



Technical note: Obtaining accurate, high-frequency and long-term seawater pH data by using coupled lab-on-chip and optode sensing technologies

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Abstract. The marine science community requires accurate, cost-effective, and reliable pH sensors capable of long-term, stable operations *in-situ* from coastal to deep-sea environments. Spectrophotometric pH sensors, based on lab-on-chip (LOC) technology, offer measurement frequencies of every 10 minutes and provide accurate data over long-term use. However, for applications where higher-frequency measurements are important, this maximum sample rate may be limiting, in addition to the power requirements needed to operate the sensor.

In contrast, commercially available pH optodes (PyroScience GmbH) are relatively inexpensive, consume little power and are contained within a comparatively small form-factor package, but with intense use the pH sensitive membrane can photo-oxidise, causing signal drift. The combination of LOC and optode technologies, however, can be used to provide long-term, high-frequency and high-stability *in-situ* pH data, but protocols to correct for sensor drift need to be developed and evaluated.

To examine sensor drift and develop protocols to account for it, we suspended two LOC pH sensors with two pH optodes at 0.5 m depth from a floating pontoon within a harbour in Southampton, UK for six months (June-December 2023). This is a highly dynamic tidal environment with substantial biofouling. The optode (AquapHOx-L-pH, PyroScience GmbH) and an independent pH sensor (Deep SeapHOx V2, Sea-Bird Scientific) measured at a high frequency (e.g., ≤ 5 min) alongside a LOC pH sensor measuring at a lower frequency (e.g., ≤ 2 hr). Triplicate lab validated co-samples were collected each week, in addition to dedicated sensors monitoring the temperature, salinity, dissolved oxygen and tidal height. We find good agreement, i.e., mean $\Delta\text{pH} = -0.022 \pm 0.023$ pH units between the SeapHOx and LOC sensors (3,182 data points in common), in addition to individual field accuracies of <0.020 pH units. As expected, we found significant signal drift (e.g., generally ≤ 0.012 pH units per day) and offsets (e.g., 0.1-0.2 pH units) with the pH optodes after intensive use in a high biofouling environment. However, by coupling accurate LOC pH data to high frequency optode data, we corrected the optode signal drift/offset and achieved a similar field accuracy (<0.02 pH units) to the SeapHOx sensor even when using ultra-low LOC pH sensor measurement frequencies (e.g., several days to weeks). Overall, this work provides the oceanographic community with guidelines on how to achieve accurate, rapid, and long-term pH measurements, while also balancing power requirements, by combining two complementary pH sensing technologies.



1 Introduction

Anthropogenic carbon dioxide (CO₂) emissions are acidifying the global oceans. If emissions are not curtailed, surface seawater pH may fall by an additional 0.3 pH units, a doubling of acidity over the 21st century, by the year 2100 (Kwiatkowski et al., 2020). On a more granular level there are several processes (e.g., photosynthesis/respiration, calcification, tidal mixing, and microbial activity) that respond to even small pH fluctuations on much shorter temporal scales. To measure these rapid processes over large spatial areas the scientific community need accurate, *in-situ* measurements of seawater pH.

The most accurate measurements of pH are made in a laboratory. While glass pH electrodes have been widely used for many decades, their accuracy (≥ 0.1 pH units) is limited due to junction potential drift (Dickson, 1993). Instead, the preferred method for accurate pH determination is done using a spectrophotometer (Dickson, 1993), and until recently, was exclusively performed in a laboratory on land or on a ship. Measurements of seawater pH can also be determined with high accuracy indirectly by calculating pH as a function of parameters that define the carbonate system (Dickson et al., 2007). These parameters, in addition to pH, are the concentration of dissolved inorganic carbon, total alkalinity (Dickson, 1981), and the fugacity of CO₂, which is typically determined from measurements of the gas phase (Wanninkhof and Thoning, 1993). There has been significant effort within the oceanographic community to develop accurate and reliable sensors capable of undertaking these measurements *in-situ* and autonomously at sea.

In the past two decades, two types of technologies have been introduced that are both capable of measuring pH with high accuracy: spectrophotometric techniques and ion-sensitive field effect transistors (ISFET). The spectrophotometric technique has been implemented on a few technologies capable of autonomous *in-situ* deployment. The SAMI-pH sensor (Sunburst Sensors) operates on a spectrophotometric reagent-based method and offers fast (response time 3 minutes), accurate (± 0.003 pH units), and stable (drift < 0.001 pH/months) measurements, but is only operable to depths of 600 m (accessed 29/08/2025: <http://sunburstsensors.com/products/oceanographic-ph-sensor.html>). A lab-on-chip (LOC) pH sensor, developed at the National Oceanography Centre (NOC), implements a spectrophotometric assay with a miniaturised fluidic manifold, valves, pumps, and electronics in a portable device (Aßmann et al., 2011; Liu et al., 2006; Martz et al., 2003). LOC pH sensors can make highly accurate measurements (uncertainty of < 0.01 pH units at pH 8.0) for several months at sea (Mowlem et al., 2021; Rérolle et al., 2014). They are also capable of operating at full ocean depth, i.e., rated for operation to 6,000 m (Yin et al., 2021). While they consume little reagent (ca. 3 μ L) and produce little waste (ca. 2 mL) per sample (Yin et al., 2021), management of reagent/waste volumes and power consumption can limit measurement frequency during long deployments. This LOC pH sensor has recently become commercially available (accessed 29/08/2025: <https://www.clearwatersensors.com/ph-sensor.html>). Conversely, pH ISFETs, which have been used on commercially available instruments such as the SeaFET and SeapHOx (Sea-Bird Scientific) for over ten years, are the most used instruments for oceanographic pH measurements. ISFETs were first adapted for pH measurements in the deep sea over twenty years ago (Shitashima et al., 2002). Their use in oceanography greatly expanded after rigorous evaluation of the DuraFET (Honeywell) pH ISFET sensor (Martz et al., 2010). The Nernstian response of the DuraFET to changes in seawater



salinity and pH, in addition to best practices, were later established (Bresnahan et al., 2014). This has been implemented in the SeaFET instrument for measurements of pH alone, and in the SeapHOx instrument, which is capable of measuring pH, dissolved oxygen, conductivity, temperature, and depth, with a modified version operating to depths of up to 2,000 m (Johnson et al., 2016). The manufacturer reported instrument accuracy is ± 0.05 pH units with a precision of ± 0.004 pH units (accessed 29/08/2025: <https://www.seabird.com/>). The accuracy can be further improved for months-long deployments by modifying the instrument with a reservoir of TRIS buffer and an additional pump to allow self-calibration (Bresnahan et al., 2021). Nonetheless, the ISFET-based pH sensors are known to have long-term electrode signal drift and require long conditioning times within the sensing environment, e.g., 1-2 day periods from the manufacturer, whereas others recommend longer ≥ 5 day conditioning periods (Saba et al., 2019; Bresnahan et al., 2014).

Two practical limitations to the more widespread use of these sensors are their size and power consumption. The commercial version of the LOC pH sensors, with a cartridge of reagents, are a cylinder 56 cm long and 16 cm in diameter. Power consumption is 1.8 W during measurement (e.g., ~ 1000 Joules of energy per sample) and 6 mA in sleep mode in between measurements. The SeaFET is 55 cm long and 11 cm in diameter (Sea-Bird Scientific). Power consumption during measurement is smaller, at a maximum of 0.4 W. Both instruments have been equipped on autonomous platforms, but the volume that these instruments require, and the power that they consume, limits the space and power available for other instruments on the platform (Takeshita et al., 2021; Saba et al., 2019; Hammermeister et al., 2025). In comparison, the pH ISFET instrumentation on an Argo profiling float uses a reported 19.7 J/sample (Bittig et al., 2019).

Newly available pH optode sensors (e.g., AquapHOx-L-pH; PyroScience GmbH) have recently begun to be explored for oceanographic applications (Wirth et al., 2024; Staudinger et al., 2019; Staudinger et al., 2018; Fritzsche et al., 2018; Monk et al., 2021). While these sensors are prone to signal drift (manufacturer reported drift < 0.005 pH units per day) as a result from deterioration of the pH sensitive coating, they can provide rapid (< 1 minute per measurement) pH data. The sensor has an internal rechargeable battery, and the manufacturer suggests it can operate for 2 months sampling every 10 seconds (accessed 29/08/2025: <https://www.pyroscience.com/en/products/all-meters/aquaphox-l-ph>). The physical size of the sensor is small (37.5 cm long and 6.3 cm in diameter) allowing for easy integration onto autonomous vehicles, and they can be procured with both shallow (100 m) and deep-sea (4,000 m depth rated) housings. Furthermore, provided there is access to the sensor, the consumable pH caps are easily changed, and the calibration procedure is straightforward enough that it can be carried out in the field. Recent work has provided guidelines for the oceanographic community regarding the calibration of the optode-based pH sensors with implications for field test data, but it indicates that the sensor is best suited for short-term (i.e., weeks to months) deployments where drift is less of a problem (Wirth et al., 2024). Nonetheless, these small optode-based sensors have the capacity to be a powerful tool for oceanographic research, but protocols need to be developed to improve their long-term accuracy.

In this paper, we demonstrate the efficacy of a combined system featuring both a LOC spectrophotometric pH sensor and an optode. We demonstrate the ability of this combined sensor package to provide accurate, rapid, and long-term pH data against an independent pH sensor (SeapHOx) during a 6-month shallow field test. We also provide a data analysis method to

correct for signal drift and offset, in addition to discussing the balance between power and accuracy of the combined system during a long-term field deployment. The assessment undertaken offers guidelines for the oceanographic community on how to obtain accurate, rapid, and long-term seawater pH data.

2 Materials and Procedures

2.1 Field test site and pH sensor setup

To demonstrate the sensor combination, we deployed sensors at a shallow test facility within a harbour in Southampton, UK (N 50° 53' 33.8496, E -1° 23' 40.7148) from late-June until mid-December 2023. The NOC is located at the head of Southampton Water, a tidal estuary site that is characterised by mixing between the marine waters of the English Channel and two principal chalk freshwater rivers (the River Itchen and the River Hamble). The quay is a busy port area that can have multiple commercial and research ships enter/exit each day. Three pH sensors (described below) were suspended at fixed points from a floating pontoon to a fixed depth of ca. 0.5 m below the seawater surface. A pressure (depth) sensor (EXO2 multi-parameter sonde; YSI) was suspended from a fixed point that did not rise/fall with the pontoon.

The relevant pH sensor specifications are provided in Table 1. The LOC sensor, manufactured at the NOC (Yin et al., 2021), is rated for deep-sea use and was powered by an external rechargeable lead-acid battery that was stored inside a waterproof box above the location where the sensor was secured to the pontoon. The battery was swapped at regular intervals (i.e., every four days). The reported accuracy and resolution of the LOC sensors are $<\pm 0.009$ and $<\pm 0.001$ pH units, respectively (accessed 29/08/2025: <https://www.clearwatersensors.com/ph-sensor.html>). The shallow-rated optode sensor (AquapHOx-L-pH; PyroScience GmbH) has an internal rechargeable Li-ion battery. The reported accuracy and resolution from the manufacturer are ± 0.050 and ± 0.003 pH units, respectively (accessed 03/09/2025: <https://www.pyroscience.com/en/products/all-sensors/phcap-pk8t-sub>). The SeapHOx sensor (Deep SeapHOx V2; Sea-Bird Scientific) is rated for deep-sea applications and is powered by internal non-rechargeable batteries (accessed 29/08/2025: <https://www.seabird.com/deep-seaphox-v2-ocean-ct-d-ph-do-sensor/product-downloads?id=60762467726>). Specifically, this sensor consists of two parts: (1) a pH sensor and (2) a conductivity-temperature-depth and dissolved oxygen (CTD-DO) sensor. These are physically connected using a support clamp and the relevant CTD-DO data feed into the pH sensor calculation. The reported accuracy and resolution from the manufacturer are ± 0.050 and ± 0.004 pH units, respectively.

Table 1. Sensor dimensions (length $\times$ diameter), weight (in air), depth rating, accuracy, resolution, and drift. *Note: the dimensions and weight are for the SeaFET (Sea-Bird Scientific) pH sensor.

Sensor	Dimensions L $\times$ D (mm)	Weight in air (kg)	Depth rating (m)	Manufacturer accuracy ($\pm$ pH units)	Manufacturer resolution ($\pm$ pH units)	Manufacturer drift (pH/time)
LOC	600 $\times$ 200	3.6	6,000	<0.009	$<<0.001$	N/A



Optode	375 × 63	0.45	100	0.050	0.003	<0.005 pH/day
SeapHOx*	549 × 114	5.4	2,000	0.050	0.004	0.003 pH/month

The optode sensor was deployed side-by-side with the LOC sensor by simply attaching the optode to the exterior housing of the LOC sensor (refer to Figure 1a). Cable zip ties were used to achieve this and never failed in our tests, but a more robust attachment could easily be constructed. The two combined LOC + optode sensors and the SeapHOx sensor were spaced ca. 0.5 m apart from each other.

2.2 Data analysis

To test the impact of measurement frequency on the resulting pH data, the sample rates of the pH sensors (i.e., SeapHOx, LOC, and optode) were changed halfway through the field trial (refer to Table 2). During phase 1 (Jun. 20 – Sep. 8, 2023) the SeapHOx and optode sensors were deployed with rapid <1 minute measurement frequencies, whereas the LOC sensor had a significantly lower measurement frequency of every 45 minutes. During phase 2 (Sep. 8 – Dec. 15, 2023) the measurement frequencies of the SeapHOx and optode sensors were lowered to sample every 5 minutes, and the LOC sensor was lowered to measure every 2 hours. A YSI EXO2 multi-parameter sonde was utilised to obtain tidal height data every 15 minutes throughout the entire study. An independent C-T (conductivity and temperature) sensor (microCAT C-T, Sea-Bird Scientific), deployed during phase 2, measured every 5 minutes and provided a back-up in case of failure of the CTD-DO portion of the SeapHOx sensor.

Table 2. Deployment dates (phase 1 and phase 2), measurement frequencies, and number of data points collected for each sensor.

Sensor	Phase 1 Jun. 20 – Sep. 8, 2023		Phase 2 Sep. 8 – Dec. 15, 2023	
	Measurement frequency	No. data points	Measurement frequency	No. data points
SeapHOx	47 sec	148,148	5 min	20,142
LOC	45 min	2,365	2 hr	1,125
Optode	30 sec	229,876	5 min	28,167
EXO2	15 min	3,711	15 min	9,316
C-T	-	-	5 min	27,075

The raw data from the LOC pH sensor was post-processed as described previously (Yin et al., 2021) using *in-situ* salinity and temperature data from an independent C-T sensor. The raw data from the optode pH sensor was also post-processed for



150 salinity and temperature from an independent C-T sensor using a Microsoft Excel-based calculator provided by the manufacturer (Pyroscience, 2025). Lastly, the SeapHOx sensor output processed pH values using the on-board salinity and temperature measured from its CTD. Therefore, all pH data presented here has been adjusted to account for the known salinity and temperature at the time of measurement.

2.3 *Sensor calibration*

155 The LOC sensor, manufactured in 2022, is a calibration-less method wherein during the manufacturing process a one-off correction to the optical system is applied to account for the wavelength non-specificity of the LEDs (Yin et al., 2021). The optode sensor was calibrated following the manufacturer's recommended procedure prior to deployment. Specifically, a fresh optode pH cap was soaked in the manufacturer-provided buffer reagents for an hour before following the calibration guide on the software. This was a two-point buffer (pH 2 and pH 11) calibration and was done once before phase 1 and once
 160 before phase 2 when a new optode pH cap was installed. The SeapHOx sensor was calibrated in September 2021 by the manufacturer. The pressure (depth) sensor was re-zeroed on land prior to deployment. The combined conductivity and temperature sensor (microCAT C-T; Sea-Bird Scientific) was calibrated in July 2017 by the manufacturer.

2.4 *Lab pH validation process*

To validate the results from the pH sensors, triplicate discrete seawater co-samples ($n = 44$, i.e., 132 samples total) were
 165 manually collected in 60 mL polypropylene syringes (Terumo Eccentric Luer-tip 3-part syringe) adjacent to the sensor inlets and measured in a lab immediately following collection using a previously outlined procedure (Yin et al., 2021). The discrete samples were not poisoned and the time between co-sampling and lab measurements was <5 minutes. Each triplicate discrete sample was copiously flushed through a 10 cm water jacketed glass optical cell, where the temperature was maintained at 20 °C, and 5 μ L injections of 4 mM purified meta-Cresol Purple (mCP) was added to ca. 8 mL of sample on a
 170 Cary 60 UV-vis (Agilent Technologies) spectrophotometer. The average of each triplicate co-sample was taken. The mean and standard deviation of the difference between replicate co-samples was 0.007 ± 0.008 pH units. The total uncertainty of the spectrophotometric measurement procedure used in this study was calculated to be 0.005 pH units, which includes individual uncertainties for the temperature, absorbance, baseline correction, deuterium lamp, and the calculation of pH from spectrophotometric data (Carter et al., 2013; Yin et al., 2021). The salinity of each discrete sample was also measured using
 175 a commercial conductivity meter (WTW Cond 3110) and probe (WTW TetraCon 325).

2.5 *Sensor maintenance*

Routine maintenance was carried out when sensors were retrieved for data download and as needed. LOC: The sample inlet filter for the LOC sensor was changed every week during the initial three months (phase 1) but remained unchanged during the final three months (phase 2). The sample inlet filter was left unchanged during phase 2 to assess if biofouling impacted
 180 the pH signal. The LOC sensor waste bag was emptied at opportunistic times throughout the study. Power was supplied to the LOC pH sensor via a rechargeable lead-acid battery, which was swapped out with a fresh battery at regular intervals (i.e., every four days) to avoid disruption to data collection. During week 10, the LOC pH sensor was flushed for 5-10 minutes each with a sequence of solutions (i. 10% Decon-90 cleaning solution, ii. ultrapure water, and iii. filtered seawater) to clean



the microfluidic channels as a result of the significant biofouling encountered. Optode: The rechargeable internal battery charge level was checked during data transfer (and opportunistically recharged). A copper mesh fabric was installed around the outer protection cage of the optode sensor at the beginning of August to help minimise the significant bioaccumulation observed and was subsequently removed near the beginning of Phase 2 (mid-September) due to the deployment of a second optode pH sensor which was equipped with an anti-fouling copper mesh guard. The spent optode cap from phase 1 was replaced with a freshly lab-calibrated optode cap for phase 2 following the manufacturer's guidance. SeapHOx: Prior to deployment the SeapHOx sensor wet cap was filled with seawater from the test site for one week to condition the sensor. The small pinhole on the attached CTD-DO half was regularly cleaned of accumulated biomass during phase 2 to prevent air buildup within the sensor. The sensor was equipped with anti-fouling technology utilising a flow-path to extend deployment durations in high-fouling environments. The on-board batteries for both the components of the SeapHOx sensor (i.e., pH and CTD-DO) were replaced on 13/11/2023, and the sensor housing was cleaned during this process. EXO2: The internal D-cell batteries of the pressure (depth) sensor were replaced at regular (monthly) intervals. Minimal fouling was observed on this sensor due to its deeper deployment depth. C-T: No maintenance was carried out on the microCAT C-T sensor after deployment.

3 Results and Discussion

3.1 Sensor performance: phase 1

The manufacturer of the optode pH sensor claim that the battery can last between 2 to 6 months with a measurement interval between 10 to 60 seconds, respectively. In our testing, the optode sensor never experienced a battery failure even during periods of high measurement frequency. When data was collected from the sensor the internal Li-ion battery did trickle charge, but this was never more than 10 minutes. For reference, the manufacturer indicates that the sensor can be fully recharged in 2 hours.

The combined LOC + optode pH sensor package (Figure 1a) provided near continuous data collection over the first three-month period (phase 1). Phase 1 occurred during the warmer summer months (i.e., the surface water temperature was relatively constant around 20 °C) and, due to the fixed 0.5 m deployment depth, we observed significant bioaccumulation on the sensors. Pictures taken during July and August show the challenging biofouling environment the pH sensors were operating in (refer to Figure 1b-d highlighting biofouling on the optode sensor). A deeper look at the chemical and physical drivers affecting the seawater pH during this study is provided in ESI 1.

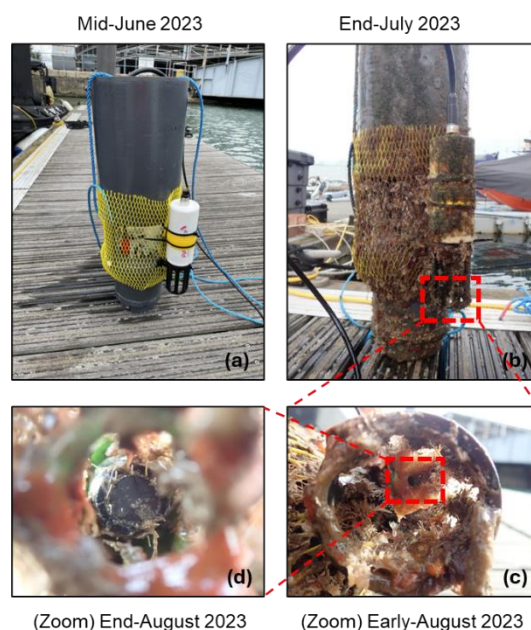


Figure 1. Pictures taken during phase 1 showing (a) clean combined optode + LOC sensor package at start of deployment in mid-June 2023 for reference, (b) combined optode + LOC sensor package at the end of July 2023 with significant bioaccumulation, (c) close-up on optode external protective cage in early-August 2023, and (d) zoom-in on pH cap protective cage showing the pH-sensitive optode surface at the end of August 2023.

During phase 1 of the study the optode was measuring at a high frequency, every 30 seconds, whereas the LOC was measuring at a low frequency every 45 minutes. An overview of the phase 1 optode and LOC pH sensor data, alongside discrete lab validated co-samples, are provided in Figure 2. The LOC data exhibit good agreement with the discrete lab validated co-samples throughout phase 1, with a -0.012 ± 0.014 (i.e., mean $\pm$ stdev; $n = 15$) pH units' difference between the discrete co-samples and LOC value closest in time to the discrete co-sample. Similar data quality has been observed from the LOC pH sensor in the past from the same deployment site (Yin et al., 2021). The optode sensor showed relatively good agreement with discrete co-samples within the first month, i.e., 0.024 ± 0.014 ($n = 10$), but thereafter we find the optode signal drifted away from the LOC and discrete co-sample signals towards unrealistic seawater pH values during the last two months of phase 1. Signal drift of 0.002 pH units per day and offsets of e.g., 0.1 to 0.4 pH units have been reported previously for optode-based pH sensors deployed in the field (Delaigue et al., 2025; Wirth et al., 2024).

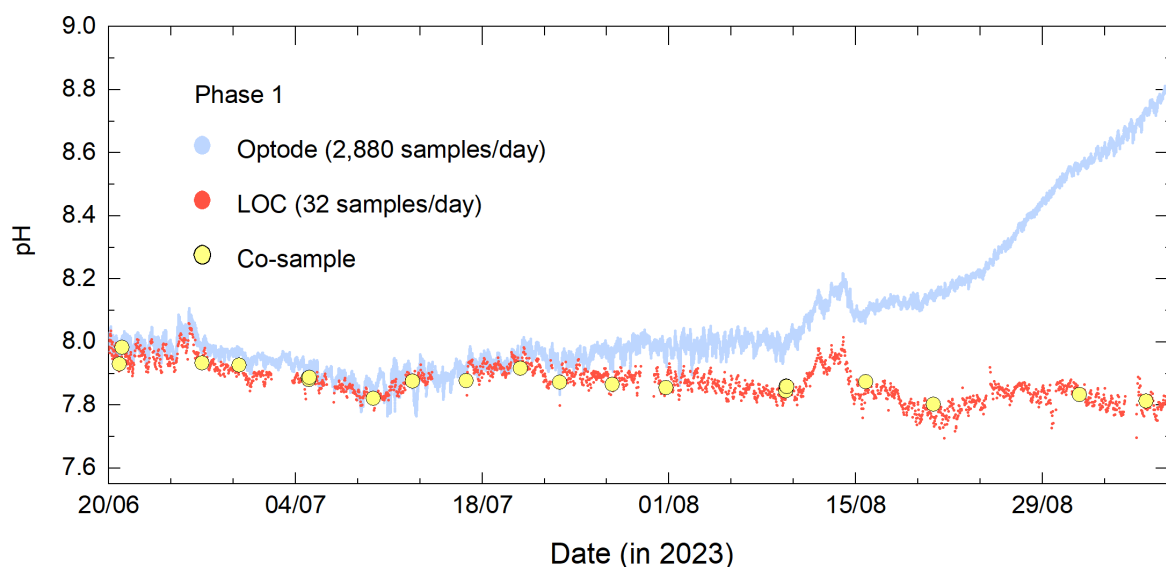


Figure 2. Overlay of optode (light blue filled circles), LOC (red filled circles), and discrete lab validated co-sample (yellow filled circles) pH data during phase 1.

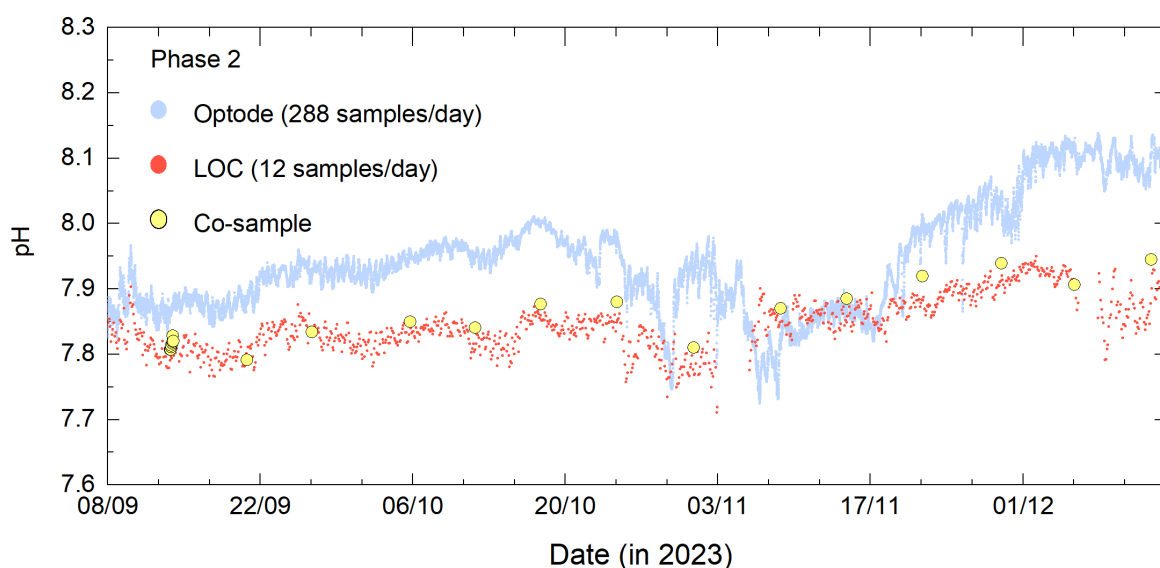
230 It should be noted that we intentionally let the optode signal drift away from the LOC reported values to test the limits of the optode device. Interestingly, the optode signal appears to maintain similar signal features to the LOC signal on relatively high-frequency timescales of hours to a few days, even with a low-frequency drift over a longer timeframe (see ESI 2). There are largely two factors at play that could cause this significant signal drift. Firstly, the high measurement frequency employed could photo-oxidise the pH sensitive coating causing rapid deterioration of the pH cap coating. These pH caps are a consumable component of the sensor device and are easily calibrated and replaced when worn. If the device can be retrieved and replenished with a freshly calibrated pH cap (as done in the present study), this can mitigate this issue, but this represents a problem when deployed in remote locations or on moving platforms. Secondly, the significant biofouling environment encountered could disrupt the long-term quality of the data. We are unable to confidently identify which of these has a greater effect but acknowledge that both factors were at play.

240 3.2 Sensor performance: phase 2

At the end of phase 1 the optode was cleaned and a new freshly calibrated pH cap was installed. The sensor was then re-deployed for phase 2 of the study. Phase 2 occurred during the end of 2023 and saw the surface water temperature decrease from ca. 20 °C to ca. 8 °C. As a result, there was less bioaccumulation on the sensors during this period. Furthermore, the measurement frequency was reduced on the sensors to sample every 5 minutes for the optode and every 2 hours for the LOC. 245 An overview of the phase 2 optode and LOC pH sensor data, alongside discrete lab validated co-samples, are provided in Figure 3. Interestingly, from the start we observed a signal offset between the optode and the LOC data. This offset is prevalent throughout the majority of phase 2. The LOC data again exhibit good agreement with the discrete lab validated co-



250 samples, with a -0.024 ± 0.011 ($n = 10$) pH units' difference. While the mean bias (pH offset) has doubled from -0.012 pH units to -0.024 pH units relative to discrete samples, this is likely a result of the significant biofouling. Again, we see indications that short-term trends in the optode signal are very similar to those of the LOC signal albeit with an offset. While the optode sensor can provide high-frequency pH data, we have demonstrated situations where optodes are not accurate, e.g., long-term drifting signal (Figure 2) and pH signals exhibiting significant offsets (Figure 3) from lab-validated samples. To improve accuracy, we propose a correction method that leverages the accurate LOC pH sensor data.



255 **Figure 3. Overlay of optode (light blue filled circles), LOC (red filled circles), and discrete lab validated co-sample (yellow filled circles) pH data during phase 2.**

3.3 Optode correction method

Linear corrections to post-deployment data have been previously utilised for oceanographic pH (Wimart-Rousseau et al., 2024; Hemming et al., 2017; Takeshita et al., 2021) and dissolved oxygen (Miller et al., 2024; Gerin et al., 2024) data. In principle, the correction method applied should take a conservative approach by aiming to remove known sources of irregularity (e.g., drifts or offsets) while preserving real variability in the sensor data. To accomplish this, our methodology leverages the accurate LOC-based pH sensor which can sample at a low frequency to conserve battery, while operating a pH optode device that may be prone to drifting/offsets, but which can sample at a much higher frequency to resolve fast pH changes. A linear rate correction was obtained by fitting a line to two LOC data points over a specified interval in time (e.g., every 1 week, every 1 day, every 1 hour) and then adding the residuals from the high frequency optode data onto this gradient. In effect, this adjusts the gradient of the optode dataset to match that from the LOC dataset while preserving the high-frequency fluctuations from the original optode data. The choice of LOC measurement interval was adjusted in this study to determine the impact of the choice of interval on the remaining error of the corrected optode data.



A brief mathematical expression of this correction process follows. A line was fitted between two LOC data points collected with the correction interval between then. This is expressed in Equation 1:

$$pH_{LOC}^{Fit}(t_i) = m_{LOC}(t_i - t_{LOC1}) + b_{LOC} \quad (1)$$

where m_{LOC} is the slope of the LOC data, t_{LOC1} is the start of the interval (based on the first LOC data point), b_{LOC} is the intercept of the LOC data fit to time, and t_i is the time of the individual sample to be corrected. It is worth noting here that this simple two-point line fit is used to mimic physically changing the LOC measurement frequency. For example, during phase 2 when a 2-hour measurement frequency was used, if the fitting correction interval was set to 24-hr, this would imply there are 12 points within that period yet only two of them are used in the line fit (i.e., the first and last data points).

A linear regression was also done to extract the best fit line from the raw optode data within the same correction interval (but in this case all the optode data was used) and is expressed in Equation 2:

$$pH_{Optode}^{Fit}(t_i) = m_{Optode}(t_i - t_{LOC1}) + b_{Optode} \quad (2)$$

where m_{Optode} is the slope of the raw optode data, t_{LOC} is the start of the interval (based on the first LOC data point), and b_{Optode} is the intercept of the optode data.

Next, the residuals (r) from the optode dataset are computed. These are the deviations of the raw optode data points from its own linear trend. The residuals are expressed in Equation 3 as:

$$r_{Optode}(t_i) = pH_{Optode}(t_i) - pH_{Optode}^{Fit}(t_i) \quad (3)$$

where $pH_{Optode}(t_i)$ is the original raw optode data point and $pH_{Optode}^{Fit}(t_i)$ is expressed as above in Equation 2.

Therefore, the corrected pH ($pH_{Corrected}$) can be mathematically defined in Equation 4, wherein the linear fit from the LOC data is added to the computed residual signal from the optode data.

$$pH_{Corrected} = pH_{LOC}^{Fit}(t_i) + r_{Optode}(t_i) \quad (4)$$

The expanded, final form of the fitting method can be mathematically expressed as below in Equation 5.

$$pH_{Corrected} = pH_{Optode}(t_i) + (m_{LOC} - m_{Optode}) \cdot (t_i - t_{LOC1}) + (b_{LOC} - b_{Optode}) \quad (5)$$

This approach maintains the low-frequency trends of the LOC while also including the high frequency features of the optode, and as a result was the chosen method used for data correction.

Figure 4 shows an example of this correction process, applied during one 24-hr correction interval. The LOC data are shown as the unfilled red circles and the two LOC data points used in the linear fit are exemplified by two filled red circles at the start/end of the window. There are 33 LOC data points within this 24-hr window but only the two filled red circles are used to generate the linear fit to the LOC data (illustrated as the solid red line). Again, the LOC linear fit sets the gradient to which the optode data will be corrected. Next, the light blue circles are the raw optode data, and for reference, there are 2,898 optode data points within this same 24-hr window. The solid black line is the linear fit to the entire set of this optode data. Finally, the corrected optode data, using Equation 5, are shown as the dark blue circles. In this instance, the offset that the entire raw optode data exhibited was corrected. Three discrete co-sample data points are also overlaid as filled yellow circles. We can see that the corrected optode data are in much better agreement with these discrete samples. Therefore, a 24-



hr correction interval (i.e., a LOC data point once per day) was sufficient to improve the optode sensor data to be in agreement with LOC pH data and discrete co-samples. Overall, this shows the power of simply using a single LOC data point once per day to mitigate any signal drift/offset in the optode dataset.

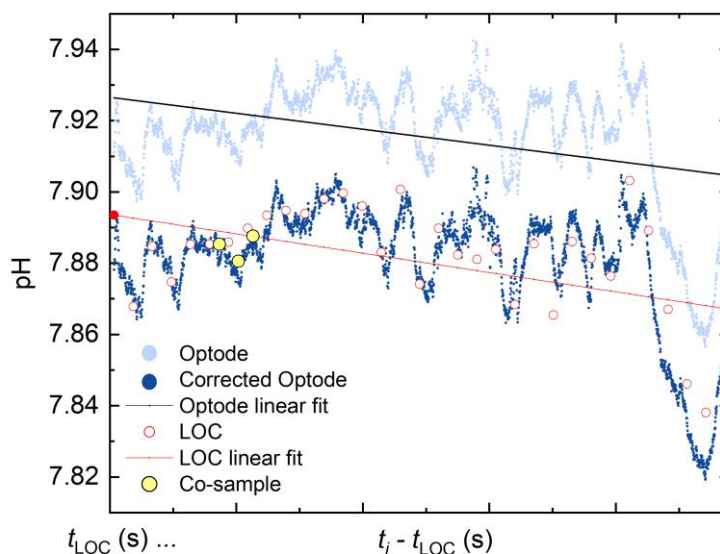


Figure 4. Exemplar data from early July 2023 showing a 24-hr period used to illustrate the correction method applied to the optode dataset. Overlaid are the raw optode data (light blue circles), corrected optode data (dark blue circles), linear fit to raw optode data (solid black line), LOC data (unfilled red circles), linear fit to LOC data (solid red line), and discrete co-samples (filled yellow circles). Note: the two filled red circles are the start and end LOC data points used in the LOC linear fit.

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While the example in Figure 4 uses a 24-hour correction interval, we repeat the analysis for several different correction intervals to evaluate the effect of the interval on the agreement between corrected optode data and lab-validated samples. The data in Table 3 report the accuracy of the corrected optode pH sensor, defined here as a mean error ($\bar{x} \Delta\text{pH}$) in addition to the standard deviation of the error ($1\sigma \Delta\text{pH}$), relative to discrete co-sample data. As can be seen the accuracy improved with more frequent correction intervals (i.e., higher LOC measurement frequencies). A correction every four weeks was sufficient to dramatically improve the accuracy of the entire set of uncorrected raw data from $+0.111 (\pm 0.172; n = 44)$ pH units to $+0.021 (\pm 0.034; n = 44)$ pH units, which is within the reported accuracy for the SeapHOx pH sensor. A correction every 1-week further improved the accuracy to $-0.007 (\pm 0.024; n = 44)$ pH units, but improvements in accuracy plateaued at higher LOC measurement frequencies (e.g., 24-hr produced an accuracy of $-0.011 (\pm 0.017; n = 44)$ pH units. Effectively, the accuracy of the optode sensor approaches the accuracy of the LOC sensor itself as the correction interval approaches the maximum sampling rate of the LOC pH sensor (i.e., in this instance every LOC data point is used to correct optode data; this is reported in Table 3 as All Data).

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Table 3. Accuracies reported as the mean sensor error ($\bar{x} \Delta\text{pH}$) and standard deviation of the error ($1\sigma \Delta\text{pH}$), in addition to the number of samples (n) at various correction intervals. Accuracies are reported with respect to discrete lab-validated samples.

Correction interval (time)	$\bar{x} \Delta\text{pH}$ (pH units)	$1\sigma \Delta\text{pH}$ ($\pm\text{pH}$ units)	n
Uncorrected raw data	+0.111	0.172	44
4 weeks	+0.021	0.034	44
2 weeks	+0.016	0.032	44
1 weeks	-0.007	0.024	44
3 days	-0.011	0.024	44
2 days	-0.009	0.023	44
1 day	-0.011	0.017	44
12 hours	-0.016	0.023	44
6 hours	-0.018	0.019	44
2 hours	-0.018	0.016	44
0 hours (All data)	-0.018	0.017	44

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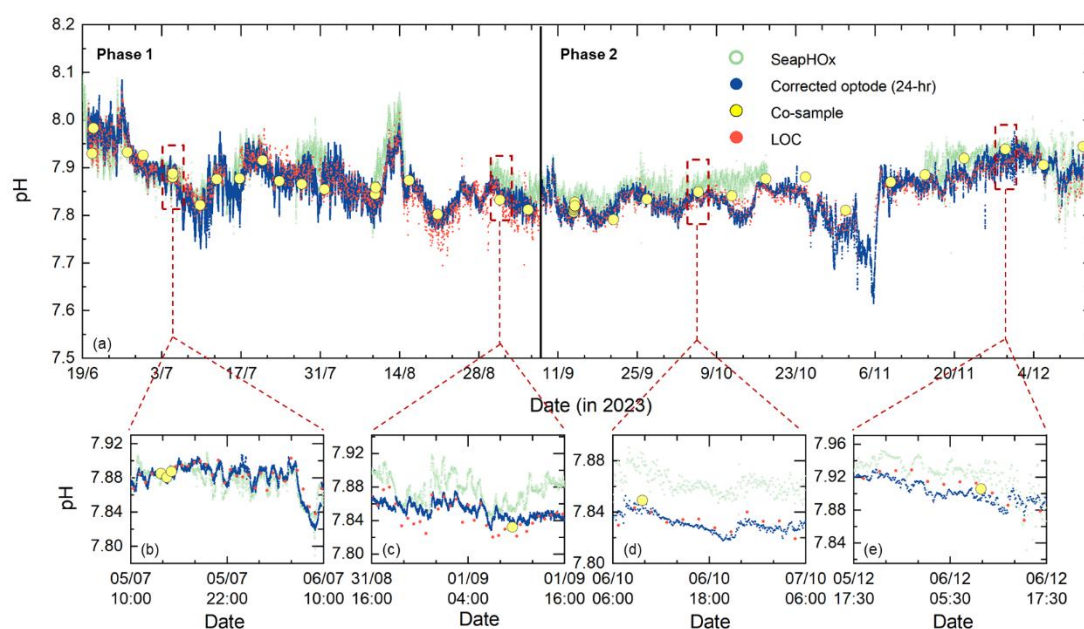
It is worth noting here that there is a local minimum in the calculated accuracy (i.e., in $\bar{x} \Delta\text{pH}$ at the 2-day point and in $1\sigma \Delta\text{pH}$ at the 1-day point) of the corrected optode data around the 1- and 2-day correction intervals. There are two possible explanations for this behaviour. Firstly, the starting point for the correction is always done from the very first LOC data point, and subsequently the fitting windows will all span according to that single starting point. To account for this, we have
330 examined the dataset using a range of different starting points and determined it has a relatively small impact on the overall result (see ESI 3). Secondly, the two-point fitting method applied to the LOC data is subject to errors in the form of outliers with respect to the line fit. For example, (referring to Figure 4) simply moving the LOC fit from the last data point (33rd data point) to the previous data point (32nd data point), would produce a significantly different gradient (note: this is not the case with the raw optode data wherein the entire dataset within the fitting window is taken into account with its linear fit). The
335 latter point is likely to have a large impact on the resulting output, and therefore the occurrence of a small local minimum of accuracy is likely an artefact of the fitting process itself.

3.4 Validation of corrected optode data

With the correction method demonstrated, it can now be applied to the optode datasets from phases 1 and 2. Therefore, the full 6-month corrected optode dataset with a 24-hr correction interval (i.e., a LOC data point collected once per day) is
340 provided in Figure 5 alongside an independent pH sensor (SeapHOx; light green unfilled circles) and the LOC pH sensor (red filled circles). The SeapHOx pH sensor was also deployed measuring at a high frequency in phase 1 (i.e., 47 sec) and lowered to match that of the optode in phase 2 (i.e., 5 min). There are four large gaps within the SeapHOx dataset. Three gaps in data from 21/07/2023 to 27/07/2023, 02/08/2023 to 09/08/2023, and 15/08/2023 to 30/08/2023 were due to stagnant



seawater buildup within the sensor, a likely result of biofouling clogging the flow path, which has been reported previously
 345 (Bresnahan et al., 2021). This caused the resulting pH data to be unusable and it has been removed from the series. The
 fourth gap from 18/10/2023 to 15/11/2023 was due to a spent internal battery within the SeapHOx sensor. Nonetheless, as
 can be seen, globally the corrected optode data are now in much better agreement with the discrete co-samples and the
 independent seawater pH sensor (SeapHOx) deployed alongside (discussed in further detail below).



350 **Figure 5. Top panel (a) shows the entire 6-month optode series with 24-hr corrected (dark blue filled circles) data with both SeapHOx (sage green unfilled circles) and LOC pH data (red filled circles) overlaid for comparison. Lab validated co-samples are provided for reference (yellow filled circles). Bottom panels (b) through (e) show four zoomed in snapshots within the larger overlaid dataset.**

The data plots in the bottom panel of Figure 5b-e show snapshots of a few exemplar data comparisons between the corrected
 355 optode, LOC and SeapHOx sensor data, in addition to lab validated co-samples. At the start of the deployment in late-June
 (Figure 5b) we find the corrected optode data and SeapHOx data agree well with each other (i.e., for this period we calculate
 a pH difference of $+0.003 \pm 0.010$; 2,880 data points in common), are both resolving fast pH fluctuations, and show good
 agreement with the three overlaid discrete co-sample data points (SeapHOx -0.003 pH unit difference and optode -0.005 pH
 unit difference). Around early-September (Figure 5c) the optode data are reporting pH values lower than the SeapHOx data
 360 (i.e., for this period we calculate a pH difference of -0.024 ± 0.014 ; 2,880 data points in common). Nonetheless, both sensors
 show good agreement with the discrete co-sample data point (SeapHOx +0.020 pH unit difference and optode +0.007 pH
 unit difference) despite the significant fouling encountered across the sensors and the fact that at this point the raw optode
 sensor data are severely drifting from the discrete lab-validated samples (refer to Figure 2). This is a significant
 demonstration of the linear rate correction methods' ability to handle challenging datasets. In early-October (Figure 5d) we
 365 find the divergence between the two datasets is still present (i.e., for this period we calculate a pH difference of $-0.028 \pm$



0.006; 287 data points in common), but this is reflective of the LOC data that was used to correct the optode data, which also appeared at lower pH values relative to the SeapHOx dataset. A new optode pH cap was installed a month prior to this point, yet it quickly drifted to a relatively constant offset (refer to Figure 3), but the correction does a good job of bringing the data to be more in line with the independent SeapHOx data. The sensors exhibit a difference from the discrete co-sample data point of +0.030 pH units (SeapHOx) and -0.006 pH units (optode). As can be seen the spread of pH values is narrower for the optode dataset, which is potentially a result of having a longer response time <60 seconds (to get 90% of the signal) due to it being an optical measurement (Wirth et al., 2024; Fritzsche et al., 2018) compared to the SeapHOx response time of ca. 16 seconds via an electrochemical measurement (Bagshaw et al., 2021). This form of signal smoothing/averaging from optode-based measurements has been noted previously (Fritzsche et al., 2018). As previously mentioned, the manufacturer reported resolution of the optode is 0.003 pH units whereas the SeapHOx has a reported resolution of 0.004 pH units. Lastly, in early-December (Figure 5e) we see that the datasets are tracking each other well (i.e., for this period we calculate a pH difference of -0.012 ± 0.012 ; 287 data points in common) and both are in agreement with the lab validated co-sample data point overlaid (SeapHOx +0.020 pH unit difference and optode +0.002 pH unit difference). Overall, we have now demonstrated that an infrequent, linear correction is sufficient to handle high frequency optode pH data even when experiencing significant signal drifts/offsets.

To exhibit this further, Figure 6 shows the difference (error) between the values of the three pH sensors and the seawater pH obtained from discrete lab validated co-samples collected throughout the study. The measurement frequencies for the optode and SeapHOx pH sensors were sufficiently rapid enough that there was always a measurement taken within ≤ 1 minute of the discrete co-sample collection time. However, due to the lower measurement frequency of the LOC pH sensor, data points collected within ≤ 30 minutes were used when comparing LOC data relative to the discrete co-sample data.

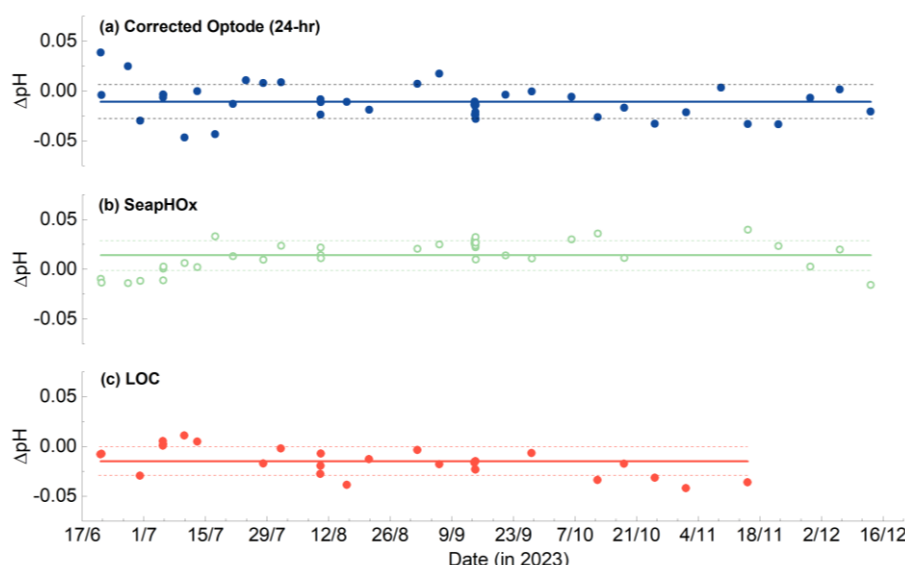


Figure 6. Performance of the three main seawater pH sensor technologies examined as a function of time throughout the deployment. Data are differences (error) relative to discrete lab validated co-samples. The accuracies are displayed as solid lines (mean error) and dashed lines (standard deviation of the error).

390 The corrected optode data in Figure 6a collectively suggest a field-obtained accuracy of $-0.011 (\pm 0.017; n = 44)$ pH units, where the solid line represents the mean error and the dashed lines represent the standard deviation of the error. This accuracy is comparable to previous reports in the field: $+0.027 (\pm 0.017)$ pH units (Wirth et al., 2024), $-0.027 (\pm 0.059)$ pH units (Fritzsche et al., 2018), and others report absolute deviations in the field ranging from 0.019 to 0.051 pH units (Staudinger et al., 2018). Furthermore, when the correction is done with our second LOC dataset (see ESI 5) the results are

395 similar e.g., an accuracy of -0.021 ± 0.025 ($n = 44$) pH units is obtained. The SeapHOx data (Figure 6b) appear at slightly higher pH values relative to the validation samples, and we calculate an accuracy of $+0.014 (\pm 0.015; n = 38)$ pH units, which is well within the manufacturer reported limits (± 0.050 pH units). The accuracy of the SeapHOx pH sensor from our trial is comparable to previous reports in the field utilising ISFET-based pH sensors: <0.025 pH units (Miller et al., 2018), $0.000 (\pm 0.019; n = 383)$ pH units (Johnson et al., 2016), $+0.007 (\pm 0.028; n = 26)$ pH units (Yin et al., 2021), and others report

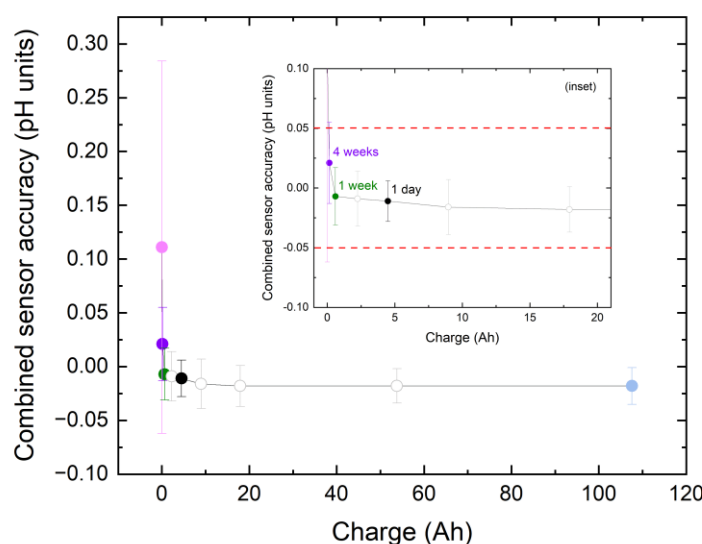
400 standard deviations between 0.011 and 0.036 pH units (Gonski et al., 2018). The LOC data in Figure 6c appear at slightly lower pH values relative to the validation sample pH, and we estimate an accuracy of $-0.015 (\pm 0.014; n = 28)$ pH units, which is comparable $+0.003 (\pm 0.022; n = 47)$ with previous work at the same test site (Yin et al., 2021). An in-depth comparison of the LOC and SeapHOx pH sensor performance is provided in ESI 4. A detailed analysis of the performance of the second optode pH sensor is provided in ESI 5.

405 3.5 Deployment considerations

As previously mentioned, the LOC + optode dual system can provide rapid and accurate pH data by leveraging low-frequency LOC data to correct drifting/offset high-frequency optode data. To help understand this, a plot of combined sensor accuracy versus battery charge for a 6-month deployment is provided in Figure 7. Each LOC measurement requires ca. 0.15



A (at 12 V) and takes approximately 10 minutes to complete. Therefore, each measurement uses 25 mAh. As can be seen, a
 410 correction interval every four weeks (i.e., filled purple circle) substantially improves the accuracy of the raw (uncorrected –
 filled pink circle) optode pH sensor data, which is approaching the manufacturer reported accuracy of a SeapHOx-based pH
 sensor (the dashed red lines indicate ± 0.050 pH units) and this accuracy requires only a small amount of power (ca. 150
 mAh for 6 months of measurements). The accuracy can be further improved by taking a LOC measurement once per week
 (e.g., filled green circle) and requires ca. 600 mAh for 6 months of operation. The improvements in accuracy largely plateau
 415 after this correction interval. Beyond this, more frequent measurements do not give significant enhancements (relative to
 discrete samples) in comparison to the charge required to achieve said accuracy. For example, the filled black circle (Figure
 7) represents 1-day correction interval and requires ca. 4,500 mAh whereas the filled blue circle represents a correction every
 1-hr and requires 107,600 mAh for 6 months. Overall, we find that a single LOC measurement every 1-7 days is sufficient to
 provide accurate and rapid pH data with this combined sensor package. Operating the LOC pH sensor at these low
 420 measurement frequencies is advantageous as it reduces reagent consumption, waste generation and power consumption,
 which taken together would also lower the sensor service intervals. This will, however, still be dictated by the specific
 deployment conditions and requirements.



425 **Figure 7. Plot of combined LOC-optode package accuracy as a function of charge required (by the LOC) to achieve the corrected accuracy. The colour- filled circle symbols are highlighted to illustrate five distinct points (i.e., uncorrected, 1 month, 1 week, 1 day, and 1 hour correction intervals). An inset provides a clearer zoomed-in region and the dashed red lines indicate ± 0.050 pH units for visual purposes.**

The above demonstrates that the accuracy of the optode sensor (<0.02 pH units) can be markedly improved to be as accurate
 as SeapHOx-based pH sensor (<0.02 pH units) by means of a simple and infrequent *in-situ* correction. Using the combined
 430 pH sensor package showcased here, the operator can select the LOC sensor measurement frequency needed to correct optode



data for a particular application. If more charge is available, then a more frequent correction interval can be used or equally this can be reduced to conserve charge with a known impact on accuracy. A commercial deep-sea rated battery the physical size of the LOC sensor itself can provide 50 Ah of charge (accessed 29/08/2025: <https://subtech.com/ocean-power/basic-batteries/>), which is sufficient to power the LOC pH sensor for a 6-month deployment measuring every 3 hours.

435 Furthermore, the small form-factor of the optode pH sensor is advantageous for incorporation onto a range of autonomous vehicles. In fact, the optode pH sensor is small enough to fit inside the standard reagent housing of the LOC pH sensor itself. For a long-term (>6 months) deployment, the low measurement frequencies from the LOC pH sensor needed to produce sufficiently accurate corrected optode data, the reagent volumes would be small (e.g., 24 mL total waste volume if sampling once every 4 weeks over a 1-year deployment) thus permitting space to incorporate the optode within the standard reagent

440 housing. Future work will look at developing an integration protocol for this combined sensor package and establish communication procedures that could allow this data correction to be done *in-situ*.

4 Conclusions

Overall, this work has demonstrated a combined pH sensor system capable of providing accurate (<0.02 pH units), rapid (<1 min/sample), and long-term (6-month) seawater pH data. This is accomplished by leveraging accurate pH data obtained from a LOC pH sensor measuring at low frequencies to correct signal drift/offset from an optode-based pH sensor measuring at a very high frequency. During a six-month shallow water deployment in a high biofouling environment, we observed significant signal drift in the optode pH sensor, whereas the LOC and SeapHOx sensors returned stable, accurate (<0.02 pH units) data relative to discrete co-samples. To improve the optode data, a linear rate correction method was demonstrated,

450 and we find that even if the LOC sensor had sampled with measurement frequencies of several days to several weeks, this is sufficient to significantly improve the performance of the high-frequency optode data (e.g., a LOC data point once every week gave an accuracy of -0.007 (± 0.024 ; $n = 44$) pH units for the corrected optode dataset). More frequent corrections improved this accuracy but only slightly (i.e., the accuracy approached that of the LOC sensor used to correct the optode data). For deployment on long-term platforms such as moorings, an optimum balance can be identified between accuracy

455 and battery capacity for the intended deployment.

Supplementary material. Electronic supplementary information is provided that shows the chemical and physical drivers (tidal height, temperature, salinity, and dissolved oxygen data) in ESI 1, zoom-in on optode drift during phase 1 in ESI 2, effect of linear fit starting point on accuracy in ESI 3, an in-depth pH sensor comparison in ESI 4, analysis of optode-2

460 performance in ESI 5, and SI References in ESI 6.

Author contributions. AL: Conceptualisation, Methodology, Software, Validation, Formal Analysis, Investigation, Data Curation, Writing – Original Draft, Writing – Review & Editing, Visualisation, Supervision, Project Administration. DK: Conceptualisation, Methodology, Software, Validation, Formal Analysis, Investigation, Writing – Original Draft, Writing –



465 Review & Editing, Visualisation. MA: Investigation, Resources, Writing – Review & Editing. SL: Conceptualisation,
Resources, Writing – Review & Editing, Supervision. AS: Conceptualisation, Resources, Writing – Review & Editing,
Supervision, Project Administration, Funding Acquisition.

470 *Competing interests.* The authors declare that the research was conducted in the absence of any commercial or financial
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