pH sensors
What a long way we have come
(in a very short amount of time)

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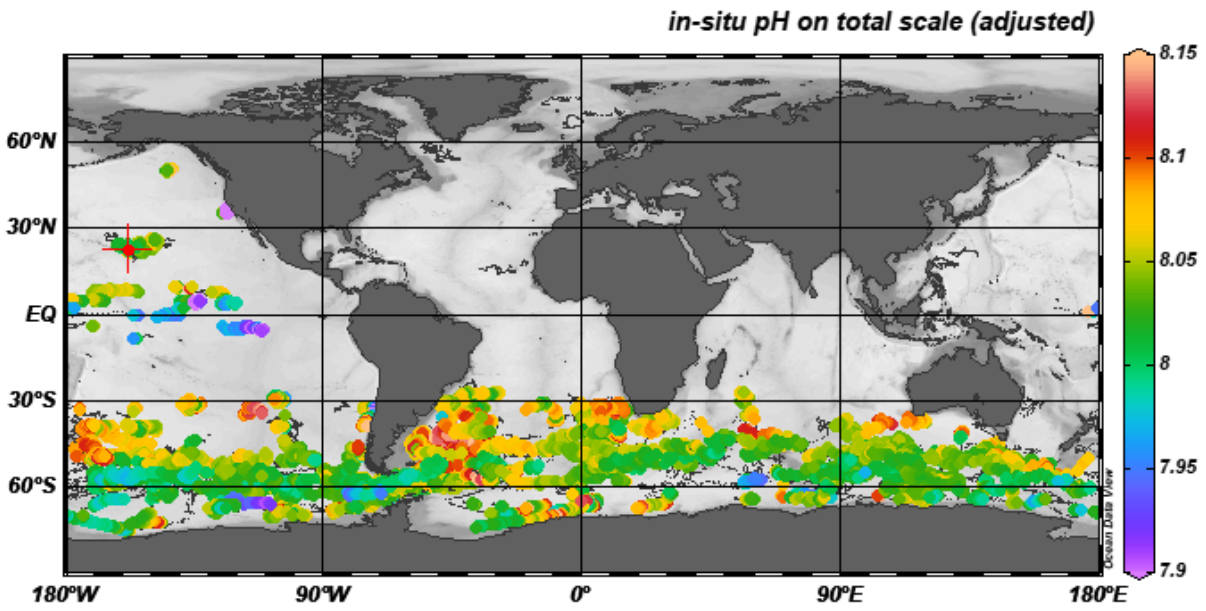
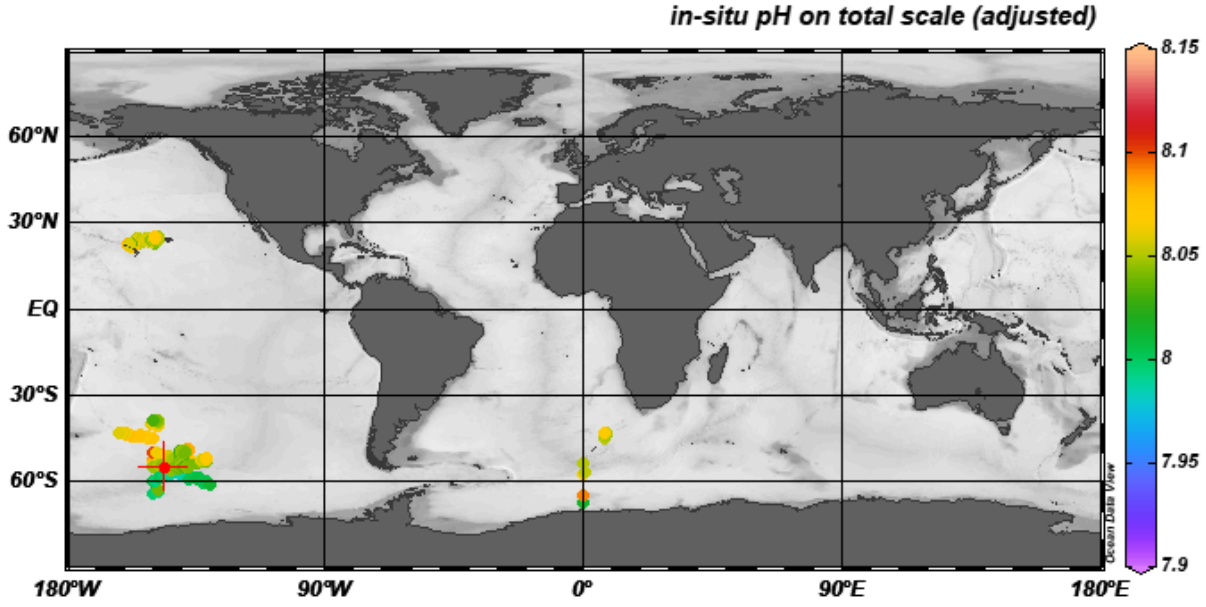
9th BGC Argo Meeting, ADMT 21
November 30 – December 1, 2020
Virtual





Today!

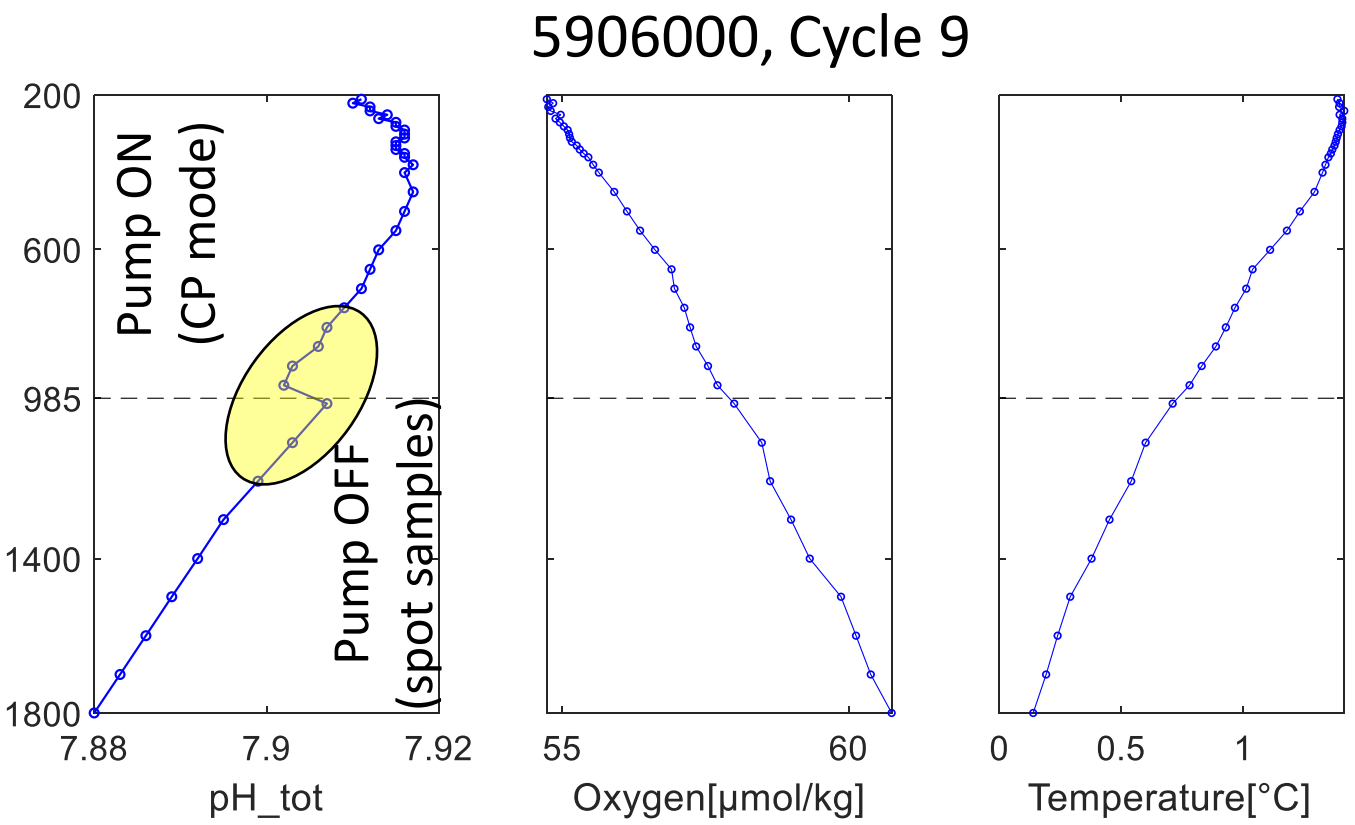
- 900,000 QC'ed pH measurements
- Largely due to SOCCOM project in the Southern Ocean
- Enabling Southern Ocean estimates of CO_2 flux, Aragonite Saturation

Just 5 years ago

- 35,000 QC'ed pH measurements
- Largely due to SOCCOM project in the Southern Ocean

pH pump offset

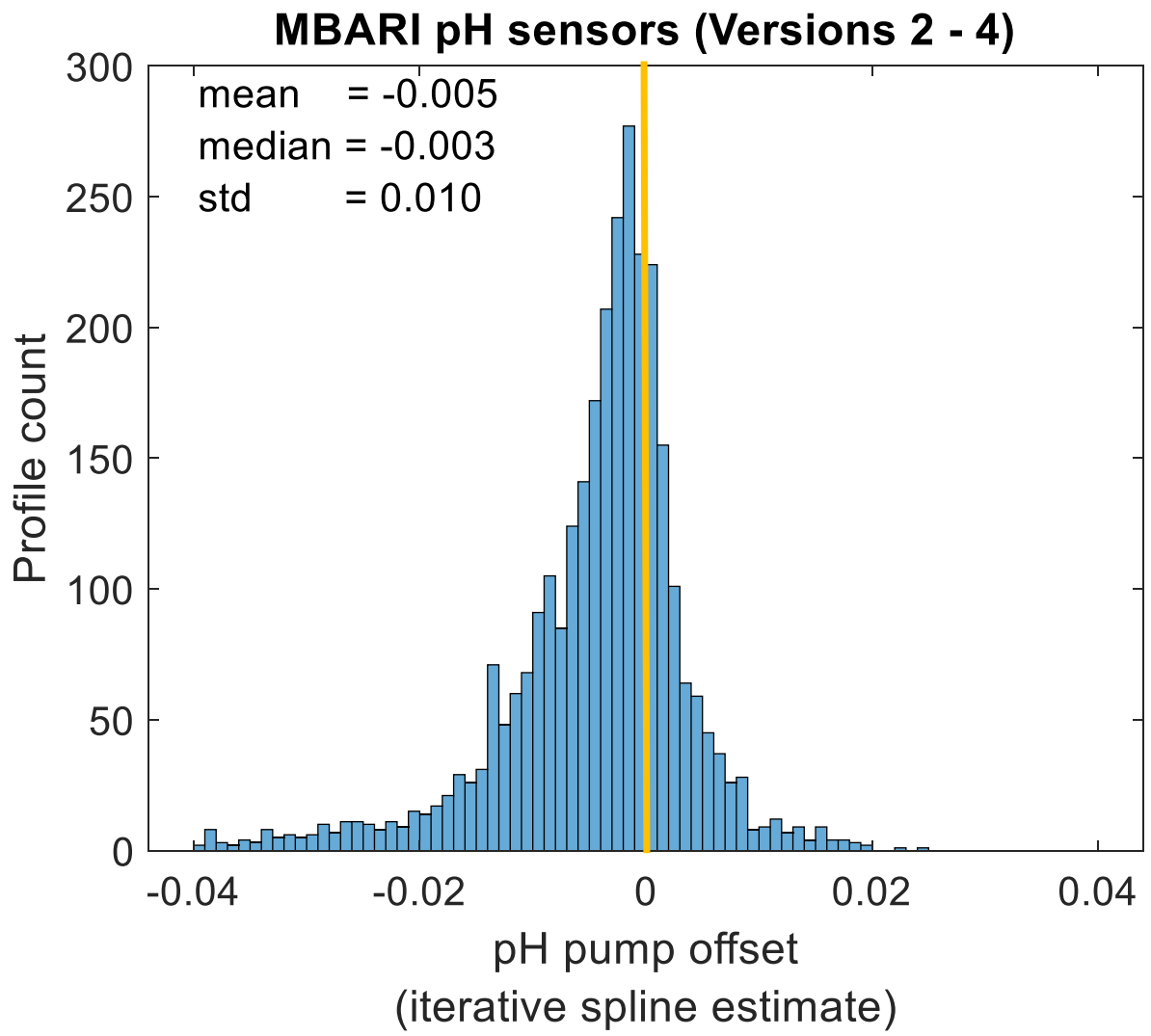
- **pH profiles exhibit a step change for some MBARI APEX floats**
- **Occurs when CTD shifts to constant profiling mode (CTD pump continuously on) at 985m**



- Oxygen & Temperature profiles smooth & linear
- pH above 985m drops by ~0.007

- Magnitude can vary from float to float
- Magnitude of offset can vary from profile to profile
- Rarely seen in NAVIS floats

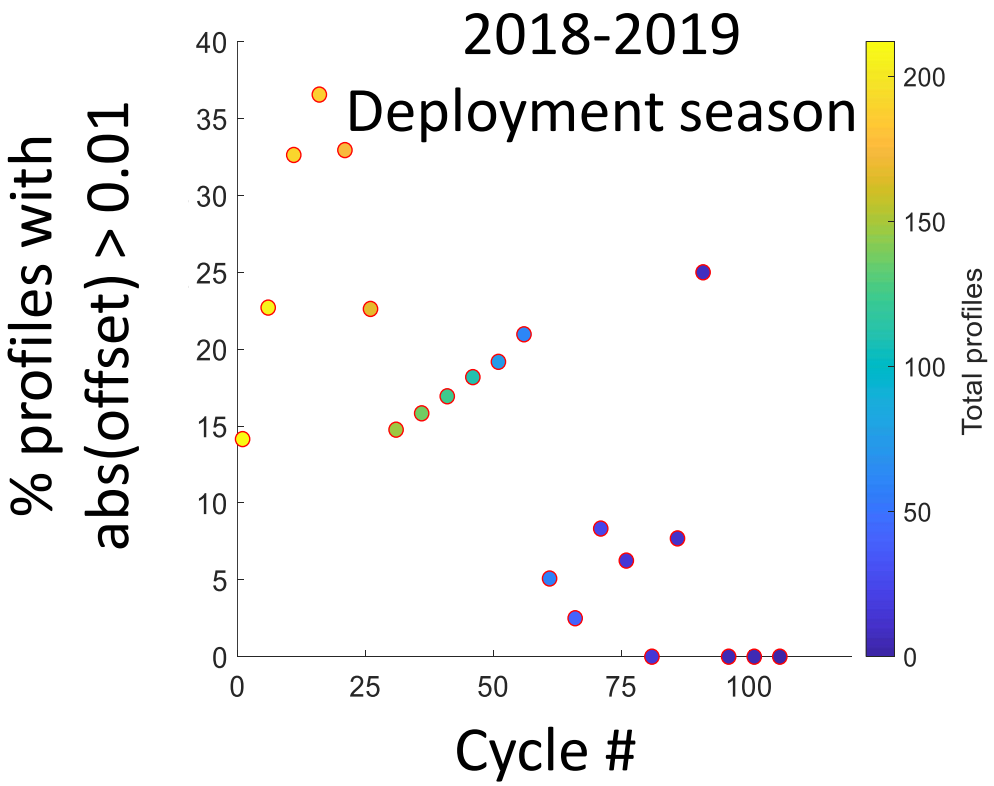
pH pump offset estimates for SOCCOM array

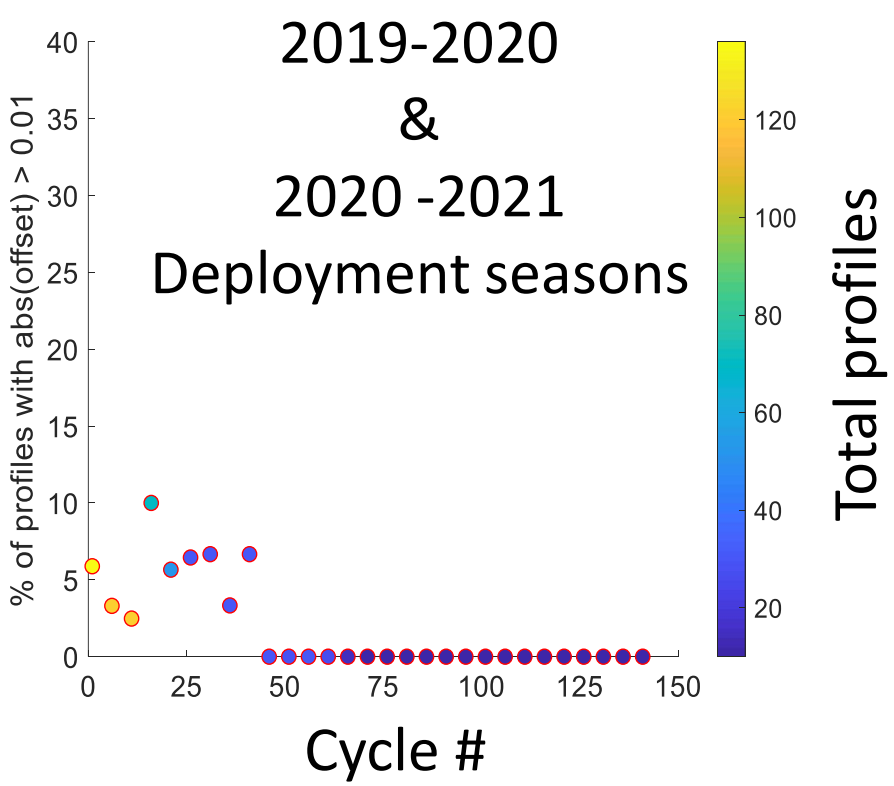


- Affects a small % of total profiles
- Overall bias small & within sensor precision (-0.005)
- Some floats affected more than others
- -1 milli pH offset => +1 µatm pCO2
- **Find root cause & fix sensor**
- **Correct existing data at GDAC affected by problem**

Find root cause & fix sensor

- Partially Related to flow over reference electrode or FET (preliminary lab work)
- Good news – Mostly isolated to 2018-2019 deployment season
- Interesting behavior over time (2018-2019 deployments)
- New sensor design may eliminate the problem completely





Correct existing data stored in the GDAC

Correction methods that have been considered:

A) Single, static offset per float

B) Perform adjustments in SAGE at 980 m vs 1500m

C) Auto-calculation of offset per float, per profile

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- Original method when few floats were affected and observed magnitudes were on the order of millipH
- Does not address time-varying nature of offset

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- Maintains accuracy of adjusted surface data
- Deep data would remain unadjusted
- Assumes offset in SAGE is independent of ref depth (980 vs 1500m)

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Correction methods that have been considered:

A) Single, static offset per float

B) Perform adjustments in SAGE at 980m vs 1500m

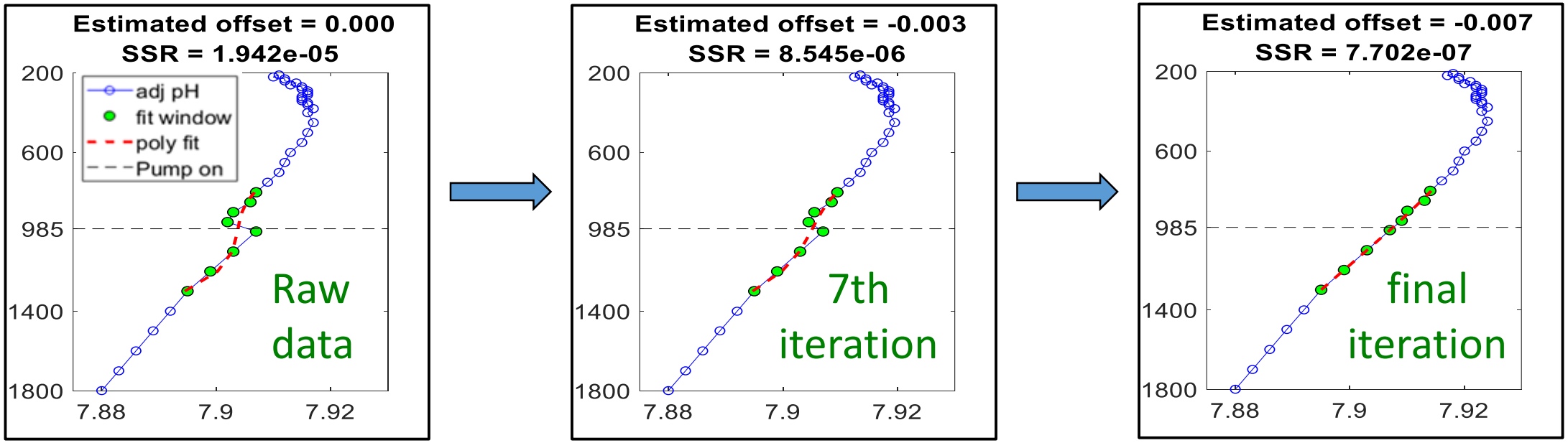
C) Auto-calculation of offset per float, per profile

- No algorithm is perfect
- Thresholds must be set
- How to record magnitude of correction and impact on error/uncertainty??
- Delayed mode or real time corrections?
- Metric for success?

Correct existing data stored in the GDAC

C) Auto calculation of pump offset – one possible approach……..

1. Assume pH is a smooth function of pressure over a narrow data window centered at 985m
2. Break data window above & below 985m
3. Add offset to shallower part of data window
4. Iterate offset value to optimize polynomial fit over data window (minimize SSR)
5. Calculate a signal to noise ratio = offset / std(fit residuals)
6. Set offset & signal to noise thresholds (+/- 0.005 & +/- 10 ??)
7. Add offsets which exceed thresholds to all data shallower than 985m

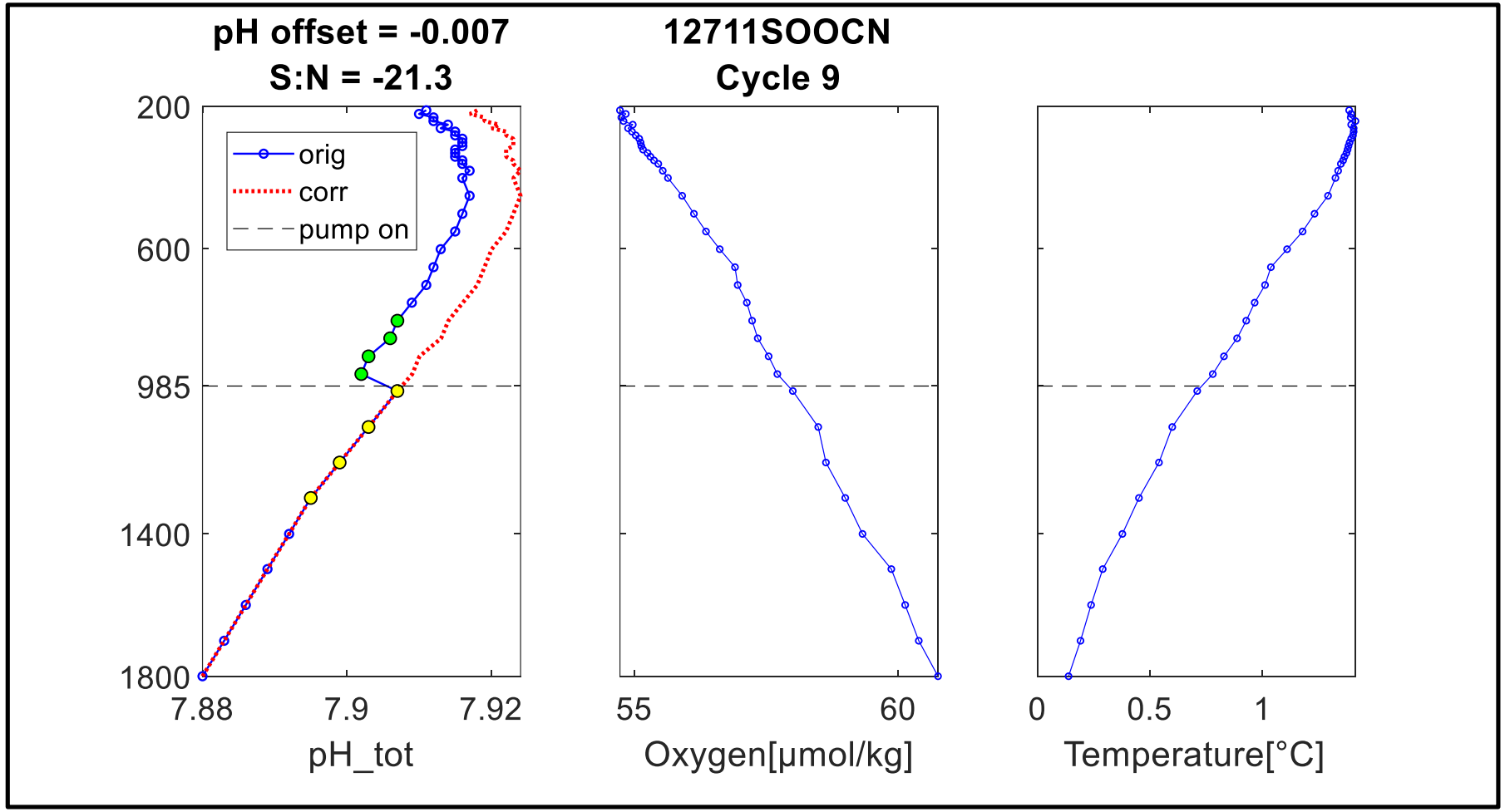


Example

5906000 Cycle 9

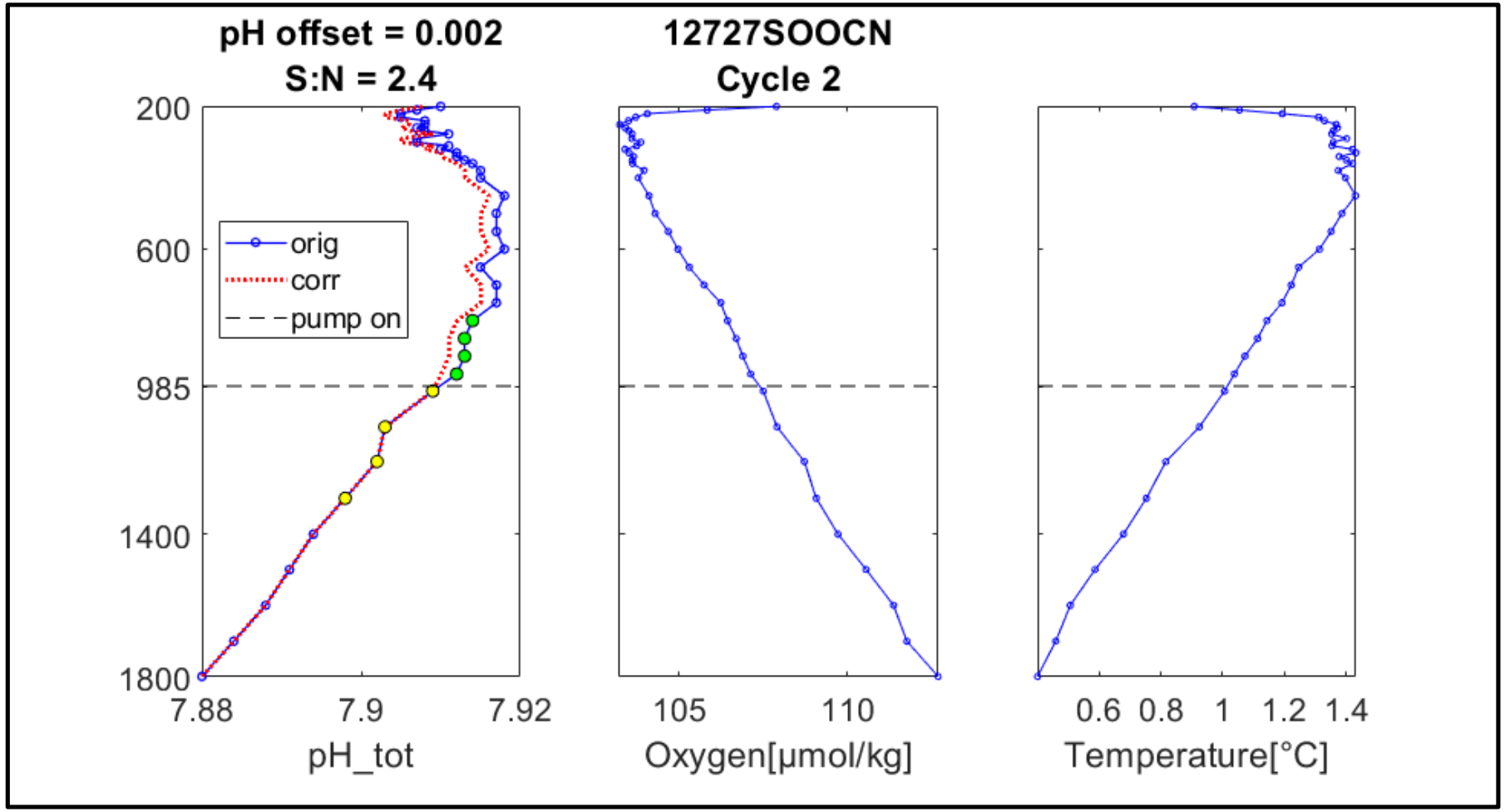
- Negative pH offset (-0.03)
- High signal to noise ratio (-21)

Apply correction



Example

5905998 Cycle 2 - No offset

- Offset small
- Signal to noise ratio low (2.4)

No correction applied