A user's guide for selected autonomous biogeochemical sensors

An outcome from the 1st International IOCCP Sensors Summer Course – Instrumenting Our Oceans for Better Observations

June 22 – July 1, 2015, Kristineberg, Sweden

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1. Introduction and Course Overview

Over the last decade, ocean observing technology has risen to the challenge of scientist by providing them with cost-effective tools that can take measurements of essential biogeochemical variables autonomously. Yet, despite these options becoming more readily available, there is still a gap between the technology and the end-user (investigators and technicians that deploy these technologies) due to a collective lack of training, in-depth knowledge, and community coordination. There is also a disconnect between data gathering by autonomous sensors and data quality, which is a major obstacle, as these sensors are already being deployed on autonomous platforms and in conjunction with ship-based sampling to broaden data coverage in space and time.

The underused state of the current biogeochemical monitoring has in part motivated the development of a "framework" for ocean observations (*Framework for Ocean Observing (FOO 2012)*), in the hopes that ocean observing systems will be able to provide more standardized and comprehensive information to address scientific and societal needs. In June 2015, the International Ocean Carbon Coordination Project, with co-sponsorship from the US Ocean Carbon and Biogeochemistry (OCB) Program, Scientific Committee on Oceanic Research (SCOR), the Royal Swedish Academy of Sciences (KVA), Global Ocean Observing System (GOOS), National Science Foundation (NSF) and the Gordon and Betty Moore Foundation, brought together 40 leading experts in the use of autonomous sensor technology for biogeochemical ocean observations. Participants of this 10-day workshop "International IOCCP Sensors Summer Course: Instrumenting Our Oceans for Better Observations" on best practices for selected biogeochemical sensors (oxygen, pH, pCO_2, nitrate) held between 21 June – 1 July, 2015 in Kristineberg, Sweden, identified an urgent need for an easy-to-use, entry-level guide addressing the use and application of selected autonomous biogeochemical sensors. Such a guide would facilitate a universally accepted set of autonomous sensor guidelines to enhance global observing capacity, especially in the face of contemporary coastal ocean challenges such as acidification (pH and pCO_2), nutrient loading (e.g., nitrogen), and deoxygenation.

This course addressed community recommendations that emerged from recent workshops (e.g., *Observing Biogeochemical Cycles at Global Scales with Profiling Floats and Gliders*) by expanding and educating the user-base for biogeochemical sensors as part of an integrated global ocean observing network. Standardized approaches to data collection and processing will enhance global data intercomparability, a fundamental requirement to enable true global ocean monitoring and detection of change. The course targeted commercial biogeochemical sensors that are readily available to the oceanographic community for measurement of oxygen, nitrate, bio-optics, and the inorganic carbon system. The goal of the course was to develop methodological protocols on sensor usage and data reporting. While this course targeted mature technologies, the discussion of emerging technologies to tackle measurements of other important biogeochemical variables was also encouraged and promoted throughout the course.

This user's guide provides easy-to-follow steps on the usage (including preparation, deployment, recovery and basic data processing) of autonomous biogeochemical sensors. It includes:

- Essential instrument know-how (instrument communication, sensor data quality control (QC), biofouling prevention, etc.)
- User recommendations
- Site-specific recommendations (preference of one type/model of instrument depending on location)
- Troubleshooting guidelines for commonly encountered problems
- Data management, quality and reporting.

Sensors for each of four parameters are addressed in separate chapters. A group of the course lecturers and participants who contributed to the document for each parameter is listed at the beginning of each section. General conclusions and recommendations are placed at the end of the document.

This is intended to be a living document, added and perfected through follow-on courses that will employ this guide and test its usefulness.

2. Biogeochemical Parameters

2.1. Oxygen

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Loucaides, S., A. Fassbender, C. L'Esperance, S. Gedela, and C. Neill, 2017: Biogeochemical Parameters: Oxygen. In: *A user's guide for selected autonomous biogeochemical sensors. An outcome from the 1st IOCCP International Sensors Summer Course* [Lorenzoni, L., M. Telszewski, H. Benway, A. P. Palacz (eds.)]. IOCCP Report No. 2/2017, pp. 9-21.

2.1.1. Background

Dissolved Oxygen (DO) is the amount of oxygen gas dissolved in water. In the ocean, sufficient levels of DO are necessary to sustain marine life. Oxygen enters the surface of the ocean through air-sea interaction with the atmosphere (i.e., namely diffusion or bubble injection) or is produced in situ by photosynthetic organisms. The DO content of water is controlled by temperature and salinity and the rates of oxygen accumulation and consumption. Marine animals consume oxygen during respiration and bacteria use DO during organic matter decomposition. In stratified waters, decomposition of organic matter below the surface mixed layer can lead to hypoxic or even anoxic conditions at depth. In the Earth's geological record, episodic widespread anoxic ocean conditions are now recognized and linked to mass marine extinction events. A reduction in DO has been observed during the last few decades throughout the ocean, suggesting a general decrease in the ocean's DO inventory. This is attributed to a number of factors, including warming (warm water can hold less oxygen than cold water), increased stratification (less mixing with oxygenated surface waters), and increased primary production in response to increased nutrient loading from land, which reduces oxygen at depth as organic matter is decomposed.

2.1.2. Measurement principles for oxygen optodes

Although there is more than one measurement type for DO, in this guide we limit ourselves to describing measurement principles for oxygen optodes. The oxygen optode is based on a principle called dynamic luminescence quenching. This phenomenon refers to the ability of certain molecules to influence the fluorescence of other molecules. Fluorescence is the ability of a molecule to absorb light of certain energy and later emit light with lower energy (longer wave length). Such a molecule, called a luminophore will, after absorbing a photon with high enough energy, enter an excited state. After some time, the luminophore will emit a photon of lower energy and return to its initial state. Some luminophores might also return to the initial state when colliding with certain other molecules. The luminophore will then transfer parts of its excitation energy to the colliding molecule, with the result that fewer photons (giving a shorter life time) are emitted from the luminophore. This effect is called dynamic luminescence quenching, and in the Oxygen Optode, the colliding molecules are oxygen (O_2). The luminophore used in the Oxygen Optode is a special molecule called platinum porphyrine. These luminophores are embedded in a polymer layer called the indicator layer (coated with a thin film of polyester for support).

To avoid potential influence from fluorescent material surrounding the sensor or direct incoming sunlight when measuring in the photic zone, the normal monitoring foil is also equipped with a black gas-permeable coating. The coating provides optical isolation between the indicator layer and the surroundings. For faster response time, foils also exist without the optical isolation layer (i.e., transparent foils) through which the blinking blue-green excitation light and red emission light can be seen (see next paragraph).

FIGURE 2.1 below describes the process of dynamic luminescence quenching used by Oxygen Optode.

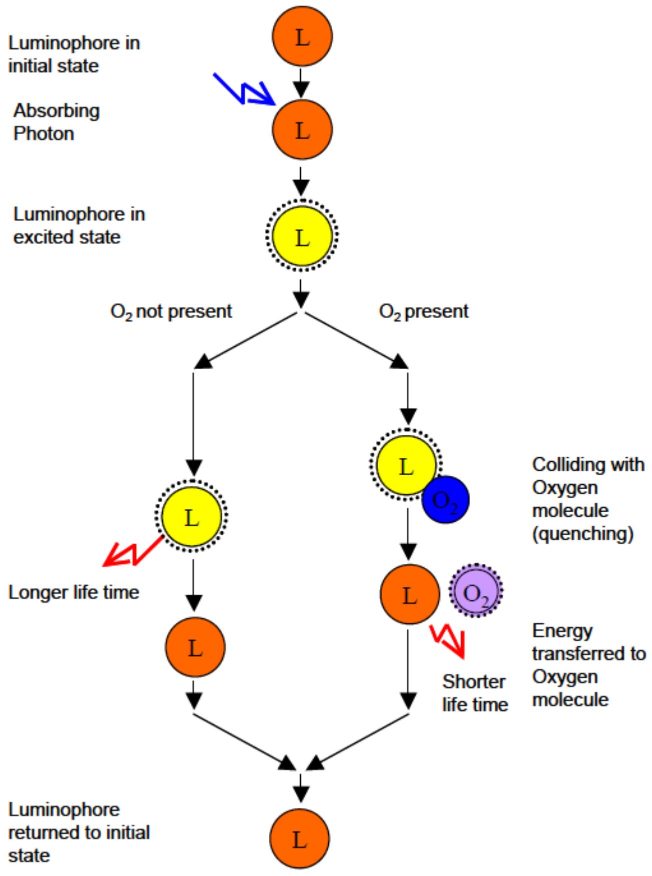

Figure 2.1. Dynamic fluorescence quenching

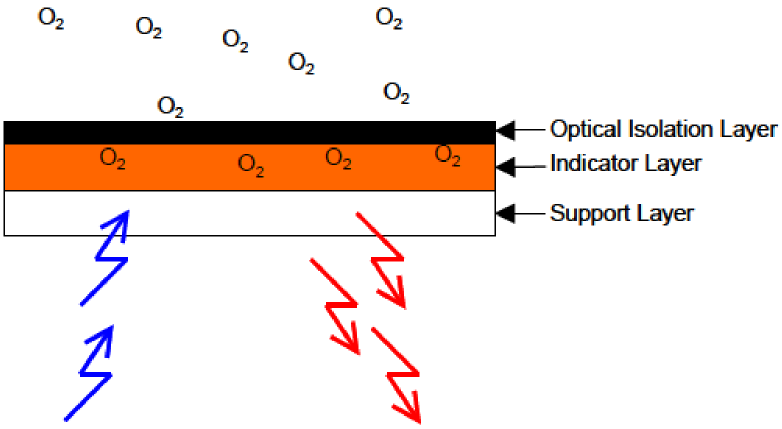

Figure 2.2. The oxygen optode foil.

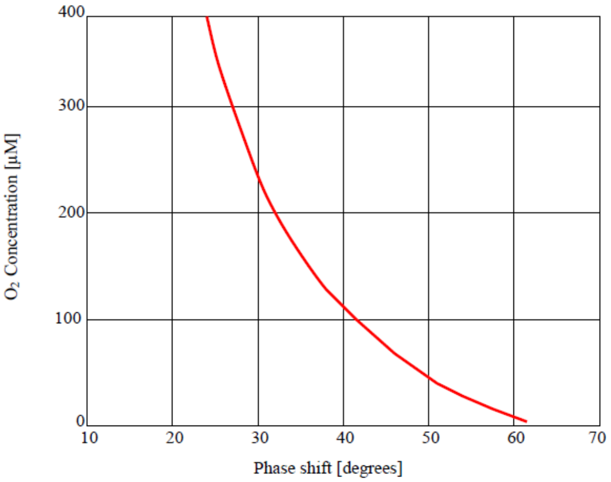

Figure 2.3. Typical phase O_2 response.

Due to its fluorescent behaviour, the sensing foil will return a red light when it is excited with a blue-green light (505 nm). If there is O_2 present, this fluorescent effect will be quenched. The amount of returned light will therefore depend on the O_2 concentration in the foil. However, the intensity of the returned light is not the optimal property to measure since it depends on many other factors, including optical coupling or bleaching of the foil. Since the returned light is delayed with respect to the excitation light, the presence of O_2 will also influence the delay. This property is called luminescence decay time (or lifetime) and it will decrease with increasing O_2 concentrations. The relationship between the O_2 concentration and the luminescence decay time can be described by the Stern-Volmer equation:

$$[O_2] = \frac{1}{K_{SV}} \left\{ \frac{\tau_0}{\tau} - 1 \right\}$$

in which:

τ = decay time
$\tau 0$ = decay time in the absence of O_2
KSV = Stern-Volmer constant (the quenching efficiency)

In order to measure this luminescence decay time, the sensing foil is excited with a blue-green light modulated at 5 kHz. The decay time is a function of the phase of the received signal. In the Oxygen Optode, the relationship between the phase and the O_2 concentration is used directly, without calculating the decay time.

An illustration of the optical design is given in FIGURE 2.4. The sensing foil is mounted outside the optical window and is exposed to the surrounding water. The foil is held in place by a screw fixed plastic plate. Two light emitting diodes (LEDs) and one photodiode are placed on the inside of the window. A blue-green LED is used for excitation of the foil. The photodiode is used for sensing the fluorescent light. Even though the sensing foil is highly fluorescent, parts of the transmitted light will be directly reflected. The photo diode is equipped with a colour filter that stops light with short wavelengths to minimize the influence of the reflected light. Further, the blue-green LED is equipped with a filter that stops light with long wavelengths. In addition, a red 'reference' LED is included to compensate for potential drift in the electronics of the transmitter and receiver circuit.

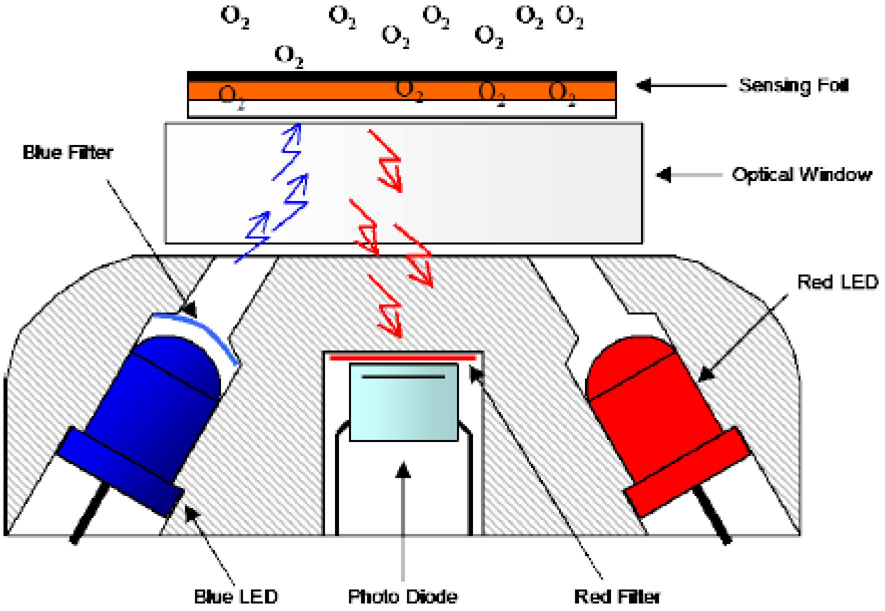

Figure 2.4. Optode optical design

2.1.3. Available Sensors

Oxygen optodes

Commercially available optodes are available from at least three sensor manufacturers including Aanderaa (*http://www.aanderaa.com/*), Sea-Bird Scientific (*http://www.seabird.com/*) and Kongsberg Maritime (*https://www.km.kongsberg.com/*; former CONTROS). Aanderaa optodes are available in deep and shallow versions with the deep version capable of full ocean depth. Fast sensing versions of the optodes are equipped with a sensitive foil recommended for fast moving platforms and profiling applications. This foil, however, is more sensitive to photo-bleaching and more prone to long term drift. Kongsberg Maritime has one commercially available DO optode; the HydroFlash uses a different sensing foil than the Aanderaa optode allowing for faster response (<3 s). The HydroFlash also has onboard data logging capabilities allowing for use as a standalone sensor. Sea-Bird Scientific has an optode based DO sensor available, the SBE 63. It provides faster measurements due to its pumped configuration. Although the SBE 63 can be used as a standalone sensor (with RS232 sensor mount) they are primarily integrated with SBE conductivity-temperature-depth (CTD) packages.

Aanderaa optodes

http://www.aanderaa.com/productsdetail.php?Oxygen-Optodes-2

Figure 2.5. Aanderaa optode 4835.

Optodes made by Aanderaa are some of the most widely used DO sensors and have been implemented on Argo floats, gliders and moorings. For the standard Aanderaa optode versions, a black optical isolation coating protects the complex from sunlight and fluorescent particles in the water. This sensing foil is attached to a sapphire window, providing optical access for the measurement system from inside a watertight housing. The sensing foil is excited by modulated blue light; the sensor measures the phase of the returned red light. For improved stability, the optode also performs a reference phase reading by use of a red LED that does not produce fluorescence in the foil. The sensor has an incorporated temperature thermistor, which enables linearization and temperature compensation of the phase measurements to provide the absolute DO concentration. Aanderaa optodes are best suited for a measurement range of 0-500 µM, with a resolution of <1 µM and an accuracy of <8 µM. Their calibration remains stable for several years, ideal for long-term autonomous deployments. Due to their small size and rapid response time, Aanderaa optodes have been integrated on a variety of mobile and stationary platforms and have been used for a wide range of applications. These sensors are equipped with serial output, which can be converted from digital to analog for data loggers that require analog input or do not have auxiliary serial inputs.

CONTROS HydroFlash O_2

https://www.km.kongsberg.com/ks/web/nokbg0240.nsf/AllWeb/2052B2A42B415092C1257EDD00269390?OpenDocument

Figure 2.6. CONTROS HydroFlash O_2.

The CONTROS HydroFlash O_2 (FIGURE 2.6) uses the same sensing principle as the Aanderaa optode, but uses a sensing foil of different chemistry. This allows for faster response times, but due to the limited number of deployment data available, it is not known if the measurement quality is compromised. One of the advantages of this sensor is that it is a stand-alone sensor that contains its own memory and can be deployed with a dedicated battery pack.

SBE 63

http://www.seabird.com/sbe63-optical-dissolved-oxygen-sensor

Figure 2.7. SBE 63 optode

The SBE 63 (FIGURE 2.7) is an individually calibrated, high-accuracy, optical oxygen sensor. The SBE 63 is designed for use in a CTD's pumped flow path, providing optimal correlation with CTD measurements. The elapsed time between the CTD and associated oxygen measurement is easily quantified and corrected for in post-processing. The plumbing includes black tubing that blocks light, reducing in situ algal growth. The pumped configuration of the SBE 63 offers relatively fast response and improved antifouling protection, especially when the antifouling chemical tributyltin (TBT) is used in-line.

2.1.4. Sensor deployment

Aanderaa optodes (FIGURE 2.5) are highly versatile in terms of deployment applications and platforms. Optodes, with a response time of a few (5-8 s) seconds, can be deployed on fast moving platforms, including gliders, profiling CTDs, floats, etc. They can easily be integrated on generic data loggers and instruments or they can be deployed on dedicated loggers/control units provided by the manufacturers. The Seaguard system made by Aanderaa is such a device, on which a number of Aanderaa sensors, including oxygen, pH, and $p\mathrm{CO_2}$ optodes, conductivity sensors, etc. can be integrated.

The foils used by DO optodes require a short (1-2 day) conditioning period to saturate with water. This is an important consideration, particularly if discrete samples are to be collected during deployment. In this scenario, the optode should be soaked in water prior to deployment to ensure high-quality optode performance at the time of taking the discrete samples. In addition to requiring conditioning, these foils are light-sensitive (even the ones with an opaque layer of black silicone); therefore, they should be stored in the dark, and many suggest a wet environment. Keeping the optodes cold (e.g., refrigerated) can slow down the storage drift.

Attention must be paid to setting the input voltage of Aanderaa optodes. When sampling the sensors at high frequencies (1-10 s intervals), there appears to be some self-heating of the sensor. The sensor has linear power regulators, which means that if you supply it with higher voltage (e.g. 8-14V), it will still consume the same amount of current as at 5V. The additional energy at higher voltages will be lost via self-heating. Therefore, it is better to supply the sensor with 5V in high-sampling frequency applications. Laboratory testing at 5V has revealed that self-heating of the sensor can introduce a 1-µM error (artificially low readings) when sampled at a 1-second sample-interval. This error drops to 0.2 µM for a 5-second interval, which is equal to the error of the internal temperature sensor when sampled at a 5-second interval.

Foils should always be covered when exposed to sunlight to avoid foil bleaching. For surface deployments when the foils are exposed to sunlight, fast optodes are not recommended. Salinity should also be set to zero (where applicable) to simplify post-processing and the conversion to in situ salinity values. If the optode is calibrated using an auxiliary temperature sensor, then the auxiliary temperature sensor should also be used in the post-deployment conversions.

2.1.5. Sensor calibration and validation

Oxygen optode performance should be evaluated using a high-quality, Winkler-referenced, multipoint calibration before and after each deployment. Aanderaa optode drift is approximately linear and proportional to the O_2 concentration, generally characterized by a gain term and no offset. Therefore, the pre- and post-deployment calibrations can be done with as little as a single point. Seabird optodes use the same sensing compound as Aanderaa and also appear to show drift that is linear with concentration. We are uncertain if this method is appropriate for the CONTROS sensors, which use a different sensing compound.

Multi-point calibrations are done commercially by the sensor manufacturers and several other laboratories. The sensors are calibrated over a matrix of temperatures and oxygen saturations, and the data are fit to various forms of the Stern Volmer equation. Seabird and Aanderaa sensors fit the oxygen concentration and CONTROS sensors fit the partial pressure. The function used by Sea-Bird has a phase-squared term that is not used by the others.

$$\text{Sea-Bird:}\qquad [O_2]\ (\text{ml l}^{-1}) = \frac{\left\{\frac{(a0+a1T+a2V^2)}{(b0+b1V)}-1\right\}}{(c0+c1T+c2T^2)}$$

$$\text{CONTROS:}\qquad [O_2]\ (\mu\text{mol l}^{-1}) = \frac{\left\{\frac{(a0+a1T)}{(b0+b1V)}-1\right\}}{(c0+c1T+c2T^2)}$$

$$\text{Aanderaa:}\qquad [O_2]\ (\mu\text{mol l}^{-1}) = \frac{\left\{\frac{(a0+a1T)}{(b0+b1V)}-1\right\}}{(c0+c1T+c2T^2)}$$

In the case of Aanderaa optodes, the multi-point calibration must be purchased as an additional option; otherwise, the calibrations are performed via polynomial fits to calibration data obtained from batches of sensor foil containing mass flow controllers as a reference. Using these batch calibrations will result in less accurate data, regardless of the quality of any subsequent one or multi-point calibration that is used for a linear correction.

There are numerous methods for performing pre- and post-deployment calibrations. Ideally, these would also be multipoint but it is probably more important that the calibrations are done as close as possible to the deployment and recovery dates. That is, a simple linear correction based on a few calibration points taken just after recovery may be better than a multipoint calibration done several months later. This is because the drift rate in storage is likely different than the drift rate during deployment.

The best linear corrections would be based on several Winkler-referenced points taken at high oxygen saturation (i.e. 100%) and zero oxygen saturation across different temperatures that span the expected temperature range during deployment. Omitting the zeroes and assuming an offset term of zero will impart a small error on very low readings but a calibration with no zeroes is far better than no calibration at all.

If Winkler measurements are not available, it is possible to get calibration points by equilibrating water with atmospheric air at a constant temperature. A standard constant temperature circulator filled with DI water and sparged with a small air pump or airstone can suffice. The bubbler should be placed just below the water surface (1 cm or so) to avoid oversaturating the water. If possible, the air should be drawn from outdoors. Monitor the optode readings, together with barometric pressure (measured in the same room). On days when barometric pressure is changing rapidly, it will not be possible to obtain complete equilibration. When the optode reading stabilizes to an extremely low rate of change, record a series of bath temperature and optode readings (FIGURE 2.8) and note the barometric pressure. The equilibrium concentration at the pressure of equilibration C_P^* can be calculated from:

$$C_P^* = C_0^* * (P - pH_2O)/(1 - pH_2O)$$

in which C_0^* is the equilibrium concentration at one atmosphere from the equations of *Garcia & Gordon* (1992) or *Benson & Krause* (1984) (the latter is probably better for pure water, the former better for sea water). P is barometric pressure in atmospheres and pH_2O is the partial pressure of water at the equilibration temperature.

A MATLAB script for the equations of *Garcia & Gordon* (1992) is available at:
http://web.uvic.ca/~rhamme/O2sol.m

MATLAB function: O2sol Version 1.1 4/4/2005. Author: Roberta C. Hamme

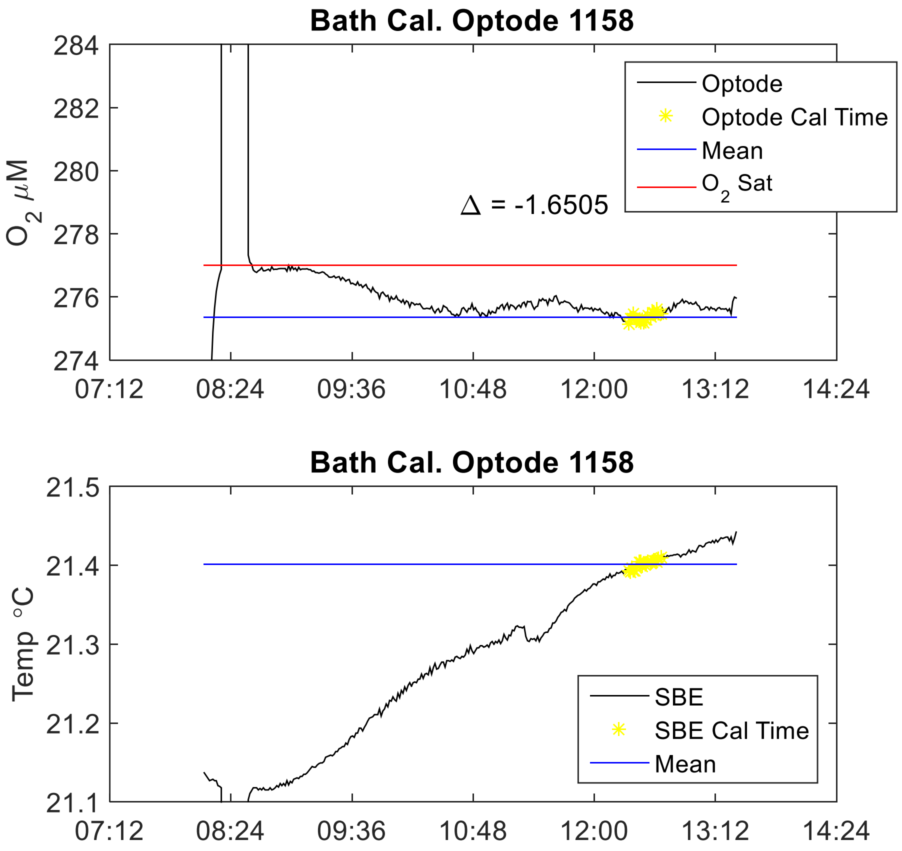

Figure 2.8. Optode oxygen readings.
Change in the optode oxygen reading with time (black). Multiple sample values from 12:30 were averaged (yellow) to give a mean oxygen reading (blue). The same time period of temperature measurements from the optode probe is averaged and used to calculate the saturation oxygen concentration with the relationship of Garcia & Gordon *(1992) at salinity of zero.*

- It is possible to gain some information about sensor drift from air measurements, which should, in theory, read 100% saturation. This method can be useful in cases in which it is impossible to recover the sensor and many air measurements are available, both of which are the case with Argo floats.
- If high-quality, in situ Winkler validation samples are available, it is also possible to correct the optode response with these data. The samples should be co-located precisely with the optode measurements in both time and space.
- For Aanderaa optodes with digital to analog (D/A) adaptors, the D/A converter and A/D converter of the logger can be calibrated, and this is worth doing (there are details in the Aanderaa manual). It is best to read the voltages with the same CTD or logger that will be used in the deployment.
- To quantify linear drift, optodes should have a multipoint calibration prior to use. An additional one- or two-point calibration just before and after deployment is also advised (*http://www.go-ship.org/Manual/Langdon_Amperometric_oxygen.pdf*).

- You can use the optode air measurement as a last resort, but this should not be relied on in place of water-based calibrations; note this may be more useful for Argo floats, from which thousands of air measurements can be integrated.

Data processing for optodes connected to SBE16 Plus

1. Perform analog to digital conversion correction (pre-deployment)
2. Set the salinity correction to zero (pre-deployment)
3. Convert output voltages to phase and temperature (post-deployment)
    - Note that this is model-dependent, so refer to the manual for the appropriate conversions
    - $P = (\text{volts}*12) + 10$
    - $T = (\text{volts}*45)/5 - 5$
4. Calculate $[O_2]_{fresh} = [(c_4+c_5*T)/(c_6+c_7*P) - 1] / (c_1+c_2T+c_3T^2)$
5. Use salinity data to convert oxygen values from fresh water to seawater values.

Further data correction and calibration

It is easy for Winkler oxygen samples to be of low quality due to improper sampling. It is thus important to ensure proper sampling technique. The sodium thiosulfate titrant solution should be calibrated with freshly made potassium iodate standard. All pipettes, dispensers, flasks and the auto-burette that are used to measure volumes in the Winkler method should be gravimetrically calibrated. Good Winkler samples are critical to carry out calibrations of optode measurements. It is important to have instruments multipoint calibrated before deployment.

The following figure (FIGURE 2.9.) shows examples of optode data calibration. To demonstrate the linear nature of optode drift, the corrections shown in FIGURE 2.9. were done with a linear gain correction based on a set of Winkler samples. For example, the Aanderaa Seaguard (light blue), which showed very low response, corrected very well to match the Winklers and multipoint-calibrated Aanderaa sensors (magenta and black lines). The Seabird SeapHOx (green line) was also reliably corrected and the CONTROS Hydroflash (dark blue) data were improved by the correction. The validity of applying such a linear correction has been well demonstrated for Aanderaa optodes and should apply also to Seabird optodes. It is unclear whether this approach is valid for the sensing chemistry used in the CONTROS Hydroflash.

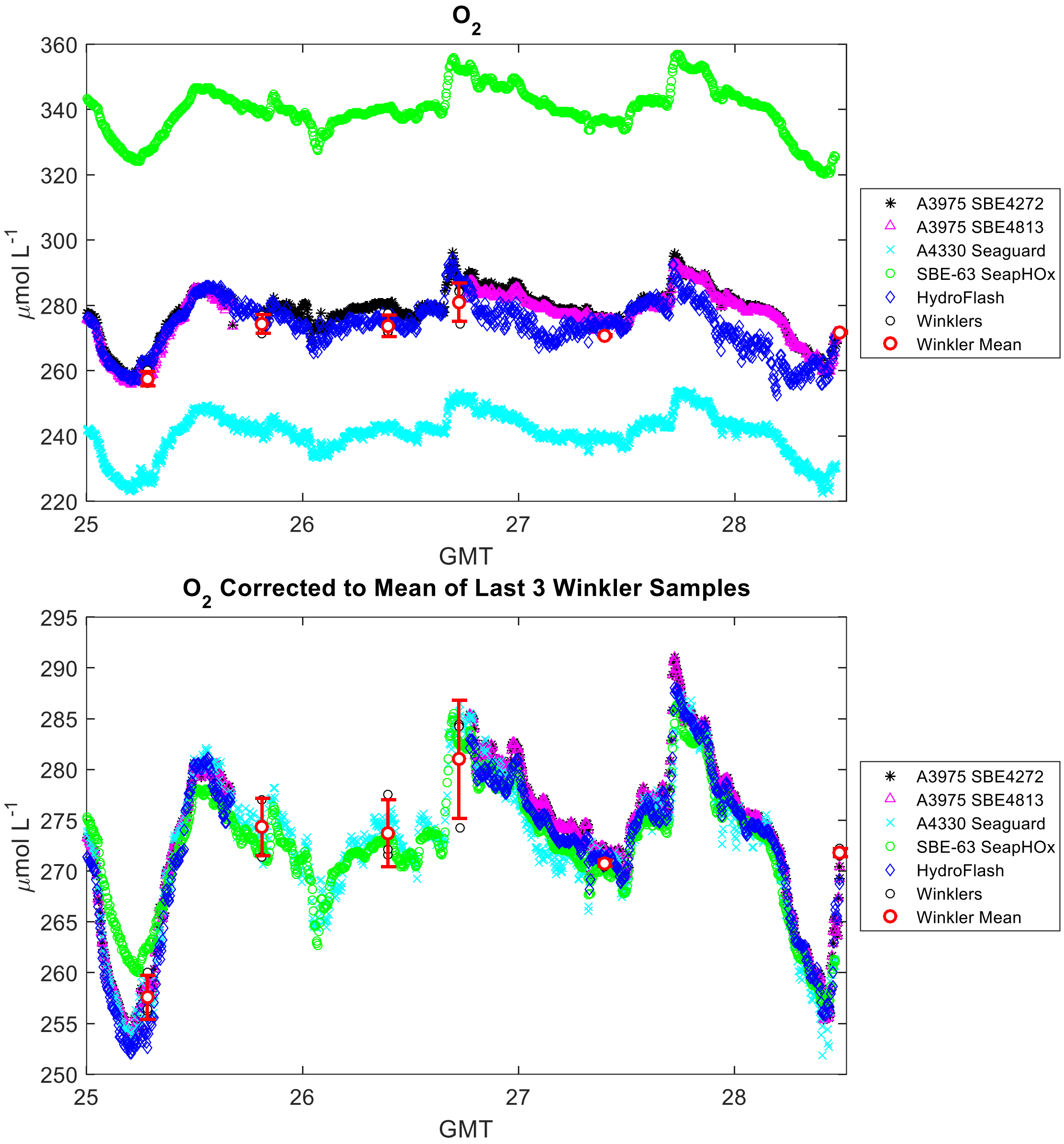

Figure 2.9. Calibration of various optode sensors.

Performing salinity corrections is also essential (FIGURE 2.10). The Aanderraa optodes should be set to a salinity of zero prior to deployment. The freshwater oxygen concentration can then be easily calculated and the salinity correction can be applied.

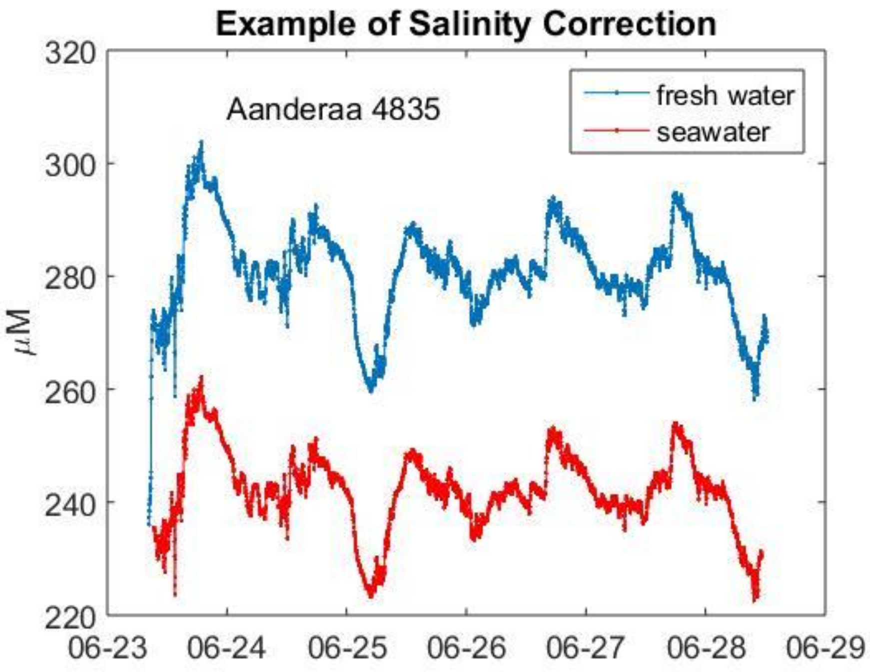

Figure 2.10. Example showing importance of salinity correction.

2.1.6. Data and metadata reporting

Information that should be documented in the metadata includes:

Pre-deployment information

- Instrument serial numbers (for all components)
- Calibration coefficients and/or statistics for all sensors, including the date of the calibration and person who performed the calibration (even if it was the manufacturer)
- Ideally, this data will include the manufacturer calibration, the analog to digital calibration, and any in-lab calibrations that are made on the optode prior to deployment
- Information about the in-lab calibration method should also be provided, including whether the optode was calibrated using the temperature probe on the sensor or an auxiliary thermistor.
- It is good practice to test the entire deployment package in the lab with all cables and battery power being used. Label cables prior to deployment for two reasons: in case someone else will be connecting all of the components in your absence, and so that you can keep track of functional and potentially faulty cables with ease post-deployment when the sensors are packaged and transported back to the lab.
- If you plan to transmit data via satellite, test the data transmission functionality prior to the deployment, including outgoing commands if the sensor package includes that capability

Post-deployment information

- Note the extent of biofouling, preferably with a picture included.
- Perform a 1- or 2-point calibration in the laboratory to assess the optode drift over the course of the deployment.
- Record the new calibration data, including the method used to perform the calibration. This will be essential for post-processing of the data and for tracking the long-term functionality of the optode over multiple deployments.

2.2. Nitrate

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2.2.1. Background

Nitrate is the most abundant form of nitrogen in the ocean, yet can be limiting to primary production. The overall oceanic nitrate inventory reflects exchanges with terrestrial and sedimentary sources, and the balance of marine microbial nitrogen fixation (nitrate production from N_2) and marine microbial denitrification (nitrate removal by conversion to N_2). Within the ocean, nitrate uptake into organic matter by primary production and return to nitrate by respiration produces large internal variations in nitrate abundance, with surface waters generally depleted and deep waters generally enriched in nitrate. This balance of processes yields an overall range in nitrate concentrations of ~0-40 μmol kg^{-1}. In addition to these natural variations, nitrate is enriched by anthropogenic inputs from fertilizers, sewage, and high temperature combustion sources, all of which lead to eutrophication.

Nitrate measurements provide information on marine metabolic processes on multiple timescales and can be a useful tool in studies aimed at characterizing oceanic circulation and nitrogen exchanges between the surface and the deep ocean. In addition, nitrate measurements help quantify anthropogenic processes and impacts, as well as associated cycling of other elements, such as carbon.

2.2.2. Measurement principles

There are two main techniques used for nitrate measurements in the ocean:

- Reduction of nitrate to nitrite using a cadmium column, followed by addition of reagent to form a purple complex quantified by spectroscopy against standard solutions (*Strickland & Parsons* (1968)). This is the standard laboratory and shipboard approach and has been implemented on some submersible systems. None of these devices were examined in the IOCCP course, and this method is not discussed further.
- Ultraviolet spectroscopy of nitrate absorption directly in seawater. This method has been implemented on several submersible sensors, including the ISUS and

SUNA sensors from Sea-Bird Scientific (Satlantic) (based on designs from MBARI) and the ProPS sensor available from ThermoFisher-TriOS. Only the SUNA sensor was examined in the IOCCP course, and the following discussion focuses on it, though the principles are essentially the same for other sensors of this type.

The basic principle of nitrate quantification by ultraviolet spectroscopy in seawater is the Beer-Lambert Law, which defines (for a single absorbing species homogeneously distributed along a specific light path) a linear relationship between molar concentration C and absorbance A at a given wavelength λ and path length x, based on the molar absorptivity ε:

$$C_{\lambda} = A_{\lambda} / x\,\varepsilon_{\lambda}$$

The absorbance is estimated from the transmitted light intensity as a fraction of that in the absence of the absorber:

$$A_{\lambda} = \log_{10}(I_{\lambda} / I_{\lambda}^{0})$$

Implicit in these equations are two key points that affect the determination of nitrate:

- Because there are multiple light paths in any real instrument, molar absorptivities must be determined for each instrument (at each wavelength). This information is provided in the instrument-specific calibration files provided by Sea-Bird Scientific (Satlantic) for each ISUS and SUNA.
- Anything else that reduces the transmittance must be accounted for; otherwise it will be interpreted as a nitrate signal. In the oxic ocean, the two main interfering absorbers are bromide and dissolved organic matter (DOM). Films or fouling of the windows, microbubbles, and particles are also problematic, mainly by affecting the spectral absorbance baseline.

The major interfering absorbance is from bromide, proportional to salinity in seawater, which shares a large portion of the nitrate spectral signal (Figure 2.11). For this reason, Sea-Bird Scientific (Satlantic) also provides a seawater adjustment that corrects for bromide absorption, including a linear approximation of its temperature dependence. DOM, on the other hand, affects the total sample absorbance, and its effect is managed by another linear term in the overall transfer function.

2.2.3. Available Sensors

In terms of sensors, while there are a variety of autonomous *in situ* measurement techniques for dissolved nitrogen species (e.g. potentiometric methods, optical techniques, traditional wet chemical analyses), currently the most reliable are the optical nitrate detectors that require no chemical reagents. The Sea-Bird Scientific (Satlantic) SUNA nitrate sensor is one such sensor.

The Sea-Bird Scientific (Satlantic) SUNA nitrate sensor

http://www.seabird.com/suna

The SUNA (Submersible Ultraviolet Nitrate Analyzer) is a chemical-free UV nitrate sensor based on the ISUS (In Situ Ultraviolet Spectroscopy) UV nitrate measurement technology developed at the Monterey Bay Aquarium Research Institute (MBARI) by Kenneth Johnson and Luke Coletti (*Johnson & Colletti* (2002)).

Principal of operation

The SUNA measures the concentration of dissolved nitrate in water. The sensor illuminates the water sample with its deuterium UV light source, and measures the throughput using its photo-spectrometer. The difference between this measurement and a prior baseline reference measurement of pure water constitutes an absorption spectrum. Absorbance characteristics of natural water components are provided in the sensor calibration file. The Beer-Lambert Law for multiple absorbers establishes the relationship between the total measured absorbance and the concentrations of individual components. Based on this relationship, the sensor obtains a best estimate for the nitrate concentration using multi-variable linear regression.

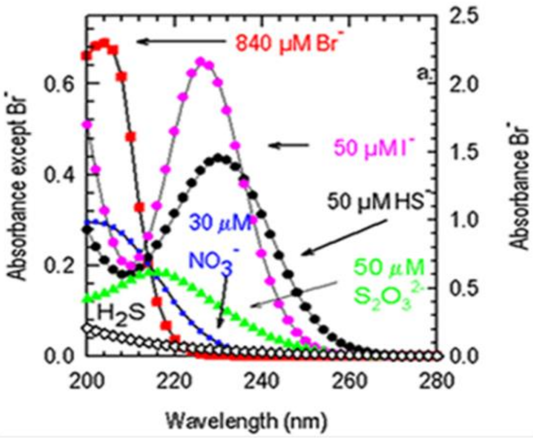

Figure 2.11. UV absorbance spectra for seawater. Source: course materials.

Electrical Specification

The required power input for the SUNA is in the 8–18 VDC range, with a supply current of 1 A (8–15 VDC in case for SUNA with an integrated wiper). Power consumption depends on the operating state. During data acquisition, it is typically 7.5 W (±20%). In standby, at the command prompt, the current draw is around 20 mA. Polled and APF operating modes will time out after a configurable time of inactivity, bringing the SUNA processor into a low power state with a consumption below 3 mA. In fixed-time operation and between periodic operation events, power control is switched over to a supervisor circuit, which reduces power consumption to less than 30 µA.

SUNA accessories

Figure 2.12. The SUNA flow cell.

- Flow cell

  The SUNA flow cell is an accessory provided by the manufacturer in order to make the sensor suitable for integration in flow-through systems such as ferry boxes or moorings with pumped flow circuits. The same cell can be used in the lab for validation tests and calibration experiments.

- Hydro-Wiper (Fouling prevention)

  The Hydro-Wiper is an active antifouling system that use a brush attached to a motor to clean the sensor optical window in user-specified intervals.

  The users must note that an instrument with hydro-wiper will have a higher power consumption that must be taken into account for deployments.

Figure 2.13. The SUNA Hydro-Wiper.

- Anti-fouling copper guard (Fouling prevention)

  The SUNA V2 is also equipped with an anti-fouling guard, which is a semi-circular piece of perforated copper that is attached direct to the sensor sample chamber. This passive antifouling guard protects the sensing element through the release of cooper ions.

Figure 2.14. SUNA V2 anti-fouling copper guard.

2.2.4. Sensor deployment

The SUNA nitrate sensor has been used on numerous platforms with different platform-driven configurations (FIGURE 2.15). In every case, the mounting of the sensor, regardless of the hosting platform, must be done in such way that it will not affect the sensing element geometry. The principle of operation for the SUNA sensor is based, among others, in the alignment of the deuterium UV light source and photo-spectrometer.

The operator must pay extra attention when using brackets or attaching mechanisms that may cause tension in the sensor housing and affect the alignment between the excitation light source and the detector.

A good practice is to attach the mechanism close to the sensing element instead of the edges of the housing.

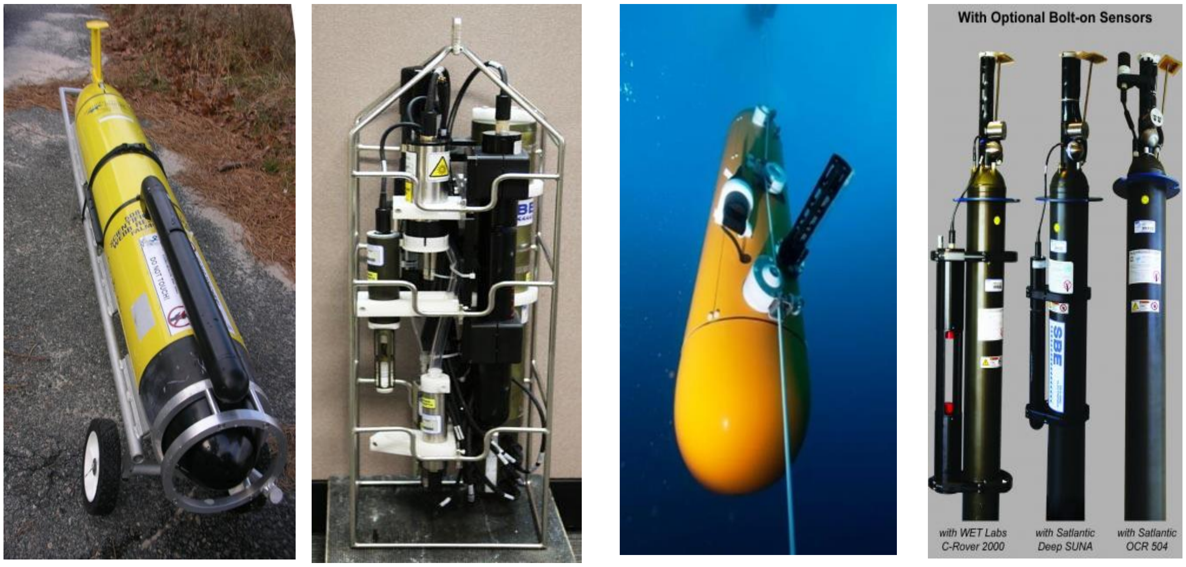

Figure 2.15. SUNA nitrate sensor attached in different platforms.
From left to right: a) glider b) CTD frame c) fixed point profiler d) Argo float.

Operating the instrument: Pre-deployment phase

Operating the instrument in the lab

- The lamp heats the instrument and this causes drift. The best practice is to *operate the instrument immersed in a constant temperature bath*.
- Because particles and micro-bubbles affect the absorbance, degassing and filtration of samples and standards is useful.
- As with any instrument, recording of instrument outputs over time for blanks and standards is recommended.

Mounting

Because the optical paths of the instrument can be affected by its mechanical mounting, pre-deployment checks and calibration should be performed as close as possible to its intended mounting arrangement. For example, the sensor can be stably mounted on a bar or plate that will then be attached to the deployment platform. For the SUNA, the mounting is best done using bands around the cylinder close to the optical gap to minimize torque across the instrument.

Optical path cleaning

Make sure instrument and the optical windows are clean; use lens tissue and non-film forming detergent followed by copious rinsing. Check clarity by measuring a deionized water sample (preferably with low dissolved organic matter, e.g., as produced by UV irradiation) in a clean bucket or flow cell. If these are not available, a less desirable but still viable option is to use an improvised flow cell made by wrapping the gap with tape or

Parafilm. Re-clean and re-measure until the sample is stable (to better than X absorbance units, equivalent to ~ 0.3 μM nitrate, the specified precision).

Lamp status

Check that the lamp provides good illumination and is stable by measuring the transmittance in deionized water (DIW).

Calibration check

Measure a working standard of seawater of known salinity (preferably close to the instrument calibration salinity) and nitrate content (with a preferably known and stable dissolved organic matter content) at known temperature. If the measured nitrate concentration is significantly different than the known value, then measure multiple nitrate standards to produce a working calibration curve for this deployment. Plan to have the instrument recalibrated by the manufacturer or perform your own full calibration against known bromide and nitrate standards in seawater.

Operating the instrument: deployment phase

- Set up the SUNA instrument using the settings recommended by the manufacturer for the mode of deployment desired (profiling, moored, periodic).
- Evaluate the power requirements and ensure the battery pack is appropriate.
- Perform and record a final DIW spectrum as close as possible in time prior to deployment.

Operating the instrument: Post-deployment phase (including storage)

- Clean the windows and record DIW and working standard spectra as close as possible after recovery. Soak the instrument in fresh water to remove salts.
- Store dry and clean

2.2.5. Sensor calibration and validation

It is possible that factory calibration is inadequate and a full range calibration by the user is required:

- Against nitrate standards made with deionized water, low nutrient seawater with constant salinity (S = 35), and local low nutrient seawater.
- Against bromide standards prepared in the same way.
- At different temperatures

Also note that:

- An indication of the response to DOM may also be useful.
- A revision of the transfer function may need to be considered, depending on results.

2.2.6. Retrieving the data

Processing of the data to obtain nitrate concentrations requires the raw spectral data, instrument calibration file, and sample temperature and salinity. Reprocessing can then be carried out using the approach developed at MBARI (*Sakamoto et al.* (2009)). All of the raw files should be recorded and archived, in addition to the nitrate concentration estimates that are derived from them.

An option to log and/or transmit data in a pre-processed format may be available. For example, the SUNA can transmit or log data in the 'concentration ascii' format, which contains time-stamp, nitrate concentration, absorbances at 254 and 300 nm, and RMSE as a measure of the data quality. Such a format can be useful if the data are to be transmitted via satellite in real time and bandwidth is limited. However, it is essential that the full spectra also be logged internally so that the processing can be repeated at a later date for validation and/or corrections.

In the case of the SUNA, the following input files are required for data reprocessing using the SUNACom software (*http://www.ott.com/en-us/products/download/sea-bird-scientific-sunacom-software-manual/*):

- The instrument package file (.xml format) describing the SUNA data.
- The calibration file (.cal format).
- The raw UV spectra to be reprocessed, which may be contained in multiple files (.csv format).
- A time series of temperature and salinity measured as close as possible to the instrument deployment. The data in that file must be in the following ASCII format: YYYY-MM-DD hh:mm:ss,Temperature[C],Salinity[PSU].

The SUNACom software will select the temperature and salinity to use for processing each spectra using a nearest neighbour method. The timestamps of the temperature and salinity time series therefore do not have to coincide with the SUNA time series, although matching the samples as closely as possible is recommended. Other things to note are:

- When processing spectra, the fitting range needs to be specified. The default range in SUNACom is 216.5 to 240 nm. The selected wavelength range should be reported in the metadata.
- If burst sampling has been used (multiple spectra gathered at defined time intervals), a smoother nitrate estimate can be obtained by averaging the bursts.

Data Validation

It is essential to collect, when possible, in situ samples to calibrate and validate the measurements of the nitrate sensor. High temporal frequency of sample collection, as well as concentration range (in case the study area experiences large concentration changes through time) will ensure that the data collected by the instrument are accurate and reliable.

In September 2015, the U.S. Integrated Ocean Observing System (IOOS) published procedures for the quality control (QC) of real-time dissolved nutrient data as part of the Quality Assurance/Quality Control of Real-Time Oceanographic Data (QARTOD) project. This manual for Real-Time Quality Control of Dissolved Nutrients Observations focuses specifically on real-time, in situ measurement of dissolved nutrients as observed by sensors deployed on fixed or mobile platforms. The document can be freely downloaded from *http://www.ioos.noaa.gov/qartod/*.

2.2.7. Troubleshooting the sensor

The general handing of a SUNA is the same as of any other instruments. Double check everything (power, cable, software, etc.) before shipping your instrument to any location or going into the field for a deployment. A checklist will always be helpful. It should be noted that the software of the SUNA (SUNACom) has different versions. Current version of the manual for SUNACom software can be downloaded from here: *http://www.ott.com/en-us/products/download/sea-bird-scientific-sunacom-software-manual/*.

Sensor weaknesses/problems

- Sensitivity of optical windows (cleanliness, sensor placement)
- Issues with reproducibility during zeroing using deionized water (2.2.5 above)
- Imperceptible changes in optical geometry
- Improper positioning on mooring or while profiling
- Bubbles on optical windows
- High concentrations of coloured dissolved organic matter (CDOM)
- Fouling
- Oligotrophic waters
- High salinity waters
- Lamp endurance

2.2.8. Choosing the right sensor for the job

It is always important to know the performance of specific sensor and the potential environmental conditions before purchasing. Simply speaking, where are you going deploy your sensor and could the sensor meet your needs? Please check these questions before you purchase a nitrate sensor:

- Do you know the nitrate concentration range of your research area? It is recommended to have basic hydrographic data from your research area such as the nitrate concentration range, temperature and salinity. If it is an oligotrophic area, the SUNA might not be able to measure nitrate in surface water.
- Will the sensor be deployed for long-term or short-term monitoring? Biofouling is a serious issue for long-term deployments; accessories such as wiper or copper protection may be needed.
- Will the SUNA be used in a mooring or profiler? For profilers in oligotrophic waters, SUNAs might not be suitable for surface measurements, but they can be

used for deep ocean measurements where the nitrate concentrations are higher than several μM.

- What is the frequency of your monitoring? This will determine how long your battery could last if the instrument will be deployed independently.
- Last but not least, what is your budget? Will it fit the price of SUNA?

2.3. pCO_2

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2.3.1. Background

Carbon dioxide (CO_2) content of the atmosphere has increased since the industrial revolution, from approx. 280 ppm in 1750 to 399 ppm in 2013, owed largely to anthropogenic use of fossil fuels and land use change (*IPCC* (2013)). CO_2 is a soluble gas in aqueous solution and it exchanges freely across the air-sea interface, with the global oceans being a net sink of atmospheric CO_2, absorbing about 2 PgC year^{-1} (*Wanninkhof et al.* (2013a)). CO_2 is a key substance involved in a number of biogeochemical processes in natural waters and the most commonly measured parameter, describing the amount of dissolved CO_2 gas in water, is its partial pressure, or pCO_2:

$$pCO_2 = P \times x(CO_2)$$

in which:

$x(CO_2)$ = molar concentration of CO_2 gas in the dissolved gas mixture (usually air)
P = total pressure of gas mixture (*Atamanchuk et al.* (2014)).

Together with dissolved inorganic carbon (DIC), total alkalinity (TA) and pH, pCO_2 helps quantify the carbonate system of seawater. In the presence of increasing atmospheric CO_2 levels, long-term pCO_2 time-series are essential in determining whether aquatic environments are long-term net sinks or sources of CO_2 (*Wayne* (2000); *Takahashi et al.* (2009); *Bozec et al.* (2011)). Both large- and small-scale studies of pCO_2 on continental shelves and in seas, rivers, lakes, fjords, bays, etc. are able to resolve major biogeochemical processes on interannual timescales (*Thomas and Schneider* (1999); *Thomas et al.* (2004); *Kaltin and Anderson* (2005); *Wesslander et al.* (2011)). All of the applications described above require continuous, uninterrupted measurements with high temporal resolution in order to provide improved understanding of pCO_2 dynamics in aquatic systems at local, regional and global scales.

2.3.2. Measurement principles

pCO_2 measurements are based on the equilibration of a carrier gas phase with a seawater sample and subsequent determination of the CO_2 in the carrier gas (*Körtzinger et al.* (1996)). What varies between pCO_2 instruments are (1) the means of equilibration of the gases' partial pressures (the 'equilibrator'), and (2) the type of detector. Since seawater pCO_2 varies strongly with temperature, a correction is necessary to compensate for the difference between equilibration temperature and the in situ seawater temperature (*Körtzinger et al.* (1996)).

Three different equilibration principles exist, each with a variety of designs:

- Liquid-gas
- Liquid-liquid
- Liquid-solid

There are also several detector types:

- Infrared:

  CO_2 concentrations are measured optically using non-dispersive infrared (NDIR) absorption spectroscopy. Examples of instruments that use this technology include the CONTROS model HydroC CO_2 (CONTROS Systems, GmbH), the Pro-Oceanus model CO_2-Pro™ instruments (with and without a flow through pump), the pCO_2 Measuring System (General Oceanics), the pCO_2 Subsea (subCtech), and the Battelle Seaology (MApCO2) System*. Other examples can be found at: *http://www.ioccp.org/index.php/instruments-and-sensors*

- Colorimetric:

  pCO_2 is measured indirectly through spectrophotometric pH determination. Examples of instruments that use this technology include the Sunburst model SAMI pCO_2 (Sunburst Sensors; *http://www.sunburstsensors.com/*). See the appropriate IOCCP page for more details:
  http://www.ioccp.org/index.php/instruments-and-sensors

- Optical:

  These sensors are not yet commercially available and at this stage advanced prototypes are being tested (for example: Aanderaa Data Instruments (*www.aadi.no*); *Atamanchuk et al.* (2014)).Their operation is based on the measurement technique identical to that of the oxygen optode; e.g. *Tengberg et al.* (2006)).

*Notes on the Batelle Seaology System: This type of system is mostly used in moorings due to its size. It has a high power demand, but can be deployed in the water for long periods of time (up to a year). It is a complex system, but can provide very reliable measurements if adequately maintained and calibrated (knowing the pressure and water temperature is critical).

Measurement Principles: Liquid-Gas

In the liquid-gas principle, the CO_2 contained in the water equilibrates with gas contained in a chamber directly (e.g. *Pierrot et al.* (2009)) or through a gas-permeable membrane (*Fietzek and Körtzinger* (2010)). This type of equilibrator is used mostly for gas phase on flow-through systems on ships. It is the simplest type of system, with very high accuracy. It does require high-quality gas standards.

Measurement Principles: Liquid-Liquid

In the liquid-liquid principle, the water equilibrates with a colorimetric pH indicator solution (meta cresol blue) in a gas permeable membrane; the shifts in the pH indicator solution are related to pCO_2 (e.g. *DeGrandpre et al.* (1995)).

Measurement Principles: Liquid-Solid

In the liquid-solid principle, a dye-embedded sensing foil is in equilibrium with the water CO_2. A comparison of the phase shift between the sensing and the reference luminophore provides estimates of pCO_2. (e.g. *Atamanchuk et al.* (2014))

2.3.3. Available Sensors

Adequately measuring the marine carbon components is critical for understanding the marine carbon cycle; technological developments to measure the marine dissolved carbon components, in particular inorganic carbon, have been ongoing for now more than two decades, which have resulted in a wide array of mature instrumentation to carry out such measurements.

CONTROS HydroC-CO_2

https://www.km.kongsberg.com/ks/web/nokbg0240.nsf/AllWeb/537648638D3F59AAC1257EDC0040495F?OpenDocument

Figure 2.16. CONTROS HydroC-CO_2.

The HydroC CO_2 is an NDIR – membrane diffusion-based submersible CO_2 analyzer that, according to manufacturer specifications, is capable of deployment in all ocean conditions and to full ocean depth (6000m). Measurements are possible at 1-s to 1-week intervals. Deployment times extending to ~18 months are possible, but with associated reductions in data frequency. The instrument has a response time (T_{63} - time to reach 63% of its final reading) of 60 s and a sample rate of 1 hz. In a cabled operation, the deployment time is limited by fouling, drift, and the auto-zeroing loop, which contains soda lime. Fully equipped versions of the sensor include the capability of cabled or autonomous deployments and come with an optional copper anti-fouling guard and a Seabird pump (to decrease the size of the boundary layer, making response time quicker). For autonomous deployments, an external battery is required. Like many other submersible instruments, the Hydro C does not collect any other oceanographic parameters such as water temperature, conductivity, or pressure. Therefore, if accompanying hydrographic parameters are required - i.e. a profiling application - then an additional sensor is needed. It is always recommended to collect CTD data so as to be able to reprocess and correct the pCO_2 measurements. Drift corrections (using the onboard zeroing), and changes in response time due to fouling of the membrane is a service that is currently offered by the manufacturer.

With this instrument, calibration by the user is not possible, only by the manufacturer. The user must therefore specify to the manufacturer a priori the expected range of temperature and pCO_2 of the environment where the sensor will be deployed. Validation samples are recommended at regular intervals. The CONTROS Hydro-C/CO_2 is available as a standalone or flow-through instrument (HydroCFT/CO_2). The underway HydroCFT is available with flow rates of 2-15 L min^{-1}. Each calibration sheet is unique to each individual sensor.

Pro-Oceanus

http://www.pro-oceanus.com/co2-pro-cv.php

Figure 2.17. Pro-Oceanus CO_2-Pro CV.

The Pro-Oceanus model CO_2-Pro CV instrument measures pCO_2 using infrared detection. The instrument is available with a standard range of 0-600 ppm and 0-2000 ppm to provide the full range of pCO_2 required for measuring ocean CO_2. The CO_2-Pro CV features an internal zeroing feature to provide a stable long-term baseline to ensure accurate and stable long-term measurements. CO_2-Pro CV instruments are factory-calibrated using WMO standard gases with detector temperature stabilization and measurement of gas stream pressure and humidity to ensure accuracy.

SAMI pCO_2

http://www.sunburstsensors.com/products/oceanographic-carbon-dioxide-sensor.html

Figure 2.18. SAMI pCO_2.

The SAMI-CO_2 uses a pH-sensitive dye housed inside a CO_2(g)-permeable membrane. CO_2(g) in the dye achieves equilibrium with the CO_2(g) in the water in which the SAMI is submersed. The CO_2(g) in the dye affects the ratio of the acid and base species of the dye and thus the response of the SAMI is dependent upon the amount of dissolved CO_2. Since the dye on the inside of the membrane is at the same pressure as the water on the outside of the membrane, the pCO_2 measured by the SAMI does not need to be corrected for pressure, regardless of sampling depth. The SAMI is generally calibrated at a single temperature for more limited CO_2 range (e.g., Hood 15°C, 240-400 µatm). Because of the non-linearity of the SAMI response, systematic errors can occur if the response is extrapolated too far outside the calibration range (e.g., low salinity waters). Manufacturers recommend comparison to field measurements where possible. However, in dynamic systems with high temporal and spatial (including depth domain) variability, substantial differences between discrete samples will still be observed. Hence, comparisons should be approached with some degree of caution in these scenarios.

Due to the way the sensor functions, outputs are a representation of the integrated response of the signal over a period of ~10 s, so it is not possible to capture events occurring on ultra-short (<10 s) time scales. Biofouling is not thought to affect instrument performance. A copper mesh cage is used to provide membrane protection (see photo above), though for heavy fouling environments, the membrane is enclosed in a chamber and a Seabird pump is used to circulate sample.

The SAMI-CO_2 system sensor is readily deployed on a variety of fixed/Eulerian measurement platforms and within inherent design limits, vertical profiling or auto profilers. One limitation of the SAMI-CO_2 is its measurement time of approximately 5 mins (TABLE 2.1). The internally fixed, non-user serviceable battery pack in the SAMI may also be a concern for long-term, unsupervised profiles. The physical size and weight of the SAMI may also prove to be an obstacle for autonomous profilers and gliders. However, depending on the application, these characteristics may not pose an obstacle. For example, response time is generally not an issue at fixed locations and depths, and winched profilers can be programmed to dwell. Unlike the SAMI-pH sensor or other pCO_2 sensors, the SAMI-CO_2 can be started in air and then deployed. In situ calibration capabilities and fouling resistance can still become performance-limiting factors, depending on the type of application.

Aanderaa pCO_2 Optode

http://www.aanderaa.com

Figure 2.19. Aanderaa pCO_2 optode.

The functioning and mechanical setup is similar to the oxygen optodes produced by Aanderaa. The sensing foil of the pCO_2 optode is comprised of two fluorescence indicators embedded in an ion-impermeable, hydrophobic and gas permeable polymer layer that are periodically excited by a blue-light LED. As CO_2 diffuses from the surrounding water into the sensing foil layer, it causes the local pH to alter by a magnitude commensurate with the pCO_2 level outside the membrane. A change in fluorescence intensity of one indicator is effected that is detected as a phase shift value of returning modulated red light. The fluorescence response of the second indicator is similar in intensity and spectra but is not affected by pH. Its longer fluorescence lifetime enables it to be used as a reference and thus for the sensor to cope with variations in background light and excitation intensity. This measurement approach is known as Dual Lifetime Referencing.

2.3.4. Sensor deployment

The following table provides some guidelines and helpful tips for instrument deployment, recovery and storage. In addition, specifics for deployment of some of the sensors are also provided.

Table 2.1. Guidelines and helpful tips for pCO_2 instrument deployment, recovery and storage.

	NDIR (e.g. Hydro C-CO_2)	Colorimetric (e.g. SAMI)	Optical (e.g. Optode)
Ensure that observations are tied to a GMT/UTC time stamp, to absolutely avoid timing issues.	X	X	X
Instruments should always be deployed with a CTD	X	X	X
Water temperature measurement must be measured independently from internal temperature			
Factory calibration coefficients are needed to compare with user calibration validation, e.g. zero and span			
Changes in response time can be helpful to identify the onset of biofouling	X	X	X
Use of a pump can slow the onset of fouling and also increase response time by reducing the boundary layer	X		

Electrical cables should always be labelled and properly maintained	X	X	X
Software – an instrument setup summary file should always be recorded and saved as a separate retrievable file	X	X	X
Power – Need to consider power budget, e.g. battery packs available, to decide on deployment endurance and sampling frequency before any deployment	X	X	X
Manufacturer's calibration interval should be stated and adhered to	X	X	X
Long term storage considerations: Instrument should be flushed with DI water to avoid continued biofouling and stored dry (not for optode).	X	X SAMI: store horizontal	
Instrument should be flushed with DI water to avoid continued bio fouling and stored wet			X
Deployment positions Instrument should always be deployed with flow through cap vertical (i.e. towards sky) or horizontal and always fully submerged underwater to prevent trapped oxygen and/or pump cavitation	Hydro C		
Deployment with/without pump When profiling or deploying in waters with high CO_2 fluctuations, it is highly recommended to use an external pump to increase the rate of water flowing past the membrane, increasing the rate of diffusion and sensor response time. When using a pump consideration needs to be given to the reliability of the pump as current pump manifolds restrict external flow. A solution to this would be to have a pump manifold that minimised the restriction of external water flow and in the event of pump failure still allowed external waters to flow in and around the sensor membrane.	Hydro C ProOceanus CV 1		
Membrane cleaning and replacement Time and cost issues must be considered. Be aware with accumulating fouling, equilibration time extends. In coastal deployments, clean or replace membrane ~ 3 months.	X		

- Membranes can be cleaned with sulphuric acid / oxalic acid washes. - Do not touch the membrane directly as this may damage / compromise its surface. - It is not advised to physically/mechanically clean the membranes due to risk of membrane damage			

Hydro C-CO_2

Proprietary 'Detect' software is provided with the sensor, but it can also be controlled by terminal commands. It is advised not to use a direct connection of sensor to serial port of the computer, as this is found to not always work. Instead, use serial to USB adaptor. You must ensure that this USB adaptor has been installed and recognized by the computer prior to trying to use it to connect to the HydroC. Once connected, the Detect software can be started and it will scan for attached sensors. If this order has not been followed and the software is already open, then it will need to be restarted in order to detect the sensor. Additionally, when setting up the sensor through computer interaction, do not connect and run the pump as it cannot run in air. The flow head directs flow from the pump directly onto the silicon membrane that sits above a sintered metal support (thus enabling the sensor to function at high pressures). The flow head can be removed to access the membrane to maintain or, if necessary, replace it.

The sensor should be deployed upright or horizontally, **NOT** downward-looking. This is to guard against bubbles accumulating on the membrane surface and causing problems with the pump.

If placed in continuous live collection mode, the baud rate can be adapted within CONTROS Detect software to suit cable length. A zero will be performed approximately every 12 hours in this mode (if in discrete mode, then a zero will be performed every time upon waking the sensor from sleep mode).

After retrieval, the Hydro C sensor must be cleaned in freshwater (to remove residual salt) and completely dried out. This is performed by running the sensor for approximately 30 minutes (with the seawater pump disconnected). This will prevent excess water condensation in the measuring cell and fluidic components behind the membrane.

Spare membranes are provided with the sensor; the length of time that these will last will depend on the working conditions and fouling. With accumulating fouling, you will see the equilibration time extending. It won't however affect the sensor's ability to reach equilibrium, just the time it takes to get there. In coastal deployments, it is typical to clean or replace the membrane every 3 months or so. Membrane replacement is easy, so it is advised against cleaning it. If cleaning is the only option, low concentration sulfuric acid (<1%) or oxalic acid (<2%) can be used. It is not advised to physically/mechanically clean the membranes due to risk of membrane damage. If the membrane is indeed mechanically cleaned, it is better to postpone the use. Even a small imperfection on the membrane will result in water penetrating in the gas loop and severely damaging the sensor. The sensor measures the molar ratio of CO_2 in wet gas that is independent of temperature and pressure. Corrected pCO_2 values are output by measuring the internal temperature and pressure and humidity and correcting the molar ratio. While humidity is needed for the final CO_2 value, it can also be used as a proxy for a damaged membrane.

Pure copper anti-fouling measures are included on the sensor, both on the pump inlet and on the main head of the sensor body. Post deployment cleaning/replacement may be needed for the pumps as well.

Aanderaa pCO_2 Optode

In order to apply point-offset adjustments to outputs, it is critical that discrete seawater samples be collected during deployment. The relative response time (about 5 minutes in cold water) precludes deployment of this sensor on profiling floats and other moving platforms. The current absolute accuracy also precludes its use in open ocean analyses of the carbonate system.

No antifouling measures have currently been adapted.

Beware:

- Hydrogen sulfide (H_2S) irreversibly poisons the sensors, so these sensors are not recommended for environments that may contain H_2S (i.e. low-O_2 conditions).
- SO_2, HCl and acetic acid also quickly and irrevocably damage the sensor (sensor foil likely oxidized).

2.3.5. Sensor calibration and validation

Calibration is essential for all sensors. All sensors drift; hence, comprehensive pre-deployment calibration, comprehensive post deployment calibration and in situ calibration (zeroing) are highly recommended. Regular re-calibration with high standard gas for the direct liquid-gas type equilibrators is also necessary, as well as occasional referencing for the membrane liquid gas equilibrators (*Fietzek et al.* (2014)). It is possible to apply the zeroing and the post-calibration to correct for the data and get that to the zero line. If possible, seeing the data in real-time (as it comes out of the instrument) is recommended, so as to know the measurements are consistent and that there are no adjustments done automatically by the sensor.

Hydro C-CO_2

During calibration, the preferred sensor operating temperature must be specified. This must be set to be always higher than the highest field temperature to be experienced so as to eliminate the possibility of condensation of water vapour occurring within the sensor body / gas flow path. Typically, this is set at ~10°C higher than the maximum sample temperature. The higher the temperature, the higher the power draw. This needs to be considered if the instrument will be operating for prolonged periods of time. The temperature at which calibration is performed is to be set by selection of the mean of the measurement range required by the end user.

Aanderaa pCO_2 Optode

Complete calibration of the pCO_2 optodes takes several months. It is important to take this into account for deployment planning. The sensor foil needs to be preconditioned, i.e., it needs to be bleached / excited a number of times before use. This takes about 1 month and appears to be independent of temperature, number of light excitations, and salinity. When the sensor is stored and transported, the foils need to be kept wet at all times using a water-filled protection cap and preconditioned in saltwater.

2.3.6. Data and metadata reporting

The golden standard for data quality protocols and associated documentation in terms of surface ocean carbon dioxide measurements comes from the Surface Ocean CO_2 Atlas (SOCAT, *http://www.socat.info/)* which is a synthesis of quality-controlled fCO_2 (fugacity of carbon dioxide) values for the global surface oceans and coastal seas. Version 3 of SOCAT has 14.7 million fCO_2 values from 3646 data sets covering the years 1957 to 2014. One of the most critical features of SOCAT is the fact that the accuracy of surface water fCO_2 has been defined for all data set quality control flags.

As of 2015, the pCO_2 sensors used during Kristineberg Course do not meet the verifiable high accuracy requirements for inclusion in the Surface Ocean CO_2 Atlas (SOCAT, *http://www.socat.info/*) data product with a QC flag of A or B, indicative of the accuracy of the fugacity of CO_2 in surface water (fCO_2sw) of 2 µatm or better and documented accuracies and standardization routines. Similarly, flags C and D are unobtainable for those sensors that lack the use of an in situ calibration comprised of two standards (one of which can be a zero). However, very useful and valuable data generated by sensors should not be discarded. For this reason, a new quality control flag 'E' has been developed and described for "alternative sensor designs" that are accurate to within 10 µatm to allow data from alternative sensors and platforms to be submitted to SOCAT. To achieve this and to be accepted by SOCAT, internal diagnostics and standardization and, when possible, post-deployment tests are necessary. As specified by the SOCAT sensor data report (*Wanninkhof et al.* (2013b)) "it is recommended that the submitting PIs provide a preliminary dataset quality flag based on the criteria in the supplied metadata. When the dataset is entered in the database the flag will have the prefix 'N' (e.g. NB, NC etc.). This should encourage submitting investigators to check their metadata and data during submission to assure they meet the appropriate SOCAT dataset QC flag criteria. The metadata form needs to be adjusted to accommodate such an entry."

To be accepted for a SOCAT flag 'E', the following criteria must be met:

- Accuracy of calculated fCO_2w (at SST) is better than 10 μatm
- Did follow approved methods/SOP criteria
- Metadata documentation complete
- Dataset quality control was deemed acceptable

2.3.7. Choosing the Right Sensor for the Job

Currently, these technologies can be deployed in a variety of platforms and can be relatively flexible, depending on the application. The sensors are mature, and it is expected that the technology will further diversify into high autonomy (large number but lower quality) and high quality (small number, best quality). Considering the amount of anthropogenic CO_2 that is entering the oceans and the effect it has on marine ecosystems, inorganic carbon has been identified as an Essential Ocean Variable (EOV; *http://www.ioccp.org/index.php/foo)*. Automated sensor technologies will be critical for monitoring the variability and changes of ocean pCO_2, and project and understand future impacts on biota and ecosystem services.

Before a sensor is purchased, the following should be considered:

- Cost of ownership: what are the associated costs with running these instruments?
  - collecting and analyzing validation samples (how many, how often)
  - annual (or sooner) factory recalibrations
  - user serviceability
  - additional equipment for ancillary data (CTD, data loggers, battery packs, cables, antifouling protection, connectors, deployment platform, driver development etc.
  - user specific training (field, software, hardware)
- Application specific considerations
  - profiling vs moored (response time)
  - pumped vs unpumped (response time + battery longevity)
  - deployment length
  - antifouling
- Data
  - access to raw data, calibration coefficients etc.
  - software for data manipulation

Consider the information in the following table when choosing a sensor.

Table 2.2. Selected criteria helpful for choosing a pCO_2 sensor.

	Controls HydroC CO_2	**Pro Oceanus CO_2-PRO CV**	**Sunburst SAMI CO_2**	**Aanderaa CO_2 Optode**
Depth range (m)	0-6000m	0– 4000 m	0-600m	0-10000 m
Quoted accuracy	+/- 1%	+/- 2 µatm	+/- 3µatm	2-75 µatm*
Quoted Precision	<1 µatm	+/- 0.01▲ ppm	<1 µatm	+/-2 µatm
CO_2 Range	200– 1000 µatm	0-2000 µatm	200 – 600 µatm	200-2000 µatm
Salinity range	any	any	any	any***
Temp. range	-2 °C to 30°C	-2 °C to 40°C	-1.5°C to 30°C	?
Response time T63	60sec	~2.5 min	~5 min	45s @40°C 4.5 min @0°C
Profiling	YES	NO	NO	Only in warm waters
Duration	~18 months@1Hz (one sampling cycle per day)	?	~10,000 measurements/ ~ 1 year @1hour	Lifetime-based (?)
Stability	<1 µatm units over 12 months	?	<1 µatm units over 6 months	1% for durations of 5 months

* *Atamanchuk et al.* (2014)
** Thermistor accuracy, precision 0.1° C, +/- 0.01ºC
*** Not be deployed in sulphidic environments
▲ *http://www.pro-oceanus.com/images/co2-pro-cv.pdf*

2.4. pH

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2.4.1. Background

The pH of seawater is a master variable in the carbonate system, and determines its carbonate speciation into carbonic acid, $H_2CO_3^*$, bicarbonate ion, HCO_3^-, and carbonate ion CO_3^{2-} (*Martz et al.* (2010)). If known precisely and accurately, this master variable can help assess the influence of anthropogenic CO_2 emissions on the ocean carbonate system. The absorption of anthropogenic CO_2 emissions by the ocean is decreasing surface seawater pH at about a rate of 0.002 units per year (*Feely et al.* (2004); *Sabine et al.* (2004)), but this assimilation rate will vary, as a function of latitudinal and seasonal changes (e.g. *Bates et al.* (2014)). To properly characterize the effect of ocean acidification, it is important to accurately capture these small scale variations, which requires measurements with a precision of 0.002 pH units or better (*Martz et al.* (2010)). In addition, to assess impacts on ocean ecosystems, it is important to monitor ocean pH changes on a global scale; this will only be achieved with the use of autonomous in situ sensors.

The pH of seawater can be used, along with other parameters such as total alkalinity (TA), dissolved inorganic carbon (DIC) or the partial pressure of carbon dioxide (pCO_2) (or a combination of these parameters), to calculate the other species in the carbonate system. However, there are limits to the accuracy of the pH measurements, and the errors associated with the accuracy have to be propagated through the equations used to calculate the rest of the carbonate parameters (*Dickson et al.* (2007)).

The lack of standard protocols for in situ autonomous measurements, combined with the uncertainty and limitations associated with various techniques (*Dickson* (2010)), make it difficult to accurately measure pH of seawater autonomously at a global level.

2.4.2. Measuring principles

There are four main techniques used for pH measurements in the ocean:

Potentiometric electrode cell

This method uses a pH sensitive electrode in combination with a reference electrode. The electric potential E_{pH} of the pH sensitive electrode is related to the pH following the Nernst equation:

$$E_{pH} = E_{ref} + R\,T / F \ln a(H^+) = E_{ref} - \ln 10\, R\,T / F\, pH$$

where $a(H^+)$ is the activity of H^+ ions, R is the gas constant ($8.3145\ J\ K^{-1}\ mol^{-1}$), T is temperature (in Kelvin) and F is the Faraday constant ($96485.33\ C\ mol^{-1}$). The measured voltage difference ($V = E_{pH} - E_{ref}$) to the potential of the reference electrode E_{ref} carries information about the pH.

Glass electrode

This method also uses two electrodes, but the glass electrode is referenced against a solution of stable pH (usually 7). In practice, pH is calculated as follows:

$$pH_X = pH_S + (E_{ref} - E_x) / (RT \ln 10 / F),$$

where pH_S is the pH of a carefully prepared standard (sea water) solution, pH_X is the pH of the sample X of interest, and E_s and E_x are the respective potential differences between the electrodes. This technique is amply used; the YSI EXO sonde is a commercially available sensor using the glass electrode principle. Its main drawbacks for seawater applications are limited accuracy (+/-0.01), sensor drift, irreproducible differences and variations in the reference electrode potential (*SCOR Working Group 75 on Methodology for oceanic CO_2 measurements* (1992)). The need for re-calibration/referencing makes it difficult to use glass electrodes for prolonged autonomous observations.

Liquid (gel) junction and/or junctionless external reference electrode

This potentiometric method uses an ion-selective field effect transistor, ISFET, which consists of a Metal Oxide Semiconductor Field Effect Transistor (MOSFET) that lacks a metal gate electrode over the conduction channel, but instead is covered by a thin insulating material (*Martz et al.* (2010)). The pH at the insulator-solution interface controls the surface charge, which then determines the strength of the electric field in the conduction channel of the FET, located between the source and drain. The ISFET operating principle is described in more detail in *Bergveld* (2003) and *Martz et al.* (2010). One of most commonly used ISFETs in seawater at the moment is a p-channel enhancement mode ISFET, operated at a constant drain source voltage and current, so that by applying a constant drain source voltage, and using a feedback circuit, the drain source current is held constant (*Martz et al.* (2010)). Institutional and commercial implementations of this measurement principle are based on the Honeywell DuraFET "hardware" and called

SeaFET sensor by Sea-Bird Scientific (Satlantic). The SeapHOx instrument is a SeaFET combined with a MicroCAT CTD and SBE63 oxygen optode.

Spectrophotometric Method

Spectrophotometric measurements of open-ocean seawater using pH-sensitive indicator dyes are simple, fast and precise (*Byrne and Breland* (1989)). The spectrophotometric method uses an indicator dye with an appropriate precisely known pKa value, for an expected sample pH, and acceptable extinction coefficient ratios of the singly protonated (HI^-) and fully de-protonated (I^{2-}) forms (*Clayton and Byrne* (1993); *Aßmann et al.* (2011)). Sulfonephtalein indicators exist in three forms, H_2I, HI^-, and I^{2-}, depending on pH, and each form has distinctive absorption characteristics. This technology is available through Sunburst Sensors as the SAMI-pH.

This method offers much higher precision and accuracy compared to the glass electrode (*Dickson* (1993)), and is often used for laboratory measurements of pH used to characterize the carbonate system. This method should not be influenced by drift, and it is highly accurate and precise, only depending on the accurate measurement of salinity and temperature, thereby circumventing problems associated with system calibration (*Aßmann et al.* (2011)).

A common indicator dye used for seawater pH measurements (*Aßmann et al.* (2011); *Seidel et al.* (2008)), *m*-cresol purple (*m*CP; log K1 of about 8.0 at 25°C and salinity = 35), has been shown to be highly accurate and reproducible when purified (*Liu et al.* (2011)). Purified *m*CP was characterized by *Liu et al.* (2011) for a temperature range of 5-35°C and a salinity range of 20-40. To the human eye, mCP as H_2I appears pink, yellow as HI^-, and purple as I^{2-}. At seawater pH ranges, where the H_2I is insignificant, the dye dissociates (second dissociation reaction):

$$\mathrm{HI}^{-}_{(aq)} = \mathrm{H}^{+}_{(aq)} + \mathrm{I}^{2-}_{(aq)} ,$$

where $\mathrm{I}^{2-}_{(aq)}$ is the fully de-protonated form of the indicator dye. pH can be determined according to the following equation, when a spectrometer with 1 nm bandpass detection is used, and includes the salinity and temperature dependence (*Clayton and Byrne* (1993)):

$$\mathrm{p}H_T = -log_{10}(K_2^T e_2) + log_{10}\left(\frac{R-e_1}{e_2-R\frac{e_3}{e_2}}\right),$$

where $-\log(K_2^T e_2) = a + (b/T) + c\ln(T) - dT$; $a = -246.64209 + 0.315971S + 2.8855\times10^{-4}S^2$; $b = 7229.23864 - 7.098137S - 0.057034S^2$; $c = 44.493382 - 0.052711S$; $d = 0.0781344$; $e_1 = -0.007762 + 4.5174\times10^{-5}T$ and $e_3/e_2 = -0.020813 + 2.60262\times10^{-4}(S-35)$. T is in Kelvin and R is the ratio of indicator absorbances ($_{\lambda 2}A/\ _{\lambda 1}A$) at the molar absorptivity maxima. The wavelengths 578 nm and 434 nm correspond to the peak maximum wavelengths for I^{2-} and HI^-, respectively.

In many cases, particularly in situ instruments, 1 nm bandpass spectrometers are not viable for cost, size, and power consumption. In this case, the equations of *DeGrandpre et al.* (2014) can be used:

$$\mathrm{pH_T(sw)} = 1245.69/T + 3.8275 + (2.11 \times 10^{-3})(35\text{-}S) + \log((R\text{-}e_1)/(e_2\text{-}R^*e_3))$$

In this case, the ratios of molar extinction coefficients can be determined on the spectrometer used as $e_1 = {}_{HI}\varepsilon_{\lambda 1}/{}_{HI}\varepsilon_{\lambda 2}$, $e_2 = {}_{I}\varepsilon_{\lambda 1}/{}_{HI}\varepsilon_{\lambda 2}$, and $e_3 = {}_{I}\varepsilon_{\lambda 2}/{}_{HI}\varepsilon_{\lambda 2}$. ${}_{HI}\varepsilon_{\lambda 1}$ is the molar extinction of HI^- at 434 nm, ${}_{HI}\varepsilon_{\lambda 2}$ is the molar extinction of HI^- at 578 nm, ${}_{I}\varepsilon_{\lambda 1}$ is the molar extinction of I^{2-} at 434 nm, and ${}_{I}\varepsilon_{\lambda 2}$ is the molar extinction of I^{2-} at 578 nm. The coefficients for the equation were determined for a temperature range of 0 - 40°C, at salinity = 35. Salinity dependence can be approximated by adding 0.00211(35-S) to the equation (*Clayton and Byrne* (1993)).

pH range is limited by dye choice. In seawater, m-cresol purple dye is usually the choice (pH 7 – 9). For lower pH, phenol red or bromo cresol purple can be used, but these dyes are not as well characterized (*Yao and Byrne* (2001)).

2.4.3. Available Sensors

YSI EXO sonde

https://www.ysi.com/EXO2

The EXO multiparameter sondes (YSI Inc., a Xylem brand, U.S.A) feature several sensor ports (depending on the model) which house a variety of sensors including pH. The EXO pH sensor is a glass electrode type with two electrodes combined into the same probe tip; one as the measuring electrode and the other as the reference electrode (*Snazelle* (2015)).

Figure 2.20. YSI EXO sonde.

SeaFET

http://www.seabird.com/seafet

Figure 2.21. SeaFET.

The SeaFET™ Ocean pH Sensor measures pH potentiometrically. SeaFETs have both an internal and an external reference electrode. Both are chloride-sensitive electrodes: The internal electrode uses an internal gel as reference while the external one uses the ambient seawater with known (measured!) salinity and a conservative relation between salinity and Cl^- as well as HSO_4^- concentration. For both electrode systems, pH From Internal Cell (FET|INT) and pH From External Cell (FET|EXT), the reference electrode-source voltage E follows a Nernst equation form:

$$E = E^* - S_{Nernst} \log(a(Cl^-)\, a(H^+)) \text{ or}$$

$$E = E^* - S_{Nernst} \log(\gamma(Cl^-)\,\gamma(H^+)) - S \log(m(Cl^-)\,m(H^+))$$

(*Martz et al.* (2010))

with $S_{Nernst} = RT \ln 10 / F$. The term E^* includes the characteristics of the two half cells, e.g., the differences between the standard potentials (E_{0pH}, $E_{0,INT}$ or $E_{0,EXT}$, etc.) and, as such, depends only on temperature and pressure but not the concentrations of the analyte (*Martz et al.* (2010)).

In the SeaFET manual (V 1.2.4), the electrode-source voltage E and E* are labeled V and V*. For the SeaFETs, V^*_{INT} is parameterized as a linear function of temperature (SeaFET manual, V1.2.4). The Cl^- activity for the ion-sensitive internal electrode is set by the internal gel and thus (ideally) a constant (included in k_{0i}). The activity coefficient γ of H^+ in seawater is also included in the relation used in the sensors, i.e.,

$$V^*_{INT} = k_{0i} + k_{2i}\,T + S_{Nernst} \log(m_{INT,gel}(Cl^-)) + S_{Nernst} \log(\gamma_{INT,gel}(Cl^-)\,\gamma_{SW}(H^+))$$

Combination with equation above from *Martz et al.* (2010) yields:

$$pH_{INT} = (V - k_{0i} - k_{2i}\,T) / S_{Nernst}$$

for the pH based on measurements of the potential difference for the cell FET|INT.
V^*_{EXT} for the external electrode follows

$$V^*_{EXT} = k_{0i} + k_{2i}\,T + S_{Nernst} \log(1 + S_T/K_S) - S_{Nernst} \log(\gamma_{SW}(Cl^-)\,\gamma_{SW}(H^+))$$

where S_T is the total sulfate in seawater and K_S is the acid dissociation constant of HSO_4^-. In combination with equation (eq:cell voltage) this yields

$$pH_{EXT} = (V - k_{0i} - k_{2i}\,T) / S_{Nernst} + \log(m_{SW}(Cl^-)) + 2 \log(\gamma_{SW}(Cl^-)\,\gamma_{SW}(H^+)) - \log(1 + S_T/K_S)$$

for the pH based on measurements of the potential difference for the cell FET|EXT.

While these sensors are accurate and reliable, they require considerable care (for example, several days' equilibration to sample conditions, frequent cleaning, etc.).

SAMI-pH

http://www.sunburstsensors.com/products/oceanographic-ph-sensor.html

The SAMI-pH (Submersible Autonomous Moored Instrument) measures pH by absorbance by mixing seawater with an indicator dye (metacresol purple).

2.4.4. Sensor deployment

General considerations:

- With pH, it is necessary to know on what pH scale the sensor data will be reported (for example NBS scale for EXO and Total pH scale for SeaFET and SAMI). It has been recommended that pH studies of the ocean be reported using the total hydrogen ion concentration scale (*Dickson* (1984); (1993)).
- If ancillary data, such as T, S, depth, are not being measured within the same sensor (such as with the YSI sonde where these are available alongside the EXO pH), then it is critical to make these measurements using another sensor deployed simultaneously. This should be noted in the metadata.
- Oxygen is a useful variable for data quality checks and is suggested as an additional measurement, if one is not already available (e.g. CTD and oxygen are integrated into the SeapHOX)
- It is convenient to log ancillary data with the same time stamp (this is further discussed in the 'ancillary data requirements' section below).

Figure 2.22. SAMI-pH (Photo from Sunburst Sensors, LLC).

EXO2

Internal-signal conditioning electronics improve the response and stability of the pH sensor, and electronic buffering in the pH sensor head reduces measurement noise (*Snazelle* (2015)).

SeaFET and SeapHOx

General housekeeping

- Make sure to replace the batteries before a long deployment. See note regarding warm-up time after a battery change in the *Conditioning time* (below). Make sure to plan the mission according to how much battery life you have.
- Sync clock to accurate time and make a decision if you want to record in UTC time.
- If you are logging data, make sure there is enough space in the hard drive of the sensor.
- Before deployment, check that your sensor has been calibrated or check for drift before and after deployment.
- Measurements of salinity and temperature are required for processing data for the SeaFET and SeapHOx. While these parameters are already measured by the SeapHOx, the SeaFET requires that additional sensors are mounted nearby to measure these variables.
- It is important to recalibrate the SeaFET instruments at appropriate salinities (i.e. salinities of the deployment location) prior to the deployment.

- If testing TRIS-buffer solutions in the lab with SeaFET sensors, use one that is made with bromide.

Conditioning time (from Bresnahan et al. (2014))

- The chloride ion selection electrode requires some conditioning time (about a week or more) in seawater prior to deployment (?). This conditioning time can be reduced by filling the storage cap with "local" seawater (collected from the deployment site).
- The ISFET requires continuous power to keep itself activated; removal of batteries even for a few minutes will require a restart of the activation period. Make sure to place batteries inside the SeaFET or SeapHOx instruments at least a few days before deployment. If batteries are removed, the sensors will still work, but it will take several days before the pH readings stabilize.

Mounting

- The SeaFET and SeapHOx instruments can be mounted vertically or horizontally; however, it is recommended to have an unpumped sensor mounted facing downward or a pumped version facing upwards. Below are some of the reasons for these recommendations.
- Sun sensitivity. Since the ISFET is sensitive to light, it should be shaded, either by mounting it vertically facing down, shading it in some other way, or by using the pumped cap.
- Sediment deposition. If mounted vertically facing up, and a pump is not available, there could be increased biofouling around the sensor due to sediment deposition. When a pump is not available, mounting the sensor facing down should reduce sediment deposition.
- Pump in/out water flow locations. Pumped systems are available for SeaFET and SeapHOx. They help to obtain faster response times and can reduce fouling. If a pump is used, it should be mounted so that it does not output water near other sensors on the same or a nearby frame. If an anti-biofouling system such as copper/nickel tubing or tributyltin is in place, water should be pumped through that system before pumping it across or past the SeaFET or SeapHOx.
- Air bubbles. Air bubbles will affect pH measurements. The plumbing system, if one is used, should have a method to minimize air bubbles. This can be achieved by using a *U* shaped tube with a hole at the top after the water intake and above the sensor; this tube will let the air bubbles escape before reaching the sensors. When using a pumped system, it is recommended to have the SeaFET or SeapHOx mounted facing up to minimize bubbles.

SAMI-pH

Preparing the SAMI-pH for deployment

- The sensor should arrive from the manufacturer ready for deployment, but with a bag containing nanopure (DI) water. In case the copper fouling guard is not wrapped around the central sampling area, wrap it in place and secure it with cable ties, being careful not to bend the inlet and outlet tubing.

- If the SAMI was previously deployed, and the nanopure bag is not attached, attach the reflective bag containing nanopure DI water (or "blank") to the inlet tubing. To program the instrument for deployment, connect your computer to the instrument using the non-submersible cable, open the proprietary SAMI software *Client*, and click on the "Serial Open" button to connect to the instrument. If you haven't connected previously to a SAMI-pH using the *Client*, you may need to also install a USB serial driver that is also available from the manufacturer.
- At first, observe whether the "Erase" button in the "Control" panel is activated. If so, it means that the data from the previous mission that were internally logged are still loaded. <u>They must be erased before a new mission is programmed</u>. Select "Download," <u>save the data file</u> (if you haven't done so already), and then "Erase."
- Next, select the "Utility" tab and look for the Cycle pump box at the bottom right corner of the window. Run the flushing routine, consisting of 50-55 cycles, to thoroughly flush the flow volume with Nanopure DI. Check the outlet tubing for a steady drip to ensure that the flow path is now free of air.
- When the flushing cycle is complete, proceed to the "Settings" tab to program the start time and the mission duration. <u>Make sure you program ample time before the start of the mission to deploy the package.</u> The SAMI must be in the water before sampling begins in order to ensure that the sample pump functions. Also, ensure the "Run duration" is set at the necessary length to ensure it covers the mission duration.
- The next aspect to program is the sampling interval. <u>This is very deployment specific, and depends on questions like</u>: how dynamic is the system in which the sampling is being carried out? What type of temporal resolution is required to answer the scientific questions driving the deployment? Reagent volume and battery power will limit either the mission duration or the sampling frequency, with the power running out well before reagent. According to the manufacturer, hourly measurements at 25 ^{o}C will allow for a 234-day deployment, which is ~5000 measurements. (*http://www.sunburstsensors.com/products/oceanographic-ph-sensor.html*).
- You may now begin the mission by selecting the "Launch" button in the "Control" tab. When you do so, the configuration data will be displayed and you have the opportunity to save them as a separate file. <u>Always do so;</u> this will be important metadata.
- Finally, disconnect with the instrument by clicking on the "Serial Close" button, remove the connection cable and replace with the dummy plug. Before deploying it in the water, <u>it is recommended that you click on the "Sample" button on the Utility tab to witness that the SAMI-pH runs properly.</u> It will draw a "sample" from the nanopure bag and dispense the reacted sample through the outlet tubing. The whole procedure should last approximately 3 min. <u>Before deploying the SAMI be sure to remove the nanopure bag from the inlet (otherwise you will not collect any samples). Once the nanopure bag is removed, it is important to be</u>

sure the SAMI is in the water before the measurements begin. If the SAMI draws in air, the pump can lock up, and can remain locked for the entire deployment.

SAMI mounting, deployment, retrieval and redeployment

- The SAMI-pH measures 55 cm in length and 15.2 cm in diameter and weighs about 7.6 kg. Therefore, it requires robust frame support or mounting in a cage with a flat bottom. Attention must be paid to ensure that the inlet tubing is not jammed and is preferably pointed towards the exterior of the package. The flexible outlet tubing must also be unjammed and its opening free. The SAMI can be deployed in any orientation.
- Before deploying, you must remove the nanopure DI bag from the inlet tubing, squeezing gently to avoid introducing any air in the flow path. Because of this, you should program the SAMI to start well after it is under water.
- Upon retrieval:
  - Immediately attach the nanopure DI reflective bag to the inlet tubing,
  - Dry the connector bulkhead of the instrument thoroughly, remove the dummy plug and connect your computer to the instrument
  - Click on the "Serial Open" button and establish connection (details on how to communicate with the sensor can be found in the previous section)
  - Stop the instrument sampling
  - Download the data to your computer and back it up onto a flash drive
  - Flush the flow path with DI using the flushing routine (under the "Utility" tab).
- After these steps, if you wish to re-deploy the instrument, follow the steps in the previous section.

Important considerations and best practices for the SAMI -pH

- Calibration is an issue in the case of coastal regions, where influx of freshwater may drive salinity below the calibration minimum (calibrated for S=25-40).
- As the name suggests, SAMI-pH is a moored instrument, and not recommended for profiling. The fastest measurement frequency is 1 min^{-1}, developed recently for the X-prize competition (2015). If needed, the SAMI-pH can be used for profiles, but it is recommended that the sensor is held at each desired depth for 3 min or more to accommodate for its "slow" response time (see following section).
- Impurities in the m-cresol purple reagent may be a problem, and they have to be considered if the precision (as determined by comparison with discrete sample measurements) is not good enough for a desired application.
- Sunburst Sensors is now providing purified mCP with all SAMI-pH units.
- The manufacturer does not have a mature solution for salinity corrections. It currently consists of a stand-alone Matlab app that often times fails to load and operate on a number of users' computers (e.g. during the IOCCP sensor course in June 2015 at Kristineberg, Sweden). However, is open ocean applications, where salinity deviates < 0.5 PSU, a constant salinity can be used to process pH data, using the SAMI Client software.

2.4.5. Sensor calibration and validation

Discrete samples (external calibration)

When possible, take frequent discrete samples alongside a sensor throughout a deployment in order to establish an error estimate in the sensor data. Preferentially, discrete pH samples would be measured using benchtop spectrophotometry following the Standard Operating Procedure (*Dickson et al.* (2007)) updated by *Liu et al.* (2011) using purified indicator. If the pH is instead calculated from any combination of the three other parameters (TA, DIC, or pCO_2), care should be taken since this adds to the overall uncertainty of the discrete pH (*Millero et al.* (2007)), which can be difficult to fully assess. TA and DIC are recommended for ship-based surveys when only two of the carbon parameters are measured (*Orr* (2009)). This recommendation is largely because of the Certified Reference Material (CRM) program for ocean CO_2 measurements (*Dickson et al.* (2003)), where the periodic analysis of a CRM allows for assessing the accuracy for DIC and TA measurements. Furthermore, TA and DIC are state variables in biogeochemical modelling due to their conservative behaviour. It is recommended to always over-determine the marine CO_2 system by measuring more than two parameters.

General recommendations

- Collect duplicate samples when possible, and routinely calculate the analytical precision for each duplicate sample (run several times)
- Utilize CO2SYS (*https://www.nodc.noaa.gov/ocads/oceans/CO2SYS/co2rprt.html*) for calculations of the DIC system.
- Always take into consideration possible processing/sample collection errors.
- If possible, utilize CRMs.
- Always know the pH scale that your instrument reports on
- Check analytical equipment performance for ambient temperature sensitivity

2.4.6. Retrieving the data, data and metadata reporting

Data correction & processing of potentiometric sensor data (e.g. SeaFET)

- In order to obtain high quality data from ISFET sensors, accurate temperature and salinity are required for processing raw sensor data. Therefore, it is recommended to couple ISFET probes with CTD sensors during deployment. For instance, instruments like the Sea-Bird Scientific (Satlantic) SeapHOx with integrated temperature and salinity data automatically reprocesses potentiometric measurements internally. Thus, if planning to deploy stand-alone ISFET probes, always make sure that accurate CTD data are being recorded in close proximity to the deployment location.
- For Sea-Bird Scientific (Satlantic) ISFET and SeapHOx instruments, software for data retrieval and reprocessing (e.g., salinity correction of the external reference electrode) is provided by the manufacturer. Data processed by this software already accounts for the factory calibration as well as for the salinity correction if

appropriate salinity data is being provided. However, within the scientific community, processing tools for Matlab and Excel software exist and are freely accessible (e.g. *Bresnahan et al.* (2014)*, suppl. material*). Such tools can be used to recalibrate or readjust sensor response in case of changes in factory calibration due to drift or unknown processes.

- External vs. internal reference electrode comparison on SeaFET is a useful parameter to track instrument drift, possible fouling, and malfunction of the electrodes. It is expected that a small difference between the internal and external junction in the ISFET would indicate proper initial calibration and lack of fouling. If there is a larger offset in processed data, but the offset does not change, this may indicate that calibration may need to be redone (see above). A changing offset between both electrodes after the reference electrode has been conditioned to ambient settings can be an indicator for ongoing biofouling processes.
- Calibrations provided by manufacturers should be treated as a "first guess" for true pH values. Even if an instrument just left factory and is being deployed soon after, <u>it is recommended to always accompany an instrument deployment with regular discrete pH samples.</u> The discrete samples should be taken at a range of temperatures and salinities, if possible, to evaluate different conditions.
- With a single-point calibration (in time) of raw sensor data (E*), the accuracy of the instrument data can be increased significantly (for details refer to *Bresnahan et al.* (2014)). In highly dynamic environments, a sufficiently high number of reference samples should be assured in order to average out any potential mismatches in time between instrument data and reference samples.
- Caution should be taken when applying corrections for data when the pH sensors (SeaFET sensor) passes quickly through a thermocline

FIGURE 2.23 and FIGURE 2.24 show examples of unprocessed and corrected SeaFET sensors, and illustrates the importance of utilizing ancillary measurements such as in situ salinity and DIC.

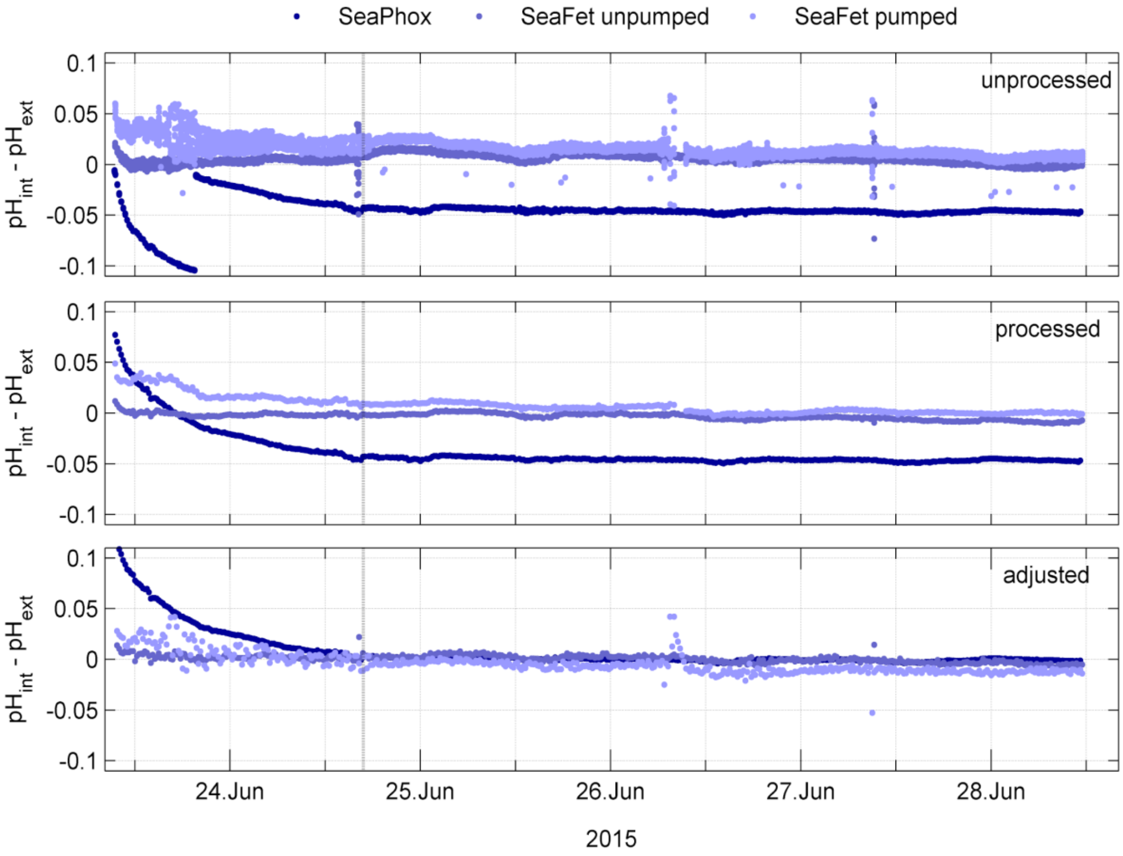

Figure 2.23. Differences between processed pH data based on the internal and the external reference electrodes collected during the IOCCP sensor course in June 2015 at Kristineberg, Sweden.
Three different ISFET sensors were used during deployment. Data prior to the date indicated by the vertical black dotted line are biased by air bubbles trapped in the pumped SEAFET.

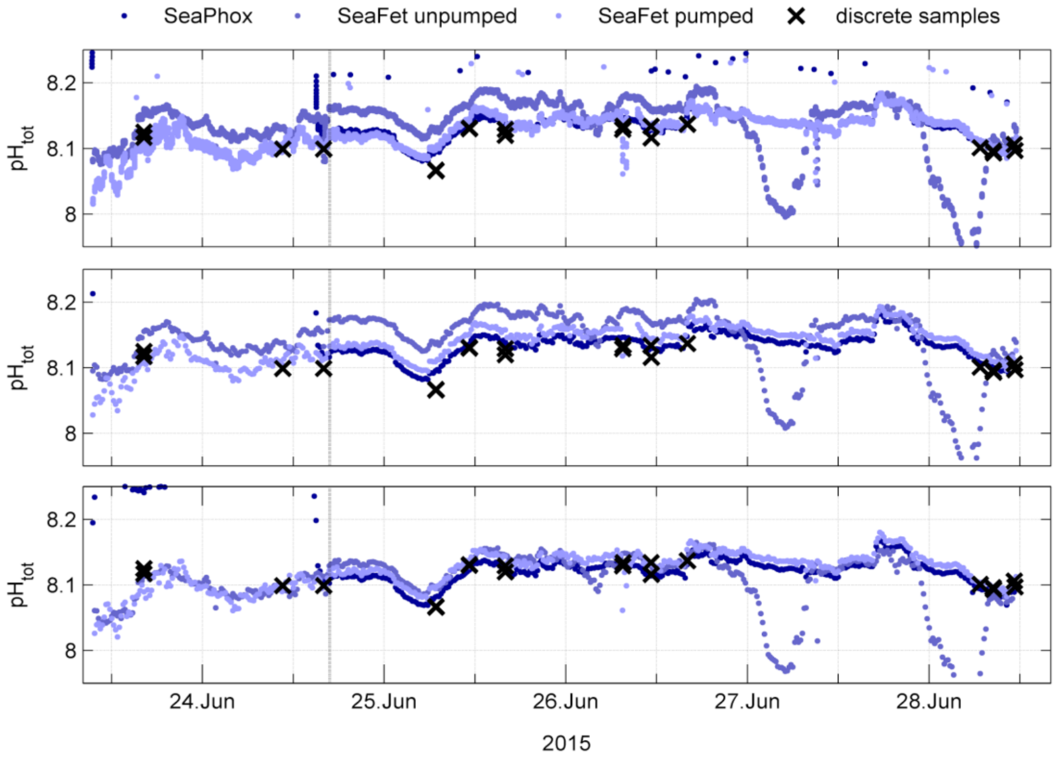

Figure 2.24. Data for all three SeaFET sensors collected during the IOCCP sensor course in June 2015 at Kristineberg, Sweden.

Top panel shows data without applying any corrections; middle panel shows data after recommended post-processing by using accompanying salinity measurements. Bottom panel shows data adjusted to collected reference samples derived from in situ DIC and TA measurements (Lueker et al. (2000)). Note: Biased data were not fully displayed in order to sufficiently illustrate remaining data of better quality.

SAMI data processing

In the previous sections, it was mentioned that the raw data can be downloaded readily from the instruments using the SAMI Client. The raw data need to be corrected for variations in temperature and salinity before generating usable pH values. Temperature is measured on-board the SAMI, therefore all pH measurements are correct for in situ temperature. These corrections may be carried out by the SAMI Client only if the SAMI-pH is interfaced with a CTD during the mission.

If the SAMI-pH is not interfaced with a CTD, the corrections for both salinity and temperature have to be performed with a manufacturer-supplied Matlab stand-alone application using the temperature recorded by each SAMI-pH and the salinity recorded from another sensor (for example a Seabird or YSI CTD). The salinity record can be supplied as a file (various formats are acceptable, including txt, csv, etc.), but the data must be formatted in three columns (or tab-delimited) as follows:

MM/DD/YY HH:MM:SS [Salinity]

The final data processing takes place at the user's discretion using software of choice. Two main necessary steps are:

- The removal of any data points generated while the SAMI was out of the water, on the dock and the inlet tubing connected to the Nanopure foil-bag,
- The removal of any major outliers that lie well outside the range of values over the duration of the deployment.
- The Matlab routine provides flags for potentially inaccurate data points.

If the SAMIs are retrieved from the water and re-deployed several instances during the deployment, resulting in multiple data files, it is recommended that the different data packages be combined in MS Excel or any other program prior to the processing of the data. The following steps should be carried out:

- Inspect the salinity and temperature-compensated pH time-series (FIGURE 2.25A).
- Identify the measurements flagged by the SAMI App; these mostly consist of anomalously pH instances and values marked as NaN by the SAMI app, typically coincident with periods when the package is out of the water and the Nanopure water bags are connected to the inlet tubing (FIGURE 2.25B), or cases where the pump has malfunctioned, air bubbles or particles are in the optical path, or the SAMI has run out of reagent. These data points should be removed from the time-series.
- Identify extreme outliers (8 for T0031 and 1 for Xprize) that lie several standard deviations away from a broad moving median as well as the general range of pH expected/observed for the location and removed them (FIGURE 2.25C).
- Produce the final data file by extracting the final time-series.

TABLE 2.3. shows examples of the types of files generated/used during a SAMI mission.

Table 2.3. Types of files generated/used during a SAMI mission.
The date stamps [DDMMYY] for the configuration file and raw data file correspond to the date of file creation, while the date stamp of the salinity and temperature-compensated file corresponds to the date of creation of the raw data file.

File type	File name structure	Generated by
Configuration file	SAMI_Cfg_[Serial no.]_[DDMMYY]	SAMI Client
Raw data file	SAMI_[Serial no.]_[DDMMYY]	SAMI Client
Salinity data file*	User-determined	User
S compensated data file	SAMI_[Serial no.]_[DDMMYY]_out	SAMI App
QC/final data file(s)	User-determined	User

** Applies in the case where a CTD isn't interfaced with the SAMI-pH*

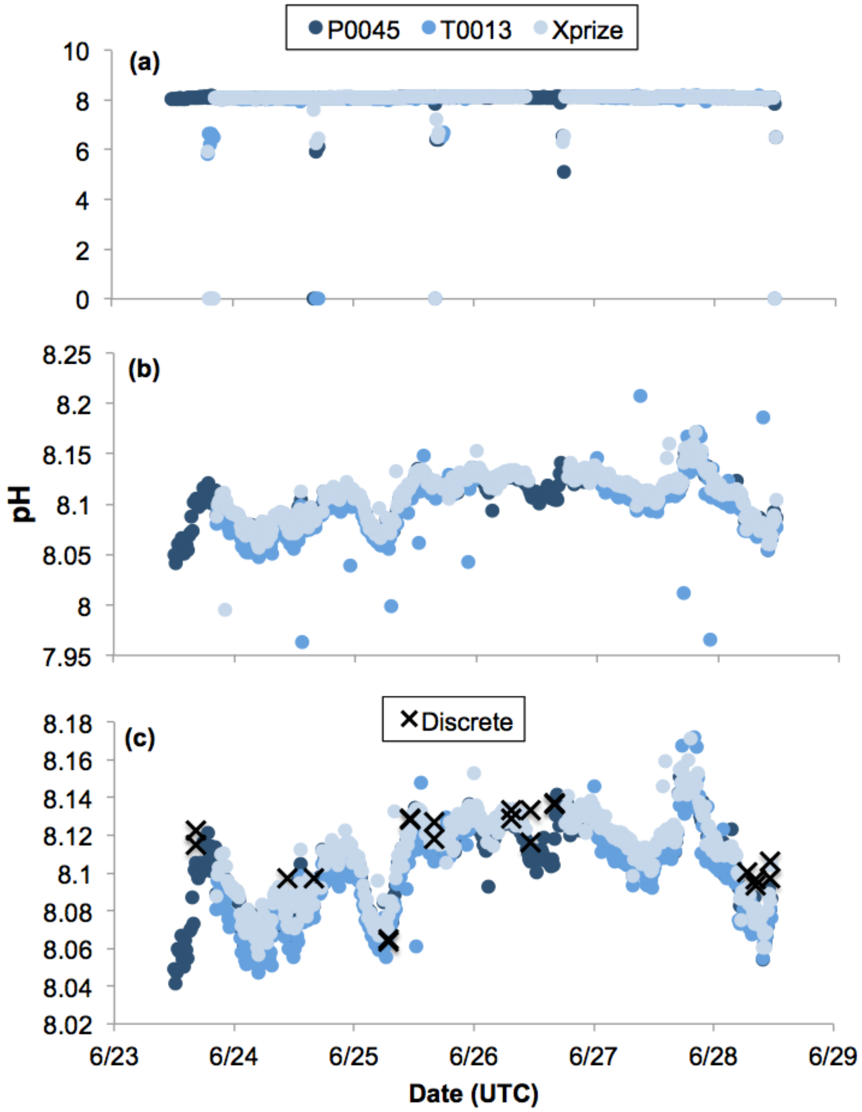

Figure 2.25. Example of a time-series of pH values from three SAMI-pH instruments collected during the IOCCP sensor course in June 2015 at Kristineberg, Sweden.

(a) Salinity-compensated data generated by the SAMI Matlab App; (b) Data in (a) with out-of-the-water (flagged) data removed; (c) Data in (b) with major outliers removed; X denotes discrete samples.

EXO2 data processing

For the EXO2 sonde, the manufacturer provides a software that retrieves the data from the instrument and applies the factory calibration to the data. However, pre-deployment adjustment of sensor response can be carried out with the software by measuring a buffer solution of known pH prior to deployment. The data are output on NBS pH scale. There is no direct conversion from NBS scale to total hydrogen ion concentration scale.

2.4.7. Choosing the Right Sensor for the Job

There are a variety of technologies from different manufacturers that can be used to measure pH in water. The sensors outlined below do not include an exhaustive list of option; it is made as to exemplify the steps suggested to make an intelligent choice on the type of technology that best suits the specific application for which the sensor is needed. In this case, three types of pH sensors are outlined below (TABLE 2.4), which were those used in the IOCCP sensors course conducted in June 2015. These include 3 measurement techniques (colorimetric, ISFET & glass electrodes, and a foil based emerging technology).

The specifications summarized were taken from the manufacturer websites. *This is a useful starting point in matching up your choice of sensor to the environment it will be used in* (e.g.: freshwater or marine) *and the platform, where it will be mounted* (e.g. deployment as a profiling sensor vs. deployment on a mooring at a single depth), *prior to purchasing*. From this we can assess applicability of each measurement type in a general sense. It is also possible that the manufacturers can amend these specifications if there was a requirement (e.g.: deep ISFET or 1-minute sampling SAMI).

Of course, a primary requirement may be cost versus data quality. There is a choice to be made between acquiring many low-cost sensors (e.g. larger spatial coverage) or one expensive one. It will all depend on your scientific question(s). Likewise, the power requirements on your platform may influence your choice of sensor and this needs to be considered before any purchase.

It is important to consider that the website specifications may be a 'best case scenario'. Manufacturers accuracy and precision are usually determined using laboratory standards and controlled environment. In situ measurements involve many uncontrolled variables, and will not result in the same degree of accuracy or precision. All sensors have been assessed and calibrated in different ways by the manufacturers and by various users (e.g. *Martz et al.* (2010); *Bresnahan et al.* (2014)). Independent validation should still be done for each research environment. A table such as the one below (TABLE 2.4) is still a good way to inform your choice for initial purchase. This type of comparative information of different types of sensors has also been collated by international groups such as ECO2 (*http://www.eco2-project.eu/home.html*).

If available, user experiences should be added to this type of table as it will amend the 'ideal' specifications to reflect real performance in the field. For example, another requirement may be 'ease of use'; it is not sufficient to refer to a scientific paper in order to make adjustments to site-specific data in all instances if you have a requirement for an 'instant' result. Likewise, access to the raw data is needed if you wish to apply your own calibration.

Table 2.4. Comparative table of pH sensors and their capabilities.

	SAMI (3)	**SeaFET** (1, 2)	**EXO** (4)
Sensor Method	Spectrophoto-meteric	ISFET	Glass electrode
Depth range (m)	0-600 0-3000m (Ti housing)	0-50	0-250
Quoted accuracy	+/-0.003	0.02 (1) 0.05 (2)	0.1 (if within 10 deg of cal) or 0.2 full range
Quoted Precision	<0.001	0.004 (1) < 0.001 pH (when averaging is applied)(2)	
Stability	<0.001/month?	0.001 pH/month (1) 0.003 pH/month (2)	
Salinity range	25-40	20-40	0-40
pH range	7 – 9	6.5-9	0-14
Temp range (°C)	0 - 40	0-50	-5-50
pH Scale	Total Hydrogen ion	Total Hydrogen ion?	NBS
Response time			
Sample Rate (seconds)	180	1 (averaged of 10 acquisition at 10Hz)	<3
Depth Profiling	YES	YES	YES
Duration (days)	~5,000 measurements @25deg C	365 (depends on frequency)	90 (when sampling every 15 minutes at 20°C)
Stability	<0.003/month Reagent life: 1 year	0.003 pH/month (1) 0.005 pH/month (2)	Significant Drift (Potential)
Conditioning Time	~2-6 hours, depending on Temp change	≤ 1 week, depending on salinity change and pre-conditioning	

(1) : Current datasheet available from *http://www.seabird.com/document/seafet%E2%84%A2-ocean-ph-sensor-datasheet*

(2): Current version of the manual available from *http://www.seabird.com/document/seafet-manual*

(3): *http://www.sunburstsensors.com/products/oceanographic-ph-sensor.html*

(4): *https://www.ysi.com/EXO2*

3. Biofouling

Biofouling in the ocean is the colonization of a submerged surface, first by marine microorganisms (e.g. bacteria, biofilms, invertebrate larvae, spores, etc.), and later by macrofouling species (e.g. barnacles, macroalgae, hydrozoids, etc.). Biofouling can cause severe disruptions to the functioning of underwater equipment by increasing drag, reducing heat transfer efficiency, degrading membranes, impeding mechanical functioning of moving parts, and for optical instrumentation, blocking the instrument's field of view, producing/consuming species to me measured (e.g. O_2 or CO_2).

Several antifouling techniques have been developed to minimize the impact of biofouling on submerged instrumentation, including materials and coatings to remove or prevent the growth of organisms, as well as mechanical devices that reduce the potential fouling. In this section, we provide examples of biofouling and summarize some of the possible antifouling solutions. We will also briefly discuss the impact of fouling on data collection. Indeed, biofouling not only hinders the functioning of sensors, but also affects the data obtained. Determining when to stop trusting the data because of biofouling is critical to ensure high-quality results. The information compiled in this section is a distillation of the experience of the IOCCP Kristineberg course participants and instructors.

3.1. Biofouling prevention techniques

Biofouling can come from a variety of organisms including tunicates, hydroids, barnacles, oysters, etc. A comprehensive list of major organisms responsible for biofouling in different geographical areas is available from a report on Joint European Research Infrastructure network for Coastal Observatories (JERICO) Biofouling Monitoring Program (BMP) (*Faimali et al.* (2016a)). Some techniques to prevent or slow down biofouling include:

- Place copper nickel tubing upstream to protect the sensor
- In the water, silicone has a long residence time and can help slow down biofouling
- Antifouling paint can help, as can copper tape on the sensor. Copper oxide is no longer useful for biofouling. If you use copper tape on metal (titanium optode), place another tape underneath or plastic wrapper to protect the sensor
- Wrap your sensor in tape – this does not prevent biofouling but facilitates sensor cleaning
- Regularly wiping a sensor improves optics (e.g., using wipers that clean the sensor on a regular time interval, depending on place of deployment)
- Diaper rash cream (zinc oxide) helps with fouling for a couple of months (has been successfully used on Acoustic Doppler Current Profilers (ADCPs))
- For instruments deployed on the bottom, a filter sock keeps sand out
- For instruments installed in a ferrybox station, acidify the water once in a while to avoid barnacle growth inside the debubbler

- Run vinegar through flowthrough systems for about a minute to clean itPhosphoric acid and oxalic acid solutions work well for removing rust
- Pumped sensors are generally better than unpumped because of water flow; taking advantage of auxiliary data helps assess instrument performance and subsequently, data quality
- Brass guards can be useful, but macrofouling organisms sometimes can bypass the brass guards and take up residence inside the instrument
- To avoid galvanic corrosion, add an anode; alternatively, fiberglass or Teflon tape can be used (for example to isolate the brush of a SUNA) if an anode is unavailable.

A comprehensive overview of biofouling prevention practices and recommendation for best practices and methodologies can be found in the JERICO Report on Biofouling Prevention Methods (*Faimali et al.* (2016b)).

3.2. Biofouled data: To use or not to use?

While it can be relatively straightforward to determine when data quality has been compromised due to biofouling, sometimes it is difficult to differentiate real signal from the effects of biofouling. As a general guideline, when faced with a biofouling situation, data are more likely to be salvageable if a robust relationship is observed between different parameters in the data set. Sometimes, it is possible to estimate the start point and time period of fouling from the sensor data (FIGURE 3.1), which can be useful for planning sensor protection measures and length of deployment. However, other contributors to variability in the data must be taken into account and it is important to know the controls and processes at work in the environment being measured as well as available tools to validate sensor performance.

In terms of data, it is important to go through it with care, as sometimes a strange data point may not necessarily be biofouling. For example, with intermittent calcification events, estimates of total alkalinity will not reflect accurately water alkalinity. The difference is due to a natural event which can provide information about a process, but there will be differences between proxy and sensor. As a rule of thumb, know your environment and the tools available for validating sensor performance. For example, in coral reef areas, it is difficult to do alkalinity proxies with salinity, because there is too much calcium carbonate. The same is true for coastal waters because of the amount of freshwater present. Hence, some proxies cannot be used in coastal waters, only in the open ocean.

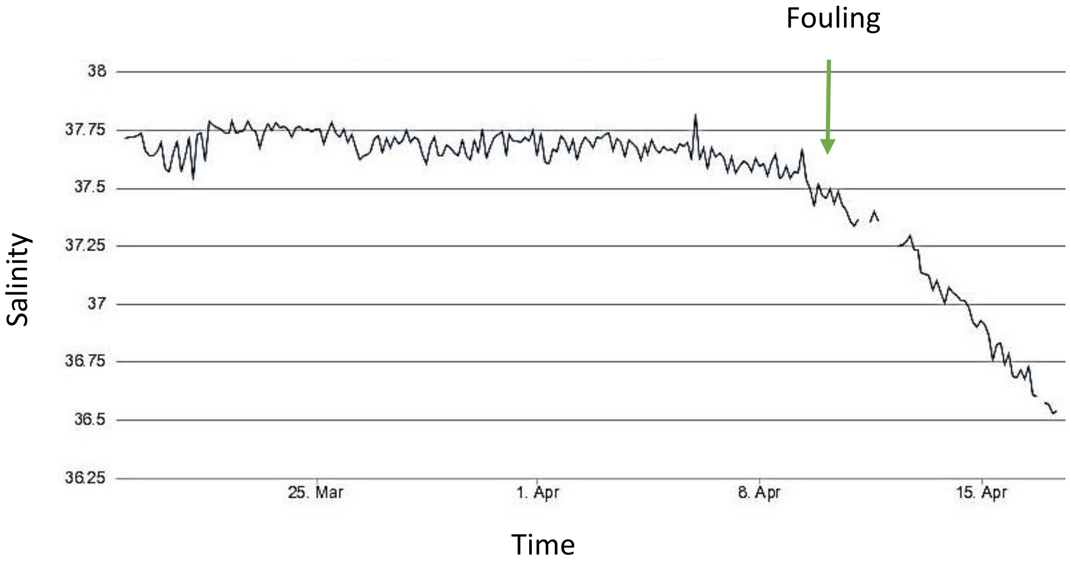

Figure 3.1. An example estimate of the start point and time period of fouling from the sensor data. Source: course materials.

4. General Tips and Recommendations

OMG! I forgot my dummy plugs!
<u>Don't panic</u>! Depending on the deployment type, there are several options you may have. <u>If a deployment is critical</u>, you can makeshift dummy plugs with silicone grease and electrical tape or tubing (bent in two). If you have dummy plugs that partially can fit your plug, you can still use these and grease the unprotected holes. <u>If a deployment is not critical</u>, you probably want to consider deploying at a later time.

<u>Consider having a field kit</u> to take with you whenever you go to a deployment. This kit should at the very least contain: dummy plugs (that match your instrument), silicone grease, electrical tape, etc.

Data is a snapshot; you cannot go back and measure the same exact thing. It's an expensive thing to maintain and time consuming. Therefore, Metadata is critical! Metadata is most useful when it provides the means to intercompare parameters.

Be sure to <u>ALWAYS</u> report your <u>metadata</u> – what sensor was used, accuracy, manufacturer uncertainty, calibration details (pre and post), standards, etc. Otherwise, there is no way you can intercompare measurements with other locations.

- Always mention where the variable was measured (e.g. CO_2 in water, air, ice, etc.).
- For nutrients it's important how you do your standards, so this is something that should be reported in the metadata, whether you're using standards, a certain method (E.g. GO-SHIP nutrient method), etc.

<u>There is nothing routine about making routine measurements.</u>

<u>Careful with manufacturer specifications!!</u> Do they give field or lab specifications? Is the response time in air or water? As a buyer, you look at the spec sheets provided and the price to make a decision. Thus, it's important to know this information.

OMG! I am in the field and need to calibrate my oxygen sensor!
If you don't have any chemicals, you can boil water for some time; put the boiled water in a glass vial and let it cool off. Put the sensor in that water and calibrate it. You can alternatively use yeast and sugar; that will consume the oxygen really quickly. If you work in an environment that has anoxic water, you can use a sample from those waters and use that as your reference zero (it should smell like sulfide).

When you test a platform/sensor, <u>test it in the configuration it will be deployed in!</u> Test the sensor extensively in the lab, then integrate it on the platform you plan to deploy it in and test it again.

One hair or piece of dirt can ruin your entire data set and destroy your instrument. Make sure you clean the connectors constantly and well.

O_2 sensors on the shelf drift intrinsically because of the technology. Be sure you know this and make appropriate pre-calibrations before you deploy. Don't take the specification sheet for granted!

All sensors drift; thus, comprehensive pre-and-post deployment calibrations, and in situ measurements are critical. <u>It is important to see the data as it comes out of the instrument</u>, and know that there's no automatic adjustment inside the sensor.
You can apply the zeroing and the post-calibration to correct for the data and get them to the zero line.

How good is good enough? It depends on the question; quality should be based on the set of requirements.

Nitrate sensors can also serve as sulfide sensors! Nitrate has a modest absorption band in the UV (217nm). Sulfide in this same range is about 10 times more absorbent than NO_3. Bromide also absorbs strongly in the UV.

If you are calibrating your own oxygen sensor, you need to be aware how pressure changes in your lab; do not use vacuum pump, as they create high overpressure. Aquarium pumps work well. Before any calibration, put your sensors in water so that they are wet.

Can I use the temperature from my Optode? Make an educated decision; the response time of the temperature sensors can be different. This is especially true depending on the application – on a mooring, using Optode temperature may be OK, because of slow ambient changes (and slow response time). On a profiler, Optode is of slower response, thus you may want temperature from a CTD. This is also true during the initial calibration of the sensors.

When you have multiple sensors, make sure all clocks are synchronized, and when possible characterize how each clock is drifting individually. This is especially important for long deployments.

Having multiple sensors allows for a better quality control of the data. Having multiple ways of measuring one parameter (auxiliary sensors) allows you to see which data is good.

Air calibrations are a way to track instrument response, and to keep instrument clean. Water calibrations are good, as long as you can find good water.

Optical instruments are particularly sensitive to how you mount them; do not bracket them at the bottom, because you may change the alignment. It is preferable to calibrate the instrument on the frame, and if it needs purging, take to depth to do so, to ensure no bubbles are left in the system.

Always look at the data in more than one way, and <u>always look at the voltages first!</u> And remember that there is also a good amount of sensor warmup time, which can be seen in the voltage.

Air calibrations are a way to track instrument response, and to keep instrument clean. Water calibrations are good, as long as you can find good water.

For instruments that have a tube intake, use black tubing and copper tubing at the entrance to reduce biofouling.

Most users just want a number, but look at the rest of the data! For nitrate, LOOK at each spectrum! You will do a disservice to yourself if you don't. Stray light is a significant problem that limits instrument accuracy at high absorbances.

A sensor does not measure concentration; it gives an estimate of what it thinks a concentration is, and while estimates can be negative, concentrations cannot. Removing negative values will bias your data in unhelpful ways (left censoring).

Relevant readings

The Alliance for Coastal Technologies has issued several sensor reports, including nutrients, oxygen, pH and pCO2. *http://www.act-us.info/evaluations.php*

The USGS published in 2015 a report on field testing and performance of nitrate measuring technologies (*https://pubs.er.usgs.gov/publication/ofr20151065*).

Do we really need detection limits? (Michael Thompson; *http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.125.88&rep=rep1&type=pdf*)

5. New Sensors on the Horizon

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The main focus for enhancement of the current biogeochemistry observing system is on sensor technology development. The sensor suite that is now available and tested throughout the array of autonomous and moored platforms (oxygen, pH, nitrate, chlorophyll fluorescence and backscattering and downwelling irradiance sensors) is hardly sufficient to address the needs and questions driving the requirements for observations described above. These biogeochemical sensors are a relatively recent development and reflect the rapid expansion of technological capabilities that has been enabled by the development of electronics and optics over the past decade. In response to the current scientific needs, it is likely that new sensors will be developed that would enable significant extensions to the current capabilities. Significant improvement of existing sensors is also contemplated to meet this goal; an example is the oxygen sensor. Early oxygen sensors were based on Clark-type oxygen electrodes. These have subsequently been replaced with optical sensors based on fluorescence lifetimes, which have improved stability and a capability for calibration in air and thus enabled more robust and reliable measurements that have furthered the understanding of oxygen in the ocean.

Another example of technology that has advanced tremendously over the past decade is that to measure pCO_2. It is following on the footsteps of oxygen, and while the current state of optode-based pCO_2 sensors has not yet reached deployment-readiness, it is expected to reach that state within the next few years? thus enabling more accurate and stable measurements. Ultimately, it may become an alternative to the pH sensor, allowing direct observation of the CO_2 saturation state at the sea surface. This sensor, when installed on autonomous platforms, would also link directly with the pCO_2 measurements provided by the global ship-based networks, adding the much-needed vertical dimension.

Other examples of new technology in the horizon might include the development of particulate inorganic carbon (PIC) sensors or fast repetition rate fluorometers. The highest accuracy pH measurements are generally made by spectrophotometry using well characterized indicator dyes. Spectrophotometric pH profiles have been measured in situ and such systems may become alternate approaches for pH determination if they are proven to have the appropriate performance needed for long-term deployments. Electrochemical sensors for nitrous oxide, phosphate, oxygen and silicate, and new optodes for pH, CO_2, O_2 and ammonia have been developed and are being tested. As new sensors are proven robust and effective, they may be considered for addition to the observing system based on performance, cost, and scientific merit.

5.1. Newly emerging technology for pH

There are quite a few advances being made in the development of autonomous pH sensors. The section below summarizes some of these advances, but by no means provides a comprehensive list of all the efforts being carried out by the international community.

5.1.1. Spectrophotometric pH sensor from NOC (National Oceanography Center, Southampton, UK) - Lab-on-chip technology

The NOC-pH sensor is based on a micro-fluidic chip, which includes a long serpentine mixer channel, a built in optical detector with a 2 wavelength LED/photo diode system, and a temperature sensor (*Rérolle et al.* (2012)*)*. The micro-fluidic design results in a low sample (550 µL per measurement) and indicator (4 µL per measurement) consumption. Sample and indicator are pumped through the system via a stepper motor and controlled using miniature solenoid valves. The seawater sample and indicator solutions are pumped at a flow rate of 34 µL/min in order to obtain an enhanced dispersion and homogenous mixing along the channel. One custom made, twin-wavelength LED is used to transmit light at two wavelengths (435 nm and 590 nm) close to the absorption maxima of the two m-CP indicator forms (HI^- and I^{2-}). Changes in light intensity are recorded by the photodiode as a slug of indicator passes through the optical path. Data from the tail-end of the absorption signal are used to calculate the pH of the sample, taking into account the pH perturbation of the indicator. Accuracy according to sensor developer is estimated to be 0.005 and precision is 0.001 pH units. Measurements are on the total hydrogen ion concentration scale.

5.1.2. pH optode

Several research groups are working simultaneously on the development of optode technology for pH measurements. This particular technology is attractive from the perspective of autonomous deployment on those platforms that have power restrictions, like gliders, profiling moorings, and floats. The measurement principle relies on patented DLR (Dual Life-Time Referencing) method that enables internally referenced measurements. A combination of different fluorescence signals is used and fluorescent intensity changes are detected in the time domain. Returning fluorescence signal reflects changes in pH of the DLR material. DLR material is deposited onto a polyester support using a sol-gel technique. This type of detection is often referred to as a solid-state detection.

Anticipated long-term stability (according to manufacturers) prompts infrequent calibration and low maintenance of the sensor. No pressure hysteresis and rugged design allows for deployments at depths down to 6000m. Sensor outputs calibrate data directly, but also allow for post-processing of raw data. Sensor features an advanced flexible interface, i.e. polled and unpolled mode, compatibility with serial loggers and controllers, making sensor integration process more straightforward.

Optode technology is set to revolutionize pH measurements by increasing spatial coverage of pH in the global ocean. However, thorough QC of optode data should be conducted on these early stages of development. Apart from this, a complete evaluation of salinity, temperature, pressure effects, response times, etc. is indispensable for the technology to be accepted by the ocean acidification research community.

5.1.3. MBARI Deep-Sea DuraFET

Pressure effect on a FET chip in commercialized versions, e.g. SeaFET (Sea-Bird Scientific (Satlantic), Halifax, Canada), currently restricts the use of this technology in profiling applications down to 50 m depth. MBARI researchers, led by Ken Johnson, have developed a deep-sea version of the sensor, which is based on a Honeywell DuraFET chip. The Deep-Sea DuraFET is repackaged to withstand pressures up to 2000 dbar, the maximum depth of most profiling floats. Initial results indicate a precision near 0.002 pH (1 SD) and an accuracy of 0.01 or better based on laboratory calibrations for the effects of pressure and temperature on sensor response. Sea-Bird Scientific (Satlantic) is currently working on implementation of the findings made by Ken Johnson's group into a commercially available product.

5.1.4. Low-cost Spectrophotometric pH sensor for surface water measurements (Sunburst Sensors)

Sunburst Sensors is developing a small, low-cost SAMI for surface water pH measurements. This instrument is based on the same principles of analysis of the SAMI-pH, but will use a small, integrated optical-fluidic design that is attached directly to the electronic board. This instrument is a newer prototype of the iSAMI, which won the affordability prize in the Ocean Health XPrize competition (*https://oceanhealth.xprize.org/*). This instrument will work at depths < 2 m, will have accuracy better than 0.008 pH units, and will measure pH on the total hydrogen ion concentration scale. It will require external power, and will be capable of integration into other systems.

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7. Appendix

7.1. Course Agenda

Instrumenting our oceans for better observation: a training course on biogeochemical sensors

June 22-July 1, 2015
Sven Lovén Center for Marine Sciences (Kristineberg, Sweden)

Course Agenda

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Main goals:

1. Teach best practices for biogeochemical sensors in general, and for selected types of sensors in particular, with the aim of improving the data currently generated by such sensors.
2. Collate the collective wisdom of participants and instructors on best practices of operation of biogeochemical sensors and distill this into a document.
3. Work on data reduction practices for sensor data, including reporting format and requirements (e.g. meta-data, accuracy/precision estimates etc.). Document this outcome for sensor data reporting and reduction.

Chosen variables where time for hands-on experience will be dedicated are listed below, together with the available sensors/technologies out in the market.

a. Oxygen (optodes, electrochemical)
b. pH: 1) Colometric reagent method (e.g. pHSAMI by Sunburst), 2) field effect transistor (ISFET) type sensor (e.g. Seafet by Sea-Bird Scientific (Satlantic))
c. pCO2: 1) membrane based sensors with NDIR (e.g. PRO-OCEANUS, CONTROS) 2) colorimetric (e.g. SAMI by Sunburst, AFT-CO2 by Sunburst), 3) otpodes (Anderaa).
d. Nitrate – ISUS/SUNA

Bio-optics (e.g. Fluorometer, backscatter and radiometers) will be included in a theoretical session.

Participants should identify the variable of choice they'd like to work with (one they have limited/no experience with).

Participants will also have the opportunity of exchanging between groups for periods of time, so that they can learn about the other sensors as well.

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Sunday, June 21, 2015

Participants arrive in Sweden

Monday, June 22, 2015

08:00-09:00	Coffee and breakfast
09:00-09:15	**Welcome and introduction** (Maciej Telszewski, IOCCP; Toste Tanhua, GEOMAR)
09:15-09:45	**Course objectives, expected outcomes, logistics and format of the course** (Laura Lorenzoni, USF)
09:45-10:45	**Plenary Session I**: *Scientific importance of instrumenting our oceans (i.e. why are we here?)* (Herve Claustre)
10:45-11:00	Coffee break
11:00-12:00	**Plenary Session II**: *Key oceanographic characteristics that will determine what sensors can be used where (i.e. you can't put whatever you want wherever you want it)* (Ken Johnson)
12:00-13:00	Lunch
13:00-17:00	**Breakout groups**: *Participants are divided into 5 groups of 5 persons each to work with each type of sensor (O2, NO3, pH and pCO2 (2 groups)). Breakout groups and familiarizing with the sensors can continue after dinner.*
17:00	Dinner

After dinner participants have time to continue working with their breakout groups

Tuesday, June 23, 2015

07:30-08:30	Coffee and breakfast
08:30-10:00	**Sensor deployment:** Participants deploy their sensors off the pier
10:00-14:00	**Plenary Session III**: *Sensors – inside out* (Anders Tengberg, Phil Bresnahan, Ken Johnson, Steffen Aßmann, Craig Neill); coffee will be available during this session; lunch will be served at noon.
14:00-17:00	**Plenary Session IV: Bio-Optical Sensors** (Collin Roesler); coffee will be available during this session
17:00	dinner

After dinner participants have time to take their discrete samples for calibration/validation

20:00-20:30	*Meet you sensors:* CONTROS
20:30-21:00	Participant presentations (10-15 minutes each)

Wednesday, June 24, 2015

08:00-09:00 Coffee and breakfast

09:00-13:30 **Plenary Session III**: *Sensors – inside out* (Anders Tengberg, Phil Bresnahan, Ken Johnson, Steffen Aßmann, Craig Neill) – Cont. Lunch will be available at 12:30.

13:30-14:30 **Plenary Session VI**: *The Carbon system: assessing and controlling measurement uncertainty in estimating the seawater CO_2 system* (Andrew Dickson)

14:30-15:30 **Plenary Session V:** *Interfacing sensors* (Craig Neill, Ronnie Van Dommelen, Anders Tengberg)

15:30-16:00 Coffee break

16:00-17:00 **Plenary Session VII (practical and theoretical)**: *Calibration and validation* (Anders Tengberg, Craig Neill, Ken Johnson, Phil Bresnahan)

17:00 Dinner

After dinner participants have time to take their discrete samples for calibration/validation

20:00-20:30 *Meet you sensors:* Sunburst

20:30-21:00 Participant presentations (10-15 minutes each)

Thursday, June 25, 2015

08:00-09:00 Coffee and breakfast

09:00-11:30 **Plenary Session VII (practical and theoretical)**: *Calibration and validation* (Anders Tengberg, Craig Neill, Ken Johnson, Phil Bresnahan)

11:30-12:30 **Plenary Session VIII (Theoretical)**: *Data, data, data!* (Andrew Dickson, Ken Johnson, Phil Bresnahan). *Coffee will be available during this session*

12:30-13:30 Lunch

13:30-14:30 **Open Discussion**: *Biofouling* (moderated by Craig Neill and Anders Tengberg, contribution by participants)

14:30-17:00 **Group activities continue: Participants at the station will continue to work with their sensor (O2, NO3, pH and pCO2).** *Coffee will be available in the afternoon.*

17:00 Dinner

After dinner participants have time to take their discrete samples for calibration/validation

20:00-20:30 *Meet you sensors:* Aanderaa

20:30-21:00 Participant presentations (10-15 minutes each)

Friday, June 26, 2015

08:00-09:00 Coffee and breakfast; Group 1 heads out to deploy the mooring at the Koljoe Fjord observatory on board of the R/V Skagerak (5 hour trip)

09:00-11:00 **Plenary Session VIII (practical)**: **Getting the data; the good, the bad and the weird** (Group 2)

11:00 Group 2 heads to meet the ship by car; group 1 returns to the station by car

15:00-17:00 **Plenary Session VIII (practical)**: **Getting the data; the good, the bad and the weird** (Group 1)

Plenary Session IX: *Assessment of the importance of sediments in continental margin ecosystems: focus on the in-situ technology in use* (Per Hall)

17:00 Dinner

After dinner participants have time to take their discrete samples for calibration/validation

20:00-20:30 *Meet you sensors:* Seabird Scientific

20:30-21:00 Participant presentations (10-15 minutes each)

Saturday, June 27, 2015

08:00-09:00 Coffee and breakfast

09:00-10:00 **Plenary Session X:** *Elusive Oxygen – How do we accurately measure it?* (Arne Kortzinger, Henry Bittig)

10:00-13:30 **Group activities continue: Participants will have a chance to go back to their sensors and download data/interact with the group expert and learn more in depth about the sensor. Participants have time to take their discrete samples for calibration/validation.** *Lunch will be served at noon*

13:30 Field trip to Lysekil, aquarium, dinner by the harbor

Sunday, June 28, 2015

08:00-09:00 Coffee and breakfast

09:00-10:00 **Plenary Session XI:** *Dogs and cats: can models and measurements get along?* (Iris Kriest)

10:00-11:00 **Plenary Session XII:** *All that you need to know about Sensor deployment but were afraid to ask* (Group led); *coffee will be available at the end of this session.*

11:00-12:30 **Plenary Session XIII/Open Discussion:** *How to take care of data: quality control and making the data available*. (Data managers included) (Moderated/led by Benjamin Pfeil)

12:30-13:30	Lunch
13:30-17:00	**Group Time: Report Writing and data analysis**
17:00	Dinner
20:00-21:00	Participant presentations (10-15 minutes each)

Monday, June 29, 2015

08:00-09:00	Coffee and breakfast
09:00-11:30	**Participants will recover their sensors**
11:30-13:30	**Group activities: Data presentations;** coffee will be available during this session. Lunch will be served at noon.
13:30-17:00	**Plenary Session XIV and discussion**: *Autonomous sensors: pushing the boundaries and developing new technology/methodology* (Doug Connelly and Eric Achterberg); this session has web conferencing. Coffee will be available during this session.
17:00	Dinner
20:00-21:00	Participant presentations (10-15 minutes each)

Tuesday, June 30, 2015

08:00-09:00	Coffee and breakfast
09:00-17:00	**Group presentations and discussion**
17:00	Dinner
20:00-21:00	Participant presentations (15 minutes each)

Wednesday, July 1, 2015

08:00-09:00	Coffee and breakfast
09:00-12:30	**Summary – review of the key aspects of the course, lessons learned and status of the 'best practices'**
12:30-13:30	Lunch
13:30-15:00	**Plenary Session XV and open discussion**: *The way forward – what happens now?* Moderated by Toste Tanhua
15:00	Adjourn

7.2. Participants list

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