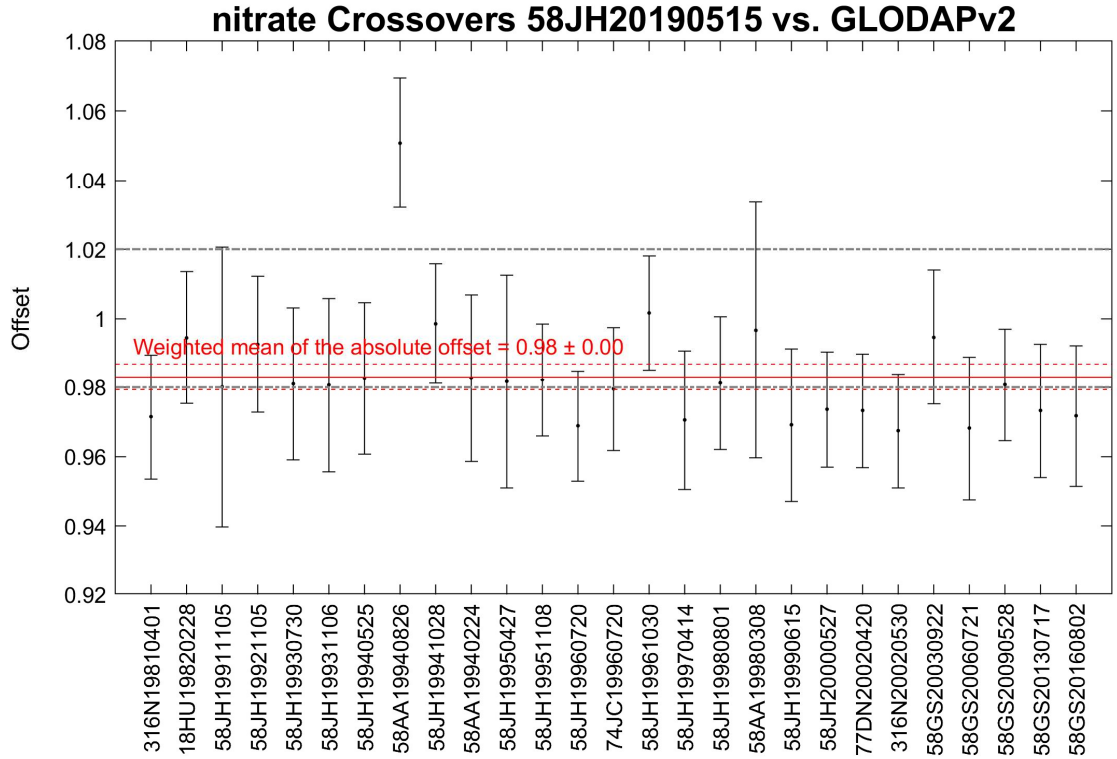
Nitrate, phosphate, and silicate were all compared with data in GLODAPv2.2019.

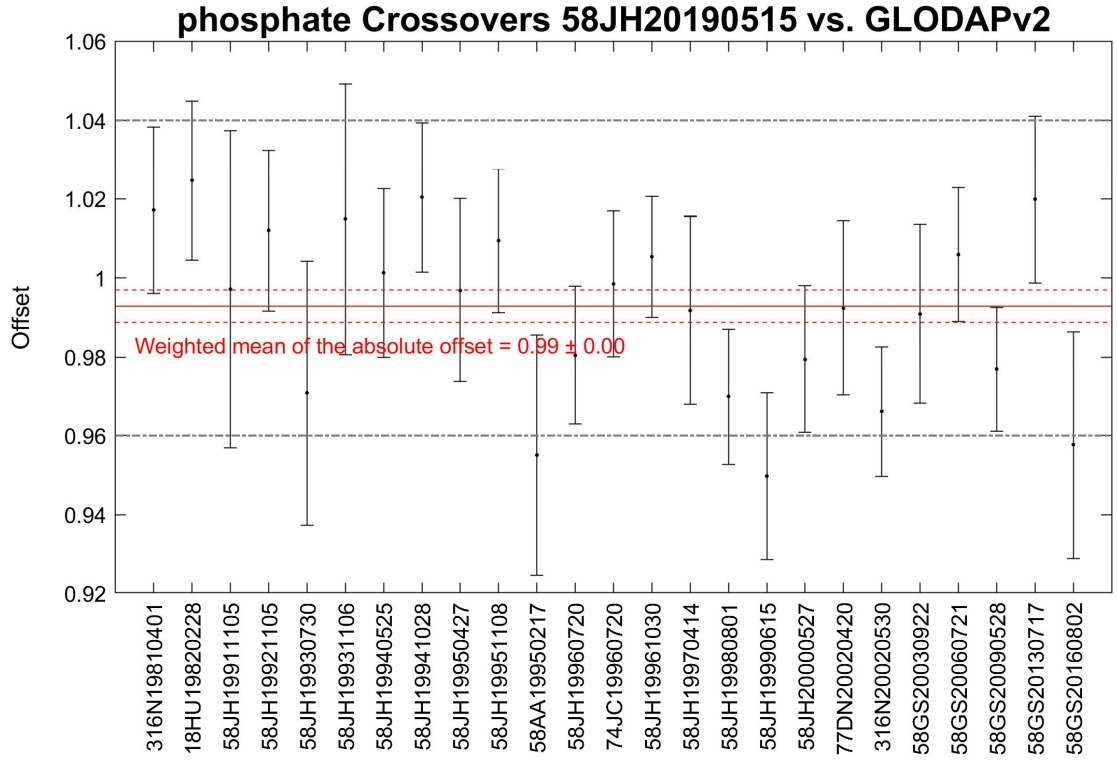
Nitrate appears to be biased slightly low (~2%). Note that nitrate in this case is NO2+NO3, even though the two are separated in the datafile.

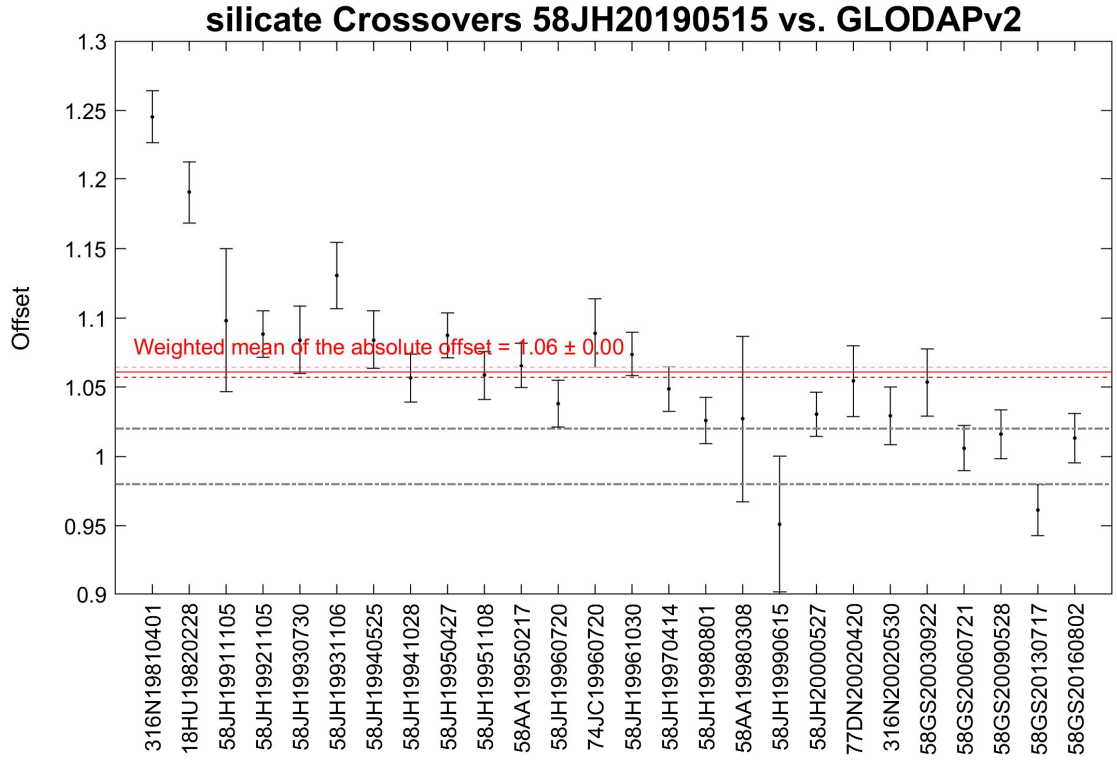
Phosphate is somewhat noisy, but within the ±4% adjustment limit.

Silicate exhibits the expected temporal trend and has no bias with the most recent cruise in GLODAPv2.2019.

Stated uncertainty (in the metadata) for all nutrients is the detection limit of the method(s) used. No other uncertainty estimate exists.






silicate Crossovers 58JH20190515 vs. GLODAPv2
Offset
Weighted mean of the absolute offset = 1.06 ± 0.00
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
316N19810401
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