

GEOTRACES Intercalibration Report

Cruise ID*: RR1815

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Parameters to be intercalibrated*:

- PH_TOT_FISH::ejuhua null

- PH_TOT_BOTTLE::wp5r6m null

***Once generated, these headings must not be changed or altered.**

Important note for CTD-sensor data submitters: it is not necessary for you to fill in and submit an intercalibration report for these parameters through D0oR (you can skip step 4). Please proceed to send the data registered in D0oR to your appropriate data centre using the data template downloaded from D0oR in step 3 as soon as possible.

Please fill in as many sections as possible.

1. Did your lab participate in an intercalibration exercise (<http://www.geotraces.org/sic/intercalibrate-data/intercalibration-exercises>)? If so, please provide a relevant figure or table, describe the results of the intercalibration, identifying your laboratory, and provide a reference for the intercalibration exercise, if published.

No, we did not participate in an intercalibration exercise for pH.

2. Did your sampling method at sea follow the GEOTRACES cookbook (available at: <http://www.geotraces.org/cookbook>)? Please give a brief description of your sampling methodology (e.g., what bottles were used, what type and size of filters were used, how the samples were treated at sea, etc.).

Yes, we followed the GEOTRACES cookbook sampling method.

60 mL of unfiltered water was subsampled from 12L GO-Flo bottles, mounted on the GTC carousel. The 60 mL polypropylene syringes were fitted with polycarbonate 3-way valves to remove air bubbles and prevent exchange of CO₂ prior to analysis and rinsed 3 times with unfiltered water. The sample syringes were then kept at room temperature in the dark until placed in a circulating water bath at

25°C for a minimum of 20 minutes to bring the samples close to analysis temperature.

3. Briefly outline the analytical methodology used in your laboratory, and provide associated metadata and references, as appropriate.

Once at analysis temperature, each syringe was attached to one of the ports on the automated syringe pump that delivered sample and dye to a 10 cm cell with an inner volume of 10 mL for sample seawater. The cell is placed in a thermostated-holder that is temperature controlled by water continuously pumped from a circulating water temperature bath, so the sample remains at $25\pm 0.1^\circ\text{C}$ during analysis. The samples were analyzed at sea within 3 hours of collection using an automated Ocean Optics UV-VIS spectrophotometric system that was modified from Carter et al. (2013) with pure m-cresol purple dye (mCP). The automated measurement sequence was initiated in LabVIEW and required a total processing time of 5 minutes and used the salinity and temperature dependent pH equation from Clayton and Byrne (1993).

Instrumentation:

The temperature of the absorbance cell is controlled using deionized water pumped from a VWR circulating water bath (Cat. No. 89202-966) and through the water-jacketed CUV-10 cuvette holder with a 10 cm pathlength, 10 mL volume cuvette with quartz windows. QP400-1-UV-VIS premium fiber optic cables are used from the HL-2000-FHSA light source to the CUV UV 10 cm cuvette holder and then to the Optics STS-VIS-L-25-400-SMA miniature spectrophotometer. The automation and data processing are controlled from a computer program written in LabVIEW. A Norgren Kloehn Versa Pump 6 syringe pump with a 4-way valve and 48000 step resolution was controlled by the LabVIEW program that delivers the sample, then dye to the cuvette.

4. Report your blank values and detection limits and explain how these were defined and evaluated.

It is difficult to report the blank values for seawater pH using spectrophotometric methods. In this study, the blank is defined by the absorbance of the sample at a wavelength (730 nm) where the mCP dye is not absorbed. Nearly all absorbance measurements at 730 nm were zero with the highest absorbance value found with our instrument being 0.01 abs which translates to <0.06% of the recorded pH value.

5. Report how you monitored the internal consistency of your data (e.g., through replicate analyses of samples).

No duplicate samples were taken on Leg 2. Samples were only analyzed in single analyses.

6. Report the external consistency of your data (e.g., results from analyses of certified reference materials and/or consensus materials).

Two reference materials (B162 and B164) from Andrew Dickson's lab at UCSD were used to evaluate the uncertainty of our pH results collected at sea. pH values of 7.9143 ± 0.0065 and 7.5532 ± 0.0030 were recorded, in comparison the reported values for these reference materials were 7.9100 ± 0.0005 and 7.5407 ± 0.0010 , respectively (Bockman and Dickson, unpublished). This translates to a 99.95% agreement for B162 and a 99.83% agreement for B164.

7. If you occupied a crossover station, include a plot and a table that show relevant data and their level of agreement, and explain any significant discrepancies (e.g., where discrepancies may reflect differences in the depth of isopycnal surfaces between occupations). If possible, please also include a profile of Temperature & Salinity.

While the second leg (RR1815) of the 2018 US GP15 GEOTRACES cruise did not have a crossover where pH was measured, the first leg (RR1814) had a crossover station with the 2017 Japanese GP02 cruise, and the 2015 P16 cruise at 47°N , 152°W , Station 8 for GP15, Station CL09 for GP02, and Station 162 for P16.

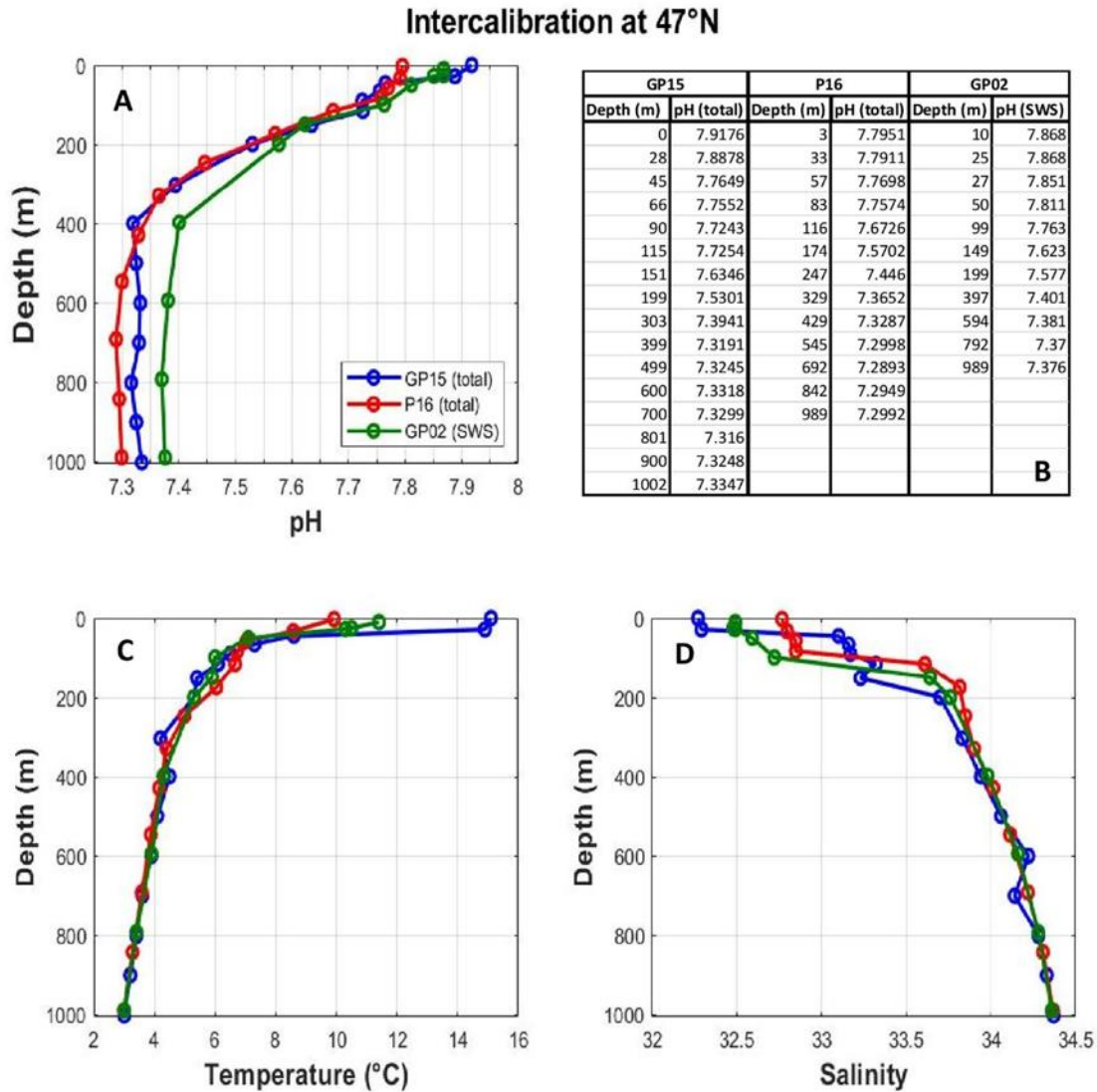


Figure 1. Comparison of data from the crossover station at 47°N, 152°W. Vertical profiles of pH (panel A), CTD temperature (panel C), and CTD salinity (panel D). pH values reported from all cruises are shown in the table (panel B). GP15 values are shown in blue, P16 values are shown in red, and GP02 values are shown in green.

There appears to be better agreement between the three measurements at pH values >7.6, with larger discrepancies in GP02 values occurring below that (Fig. 1, Panel A). The discrepancies in the upper 100 m could potentially be due to the depth of the mixing layer at that time of the year, while the larger discrepancies below 200 m are likely a result of analysis methodology between GP15/P16 and GP02. The pH values from GP15 and P16 were measured using a spectrophotometric method with a purified m-cresol purple dye, whereas GP02 measured pH using an electrode.

The report by Bockman and Dickson (unpublished) on the inter-laboratory comparison of the reference materials (B162 and B164) supports the possible

reason for discrepancies between the two methods. The report stated that while the spectrophotometric method with purified mCP dye had better agreement with values measured by the Scripps Institution of Oceanography than electrode measurements, the results from the electrode were worse for the lower pH reference, B164 (pH ~7.54), than for the higher pH reference, B162 (pH ~7.91). Figure 2 shown below reiterates the observation by Bockman and Dickson (unpublished) that in general, there are larger discrepancies between the spectrophotometric and electrode method at greater depths that relate to lower pH values.

Since GP15 had better depth resolution in the upper 1,000 m, the pH from GP15 were linearly interpolated to match the depths that correspond to the reported values from P16 (Fig. 3) and GP02 (Fig. 4), respectively. The interpolated GP15 pH values were plotted versus the actual P16 (Fig. 3) and GP02 (Fig. 4) pH values and fit with a linear relationship which shows there is a strong correlation between the two where $r=0.9875$ ($r^2=0.9752$) and $r=0.993$ ($r^2=0.9863$), respectively, for P16 and GP02.

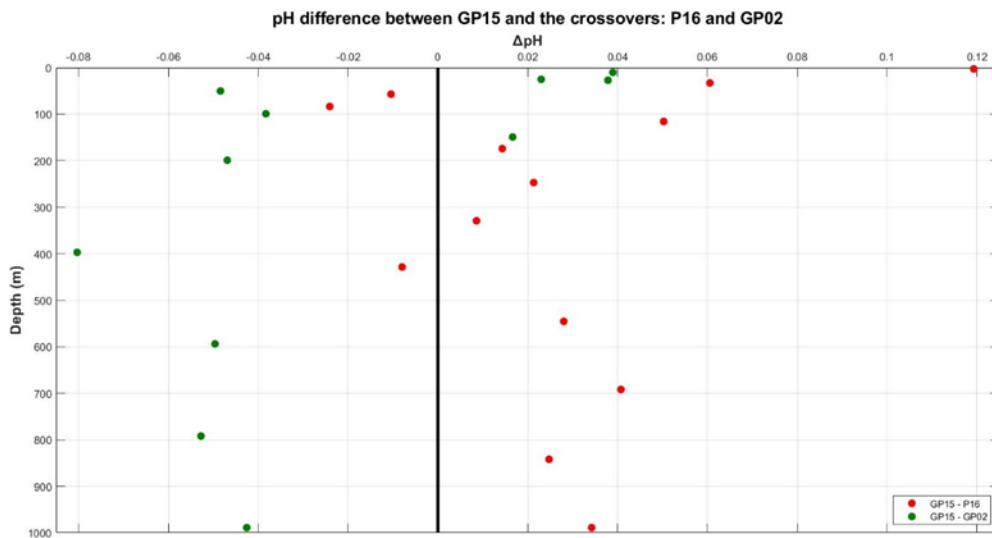


Figure 2. Difference between GP15 pH values and P16 ($\Delta pH = GP15 \text{ pH} - P16 \text{ pH}$, red) and GP02 ($\Delta pH = GP15 \text{ pH} - GP02 \text{ pH}$, green). GP15 values were linearly interpolated to match the depths reported by P16 and GP02.

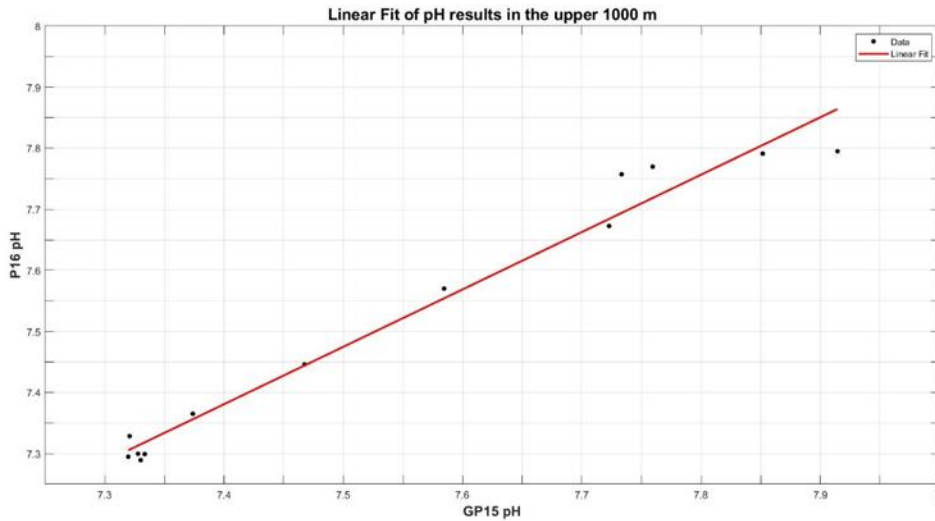


Figure 3. Linearly interpolated GP15 pH values vs. P16 pH results from 9 depths between 3-989m are represented as black dots. The linear fit of the data is shown in red. ($y = 0.9392x + 0.4306$, $r = 0.9875$, $r^2 = 0.9752$, $p = 3.52 \times 10^{-10}$).

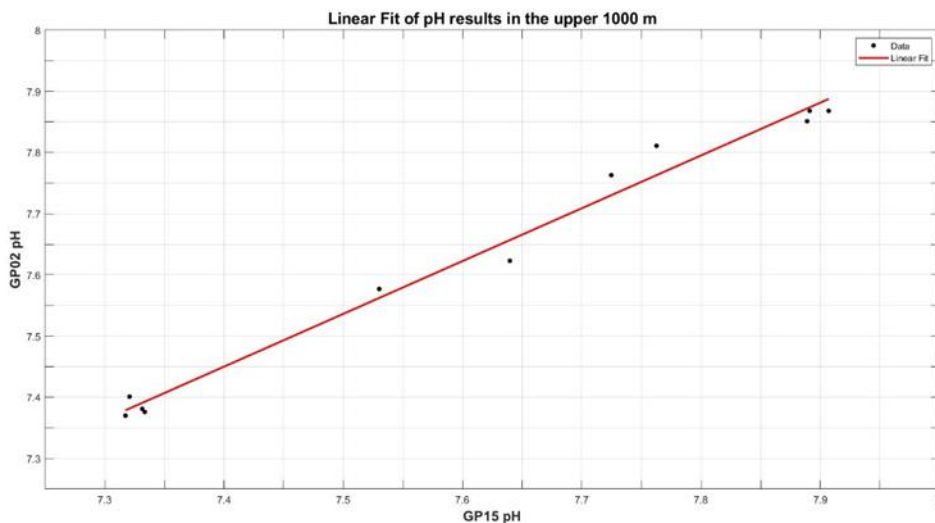


Figure 4. Linearly interpolated GP15 pH values vs. GP02 pH results from 11 depths between 10-989m are represented as black dots. The linear fit of the data is shown in red. ($y = 0.8628x + 1.0654$, $r = 0.9930$, $r^2 = 0.9863$, $p = 1.14 \times 10^{-9}$).

8. If you did not occupy a crossover station, report replicate analyses from a different laboratory, or if there were no replicate analyses (e.g., due to large volumes or short half-lives), explain how your data compare to historical data including results from nearby stations, even though they may not be true crossover stations.

N/A. Crossover station was occupied in the first leg (RR1814).

9. If not already included in your responses to the questions above, please provide a representative vertical profile or report the range of values, for the parameter(s) that are addressed in this intercalibration report.

The pH ranged from 7.2598 to 8.3021 throughout the second leg (RR1815). Figure 5 shows a representation vertical profile from Leg 2.

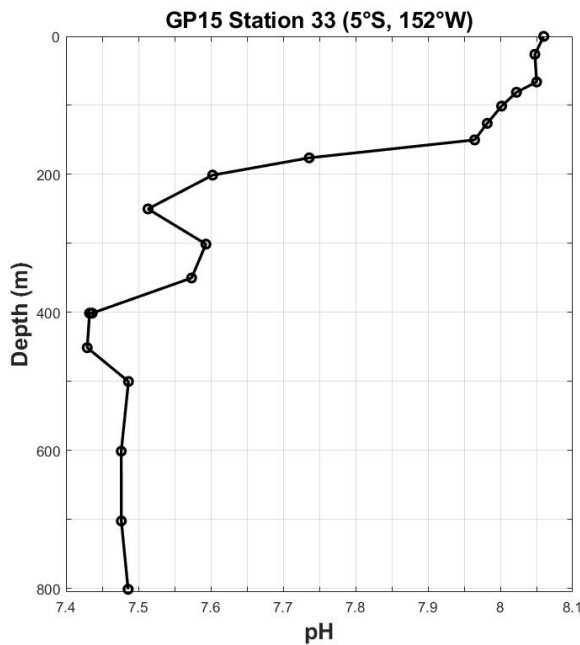


Figure 6. Vertical profile of pH values reported at 5°S, 152°W on GP15 in 2018.

References

- Byrne, R. H., Mecking, S., Feely, R. A., and Zuewu Liy. 2010. Direct observations of basin-wide acidification of the North Pacific Ocean. *Geophys. Res.*, 37(2).
- Carter, B. R., Radich, J. A., Doyle, H. L., and A. G. Dickson. 2013. An automated system for spectrophotometric seawater pH measurements. *Limnol. Oceanogr.: Methods*, 11: 16-27.
- Carter, B. R., Feely, R. A., Mecking, S., Cross, J. N., Macdonald, A. M., Siedlecki, S. A., Talley, L. D., Sabine, C. L., Millero, F. J., Swift, J. H., Dickson, A. G., and K. B. Rodgers. 2017. Two decades of Pacific anthropogenic carbon storage and ocean acidification

along Global Ocean Ship-based Hydrographic Investigations Program sections P16 and P02. *Global Biogeochemical Cycles*, 31: 306-327.

Clayton, T.D. and Byrne, R.H., 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep Sea Res.*, 40(10), 2115-2129.

Once completed, please upload the report here:

<https://geotraces-portal.sedoo.fr/pi/>