FIELD PERFORMANCE OF AN ISFET BASED PROFILING PH SENSOR

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Introduction

Project Goal: Assess the field performance of an ISFET based Profiling pH Sensor for use with shipboard CTDs, like SBS 25 and SBS 9.

- The Profiling pH Sensor is based off the board set and firmware from the SeaFET V2 and the hardware was modified from the SBS 39.
- The Profiling pH Sensor was calibrated using the standard calibration methods developed by Sea-Bird Electronics for their ISFET pH sensor line.
- The evaluation was performed in May 2019 during the Central California Carbon, pH, and Oxygen (C3PO) research cruise, operated by MBARI.
- The predicted pH values from the sensor were validated against pH bottle samples measured using spectrophotometry.

Why is this important?

Historically, ocean pH on a shipboard CTD cast was either measured using spectrophotometry or with a glass electrode. Spectrophotometry using m-cresol is the gold standard to measure seawater pH, but this method is expensive, labor intensive, and can only be measured at depths where bottle samples were taken. This greatly reduces the pH data density obtained from a given cast. The glass electrode can provide more data density when used in conjunction with a CTD, but suffers from depth limitations (<1200m), calibration drift, offsets caused by undeterminable liquid junction potentials, and interferences. However with the introduction of robust and stable ISFET pH sensors for use in ocean applications, a paradigm shift in the methods used to acquire reliable high density pH data has occurred. Due to this technological advancement, pH is beginning to be recognized as critical for the understanding of long and short time scale biological productivity, food chain cycles, and carbon fluxes.

Technology:

Sensor was design around existing SBE technology:

- Sensor: Deep ISFET pH sensor sub-assemblies
- Board-set: SeaFET V2 Board Set
- Housing: SBS 39 Ti Housing(12 in length by 2 in diameter)

Integration with current SBE shipboard profiling CTDs was made possible by modifying the SeaFET V2 Firmware:

- Enabled DAC to take samples at 1Hz by optimizing board level sampling methods and reducing number of variables recorded (only Vrs, Temp, and Humidity; no health values)
- Enabled DAC to output in analog mode 0-2.5 V
- Created transfer function from 12-bit counts to Vrs (V)

pH data is integrated into the data stream from the CTD, making data analysis easier and reducing the barrier of entry to scientists who want shipboard profiling pH data

Fig. 1 Profiling pH Sensor

Sensing Mechanism Basics

The ISFET is a type of MOSFET (Fig. 2)

- *The gate is an ion sensitive material that is sensitive and selective to the analyte of interest, here H^+*
- *Constant current flows from Drain to Source controlled by pH and the counter electrode voltage, which creates a feedback loop*
- *The reference is a pressure tolerant Cl^- sensitive solid state electrode*
- *When the half cells are combined, the voltage on the reference electrode is proportional to pH*

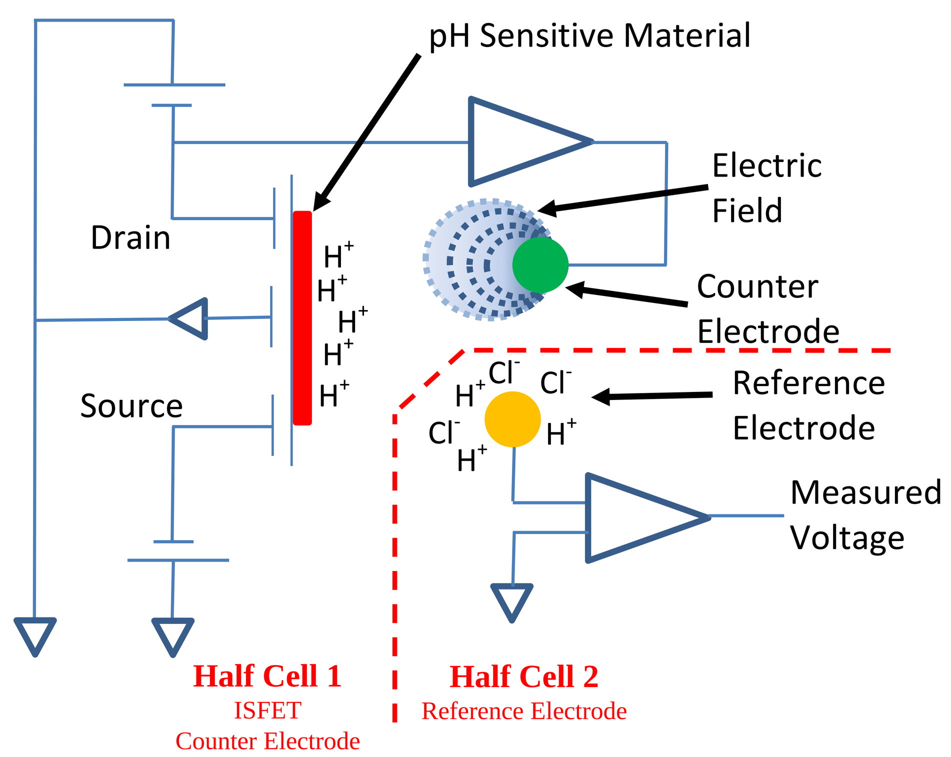


Fig. 2 Schematic representation of the ISFET, counter electrode, reference electrode and operating components.

Results

The evaluation of the Profiling pH Sensor was performed as part of the research cruise (C3PO) operated by MBARI off the continental shelf of central California. This research cruise's purpose was to validate the in situ calibration performance of their pH enabled glider (also using SBS pH sensor technology). During this cruise 33 casts were performed with depths ranging from 200m to 2000m and with >300 bottle samples taken to be analyzed by spectrophotometry. Figure 3c shows the response of the Profiling pH Sensor during 31 casts performed during the C3PO research cruise, two casts were removed due to human sampling errors. The repeat performance of the Profiling pH Sensor is exceptional in the thermocline (0-500m). While hysteresis is observed between the ascending and descending cast in the lower depths (500-1200m). This hysteresis is theorized to be an artifact of piezoelectric response of the ISFET die. Overall, the performance of the Profiling pH Sensor was excellent and work is being performed to mature this sensor into a future product.

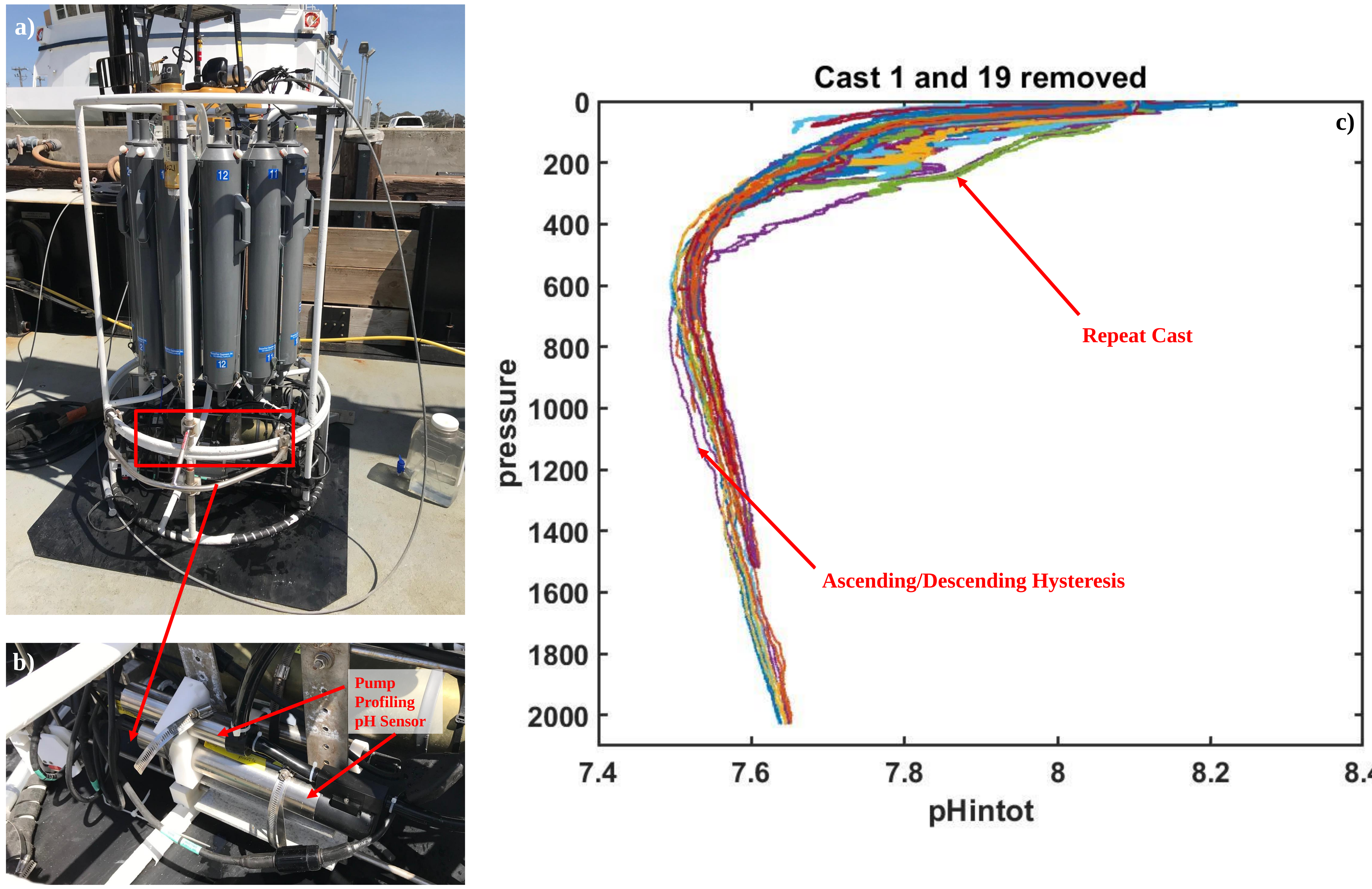


Fig. 3 a) A picture of the SBS 9 used on the RV Racheal Carson during the C3PO research cruise operated by MBARI. The location of the Profiling pH Sensor package is highlighted in red. b) The Profiling pH Sensor was integrated with a 5T pump and mounted next to the SBS 9 at the bottom of the carousel. The Profiling pH Sensor elements were constantly submerged in seawater with a P-trap made of hosing attached to the pump outlet and Profiling pH Sensor inlet. c) Shows the pH response of the Profiling pH Sensor during 30 casts performed during the C3PO research cruise with depths ranging from 200m to 2000m against pressure.

Experimental Setup

The Profiling pH Sensor was installed next to the SBS 9 on the lower section of the carousel water sampler on the RV Rachel Carson operated by MBARI, shown in Figure 3a&b. Integration with the CTD package was achieved by using a wet pluggable Y-cable with the distal section connected to one of the SBS 9's analog in channels (V0). The proximal Y sections were split between the titanium 5T pump and the titanium Profiling pH Sensor. A P-trap was constructed from two pieces of black tubing, one connected to the 5T pump outlet and the other connect to the inlet of the Profiling pH Sensor. The P-trap was used to ensure the sensing elements of Profiling pH Sensor remained submerged in seawater at all times. This design guaranteed the counter electrode did not lose polarization between casts.

Calculating pH

$$pH_{Cell} = \frac{V_{RS} - V_{ref}\,(T,P)}{S_{nernst}} + \log(Cl_T) + 2 * \log(\gamma_{HCl})$$

$$S_{nernst} = \frac{R * T * \ln(10)}{F}$$

- V_{RS} is the potential that forms on the reference electrode when the two half cells are combined. It is proportional to pH and is the signal that is measured
- Cl_T is the chloride concentration and is calculated from salinity
- γ_{HCl} is the activity of HCl is calculated from salinity and temperature
- V_{ref} is calculated using temperature and pressure calibration coefficients
- pH_{cell} can be calculated from V_{rs} with *in situ* temperature, pressure, and salinity

pH Sensor Calibration

$$V_{ref}\,(T,P) = k_0 + k_2 * T + f(P) - \bar{V}_{HCl}\frac{P}{F}$$

- k_0 is an offset that is determined by conditioning the sensor to seawater
- k_2 is a linear estimate of the temperature dependency of the ISFET determined in a 0.01N HCl solution
- f(P) is a polynomial estimate of the pressure dependency of the ISFET determined in a 0.01N HCl solution
- Note, the last term compensates for the compressibility of seawater and is set to zero for calibration in HCl

Accuracy Performance

The accuracy of the Profiling pH Sensor was assessed against bottle samples taken at each cast during the C3PO research cruise. The pH of these bottle samples were evaluated with a spectrophotometer. Figure 4 shows the difference between the pH predicted by the Profiling pH Sensor and the pH measured from the bottle samples taken from the 30 casts with surface outliers removed. A heatmap is overlaid to show the response of the sensor through time represented by the station number, Station 1 (blue) to Station 32 (yellow).

The accuracy of the Profiling pH Sensor for the first 10 stations was excellent, with residuals of 0.02 pH or below. Some drift in the sensor's response is observed, but the sensor remains within SeaFET V2 specification (<0.05 pH) through out the entire cruise. This drift could be from many sources, but biofouling is the most probable cause. The sensor was not protected from biofouling between casts and the sensor showed evidence of biofouling when returned to SBS for evaluation. SBS is working on new methods to mitigate biofouling in future field evaluations.

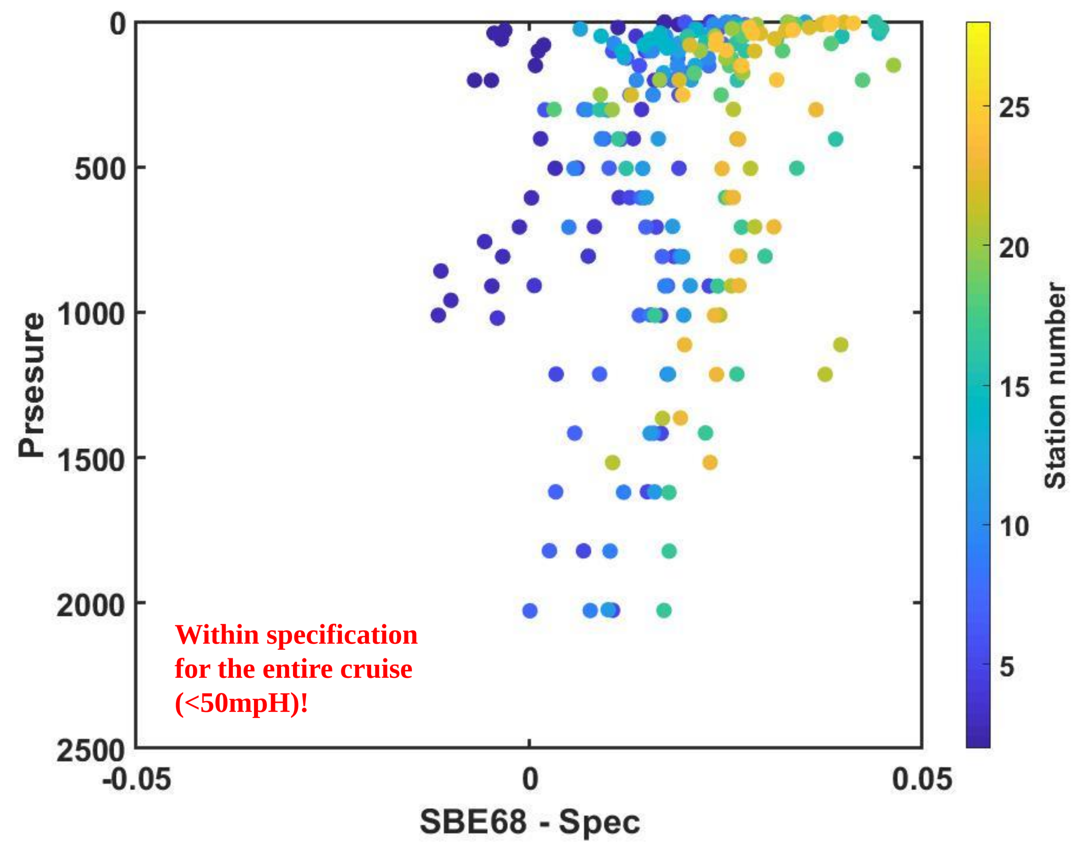


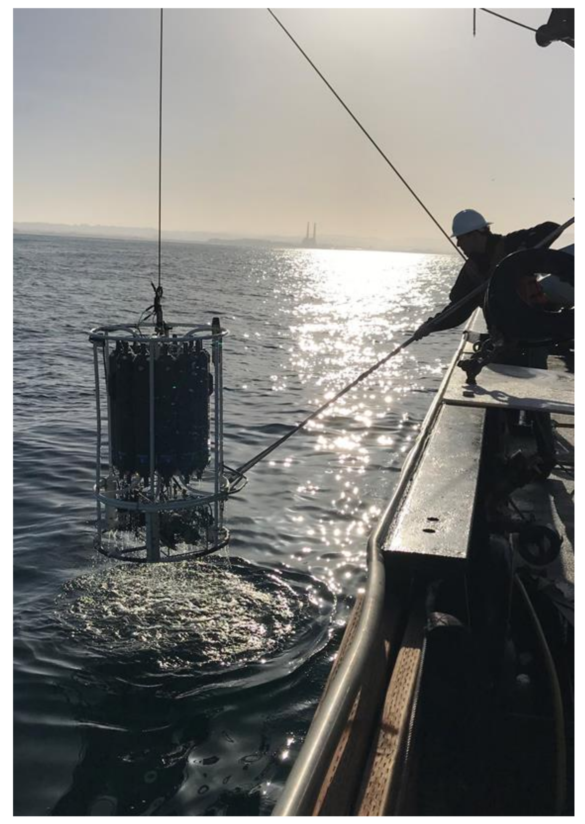
Fig. 4 Shows the difference between the Profiling pH Sensor and the spectrophotometric pH values measured from the bottle samples taken during each cast of the C3PO research cruise against pressure. The station number is also shown as a heat map from blue (Station 1) to yellow (Station 32).

Conclusions

The initial field tests of the Profiling pH Sensor have demonstrated that it is a stable and accurate pH sensor for shipboard ocean acidification monitoring. These field tests have also laid the foundation to establish the Profiling pH Sensor as an essential tool for understanding one of the critical parameters that controls many of the biological and chemical cycles in our ocean. Currently Sea-Bird Scientific engineers and scientists in conjunction with the MBARI Chemical Sensor Group are working closely to evaluate this sensor's analytical performance in the hopes of maturing it into a future product.

Acknowledgements:

Many thanks to the Science and R&D team, and all of the Sea-Bird team members who helped with the development of the Profiling pH Sensor and fieldwork. Thanks to Bob Kruger, Stephanie Jaeger and the crew of the RV Sound Guardian at King County Environmental Lab for their ongoing support and enthusiasm to test new sensors with us. Countless thanks to Ken Johnson, Hans Jannasch, Luke Coletti and the other scientists at Monterey Bay Aquarium Research Institute for the many discussions, sharing of data and insightful feedback. Without all of this support none of this would be possible.



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