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1. Executive Summary

WP3 task 3.5 developed combined carbonate system sensors to provide contemporaneous measurements to improve carbonate sensor measurements and calculations in coastal observing systems. While each of the three subtasks encountered issues related to development and deployment, three novel systems have been developed for underway operation on moving platforms to improve the observation and characterisation of carbonate system variability in coastal waters.

2. Introduction

The marine carbonate system reflects changes in air-sea CO₂ equilibration, the balance between photosynthesis and respiration, and longer-term patterns such as seasonal mixing and the rise in atmospheric CO₂ due to fossil fuel burning. It includes several variables that are important for coastal biology and chemistry that includes pH, pCO₂, and saturation state of aragonite and calcite (Ω). Traditionally, total dissolved inorganic carbon and total alkalinity samples are collected and preserved for analysis in the lab. Using these two carbonate system variables, other carbonate system variables using carbonate system dissociation constants (CO2SYS). But sample collection and analysis in the lab have some drawbacks including the use of HgCl₂ which is a long-term environmental hazard, a time lag between sample collection and results, and error propagation when using CO2SYS, especially in the case of total alkalinity in coastal waters where non-carbonate alkalinity can affect total alkalinity measurements.

For these reasons, the subtasks in the WP aimed to develop carbonate system sensors for near real-time coastal observing of two carbonate system variables. This provides data on the two targeted variables, and also afforded the traditional approach of using CO2SYS (and auxiliary data) to calculate the other carbonate system variables. The subtasks comprised of the following:

Subtask 3.5.1: Combined spectrophotometric pH and CO₃ determination

Subtask 3.5.2: Combined spectrophotometric pH and total alkalinity determination

Subtask 3.5.3: Combined electrode and spectrophotometric technology for high-accuracy, high-resolution pH determination

Below is the report relating to each of the subtasks and their activities.

3. Main report

Subtask 3.5.1: Combined spectrophotometric pH and CO₃ determination (NIVA)

Development

A combination spectrophotometric pH and CO₃²⁻ sensor was designed and fabricated by NIVA (Fig. 3.1). The pH portion of the sensor was based on a spectrophotometric technique using a pH-sensitive indicator dye, thymol blue (cite). It is a flow through system that uses LEDs and an Ocean Optics spectrophotometer (STS-VIS) to measure absorbance at 435 nm, 596 nm, and 730 nm, with the first two wavelengths used to calculate pH and the last wavelength the non-absorbing (control) wavelength. The reaction cuvette that is about ~8 ml in volume and a pathlength of ~38 mm. Indicator dye addition



is automated with a solenoid pump, and temperature inside the cuvette is continuously monitored using a glass encapsulated thermistor (Honeywell). Each sample is subjected to a series of dye additions to characterize the pH and temperature perturbation to the original sample pH. The design and operation of the pH portion of the sensor is described in Reggiani et al. (2016).

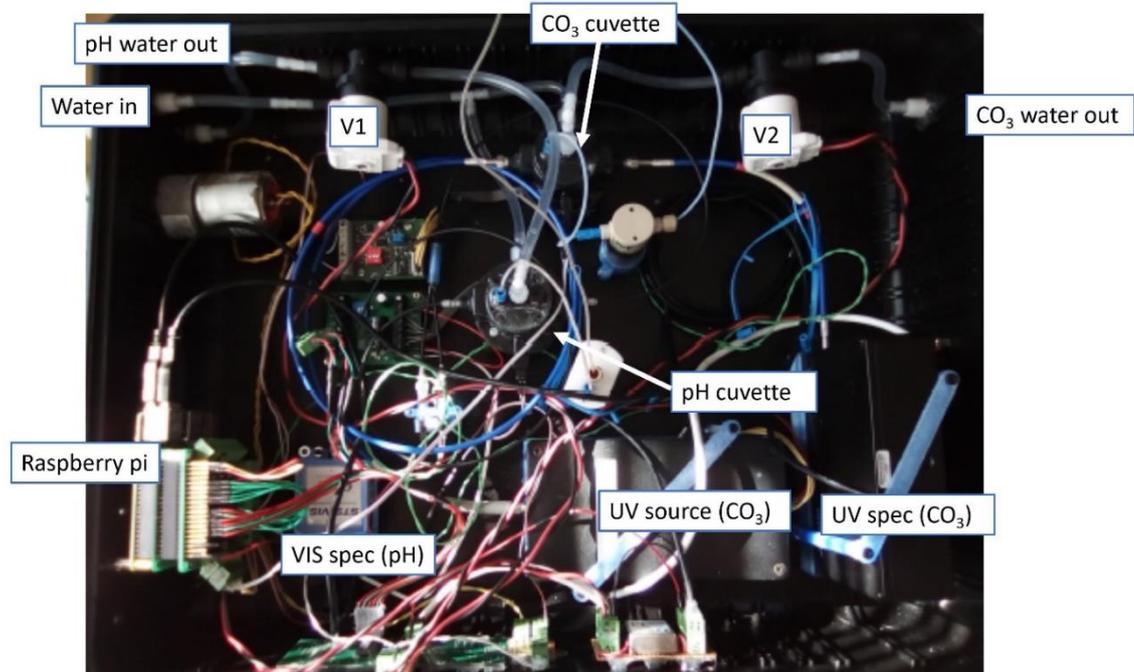


Figure 3.1. Schematic of combined pH and CO_3^{2-} sensor. Water enters the flow through system at the top left of the schematic and flow to each of the two cuvettes (CO_3^{2-} and pH) is controlled by two stop flow valves (V1 and V2). Each cuvette has separate “water out” lines to facilitate separate waste collection. The operation/sequence programming and VIS LED sources are from the Raspberry pi in the bottom left corner of the schematic, and the VIS spectrophotometer lies to the right of the Raspberry pi. The UV source and spectrophotometer are in the bottom right corner of the schematic.

The CO_3^{2-} portion of the sensor is based on a similar flow through/cuvette design as the pH portion of the sensor, but instead of using a pH sensitive dye, the measurements are made on PbCO_3^0 formation with the addition of PbCl_2 (Byrne and Yao, 2008; Easley et al., 2013). The geometry and construction of the cuvette is identical, except for the use of UV compatible components (windows, lenses, source - Heraeus Noblelight GmbH, spectrophotometer - MightyEx CCD spectrophotometer). This technique uses PbCl_2 to form PbCO_3^0 which is measured at absorbances of 234 and 250 nm with a non-absorbing (control) wavelength at 350 nm. PbCl_2 addition is automated and temperature is also continuously monitored with a glass encapsulated thermistor. While the Pb concentrations in the outflow of the system is relatively low to coastal values, the waste stream has been collected and an activated carbon filtration system is being developed for removing Pb from the waste stream before disposal.

The combined operation of pH and CO_3^{2-} sensors is performed using a Python-based graphical interface program. The cuvettes are connected to tubing/valves that enable alternating flow and operation of each sensor. The attributes of source strength, spectrophotometer integration time, sampling frequency, etc. are controlled in the program. The program also uses salinity provided by the



FerryBox system that the combined sensor is linked to, which is subsequently used for calculations of various pH and $[\text{CO}_3^{2-}]$ related constants and density.

Testing (field and lab)

Lab-based testing was focused on finetuning operation of each individual measurement “circuit”. Based on the previous development of the pH system, the implementation and operation was relatively straightforward. Most effort was spent on interfacing the UV source and spectrophotometer for use with the CO_3^{2-} portion of the sensor, requiring extra coding in Python for operation and data acquisition, in addition to some signal processing of the UV signal. Lab-based testing using coastal seawater at NIVA’s Solbergstrand field station’s FerryBox system and at a collaborator’s lab near the Gulf of Trieste indicated that the pH portion of the sensor operated as expected (in comparison with a similarly-designed standalone pH sensor – uncertainty of <0.003) and the CO_3^{2-} portion of the sensor achieved an uncertainty of $<2 \mu\text{mol/kg CO}_3^{2-}$.

Field deployment for the combined system was on NIVA’s M/S Color Fantasy FerryBox system from 16 July-9 August 2018. The CO_3^{2-} portion of the system was in operation for the first few days, but it was disconnected until 7 August due to problems related to handling seawater in and out of the sensor. However, a leak developed from the CO_3^{2-} cuvette when operation was resumed on 7 August, and it was therefore disconnected. On 23 July, the flow to the pH portion of the sensor was obstructed and the system was offline until the obstruction was removed and pH measurements resumed on 1 August. On 9 August the sensor was removed from the FerryBox system for repair of the CO_3^{2-} portion of the sensor and for new quick connects that are believed to have caused the seawater flow obstruction. The sensor measurements were ground-truthed by measurements made using 10 cm cuvettes in a benchtop UV-VIS spectrophotometer using thymol blue and PbCl_2 addition for pH and CO_3^{2-} measurements, respectively.

The data collected between 16 July-9 Aug using the combined pH and CO_3^{2-} sensor are shown in **Fig. 3.2**. pH and CO_3^{2-} data shown are preliminary values as pH still requires a salinity correction and CO_3^{2-} requires a temperature correction. Temperature-dependent constants must still be developed for CO_3^{2-} calculations. **Fig. 3.2a** show pH and CO_3^{2-} data for the entire period, **Fig. 3.2b** shows a 6 day period of pH data indicating regional variability observed between Oslo and Kiel, and **Fig. 3.2c** shows a period with concurrent pH and CO_3^{2-} data in finer detail. In terms of the pH observed during the entire period, the sensor acquired pH agrees well with benchtop ground-truth pH spectrophotometric analyses as well as with CO_2SYS -calculated pH from manually collected samples analysed for total dissolved inorganic carbon and total alkalinity. Regional variability in pH indicate that pH minima were observed during the deployment period in the Kattegat (~ 56.3 - 57.3 deg N) as well as in the Inner Oslofjord (~ 59.9 deg N), while pH maxima occurred near Kiel (**Fig. 3.2b**). CO_3^{2-} values shown in **Fig. 3.2c** agree well with a subset of measurements made with a benchtop spectrophotometer, and the positive correlation between CO_3^{2-} and pH are also consistent with carbonate system chemistry, i.e., CO_3^{2-} increases as pH increases. Unfortunately, the CO_3^{2-} portion of the sensor developed issues before testing could be fully completed. Further tests are forthcoming in October-November 2018.

Recommendations

pH portion

- Fabrication and operation of the pH portion of the sensor was relatively non-problematic. This was based on a robust initial design.



- Sensor failure was due to obstruction of seawater supply to the box. This was due certain components in the quick connectors. New connectors with fewer moving pieces will be adapted.

CO₃²⁻ portion

- Fabrication and operation of the CO₃²⁻ portion was a more challenging due to the incorporation of new components (windows, lenses, fiber, source, spectrophotometer) that were needed for UV compatible spectral analysis. Future work on finding new products that improve upon UV source intensity and miniaturized UV spectrophotometer sensitivity is needed.
- Constants have been developed for CO₃²⁻ calculations at a fixed temperature of 25 deg C. While the temperature effect is not very large, new constants need to be determined for absorbance calculations at different temperatures (e.g., 0-25 deg C). Further, constants have been developed for salinity ranging from 18-40 – some coastal waters (especially in the Baltic) can regularly be S<18. Work developing new constants for lower salinity waters is needed.

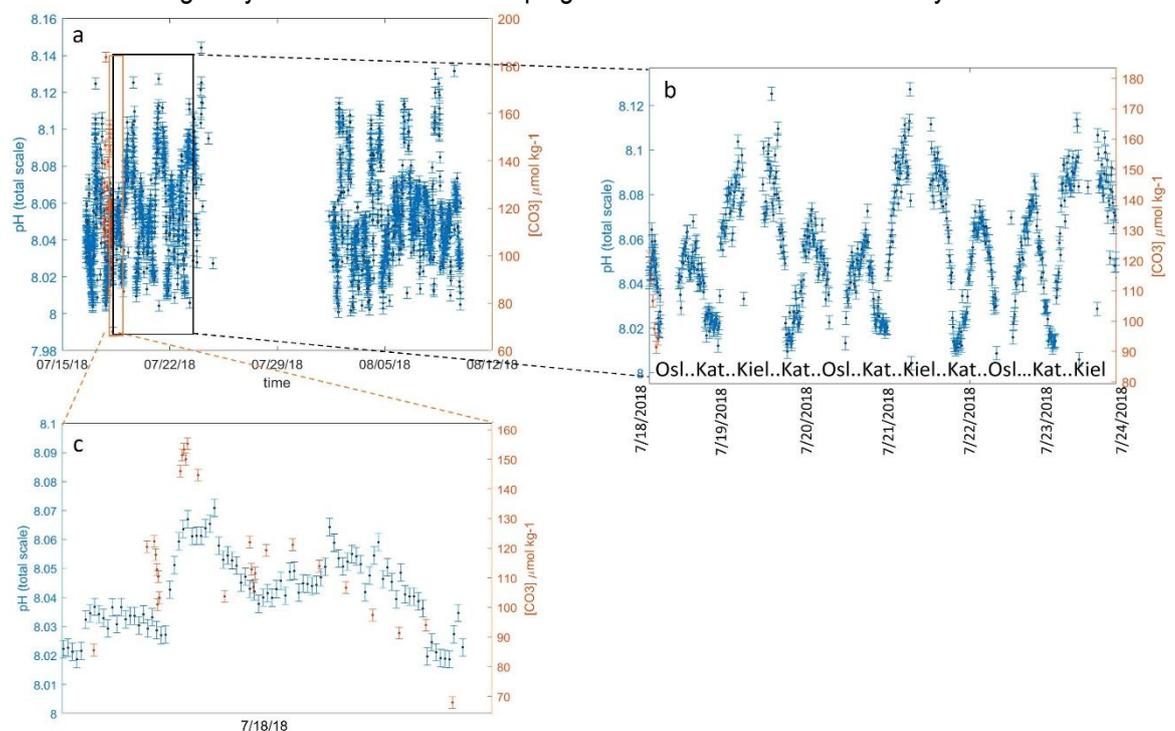


Figure 3.2. pH and CO₃²⁻ data collected during 16 July-9 Aug. pH data are uncorrected for variation due to salinity and CO₃²⁻ data are uncorrected for variation due to temperature. Panel (a) is data for the entire period: blue symbols represent pH and orange symbols represent [CO₃²⁻]. Panel (b) is a shorter time period between 18-24 July to show regional variability in pH – Osl: Oslo, Norway; Kat: Kattegat; Kiel: Kiel, Germany. Panel (c) is a shorter time period of 17-18 July to show the coherence of measurements of pH and CO₃²⁻. Error bars represent *in situ* uncertainty of 0.003 and 2 µmol kg⁻¹ for pH and CO₃²⁻, respectively.

Subtask 3.5.2: Combined spectrophotometric pH and total alkalinity determination (HZG) Development

A state-of-the-art spectrophotometric pH analyser, the CONTROS HydroFIA pH (Kongsberg Maritime Contros GmbH, Kiel, Germany), was developed by Steffen Aßmann, within the research group of Wilhelm Petersen. It was first made commercially available in 2018. The analyser was obtained by our research group in April 2018, and therefore so far we have limited experience with this instrument.



Further laboratory and field testing, as well as communications setup to the FerryBox (Petersen et al. 2011; Petersen, 2014) in a flow-through setup are planned within the next few months. We should have a better overview of the system by spring 2019.

Features of the HydroFIA@pH

- Power supply: 100-240 V AC for the 15V DC, 13.4A power supply; no battery option available.
- Sensing principle: analyser for spectrophotometric pH determination. Seawater pH is measured using an indicator dye (m-Cresol purple) and VIS absorption spectrometry as an absolute measurement method. While temperature of the sample is kept constant at 25°C, external input of salinity is necessary for pH calculation in a flow-through system.
- Latest specifications (based on manufacturer technical specifications):
 - range: pH 7-9, salinity 20-40 psu
 - accuracy: ± 0.003 (based on CRM testing)
 - precision: ± 0.001
 - stability: should be stable over many months, but not yet tested in the lab/field.
- Fouling issues: none indicated.
- Electronics: Data interface is RS-232 (live data, baud rate 115200, data bits 8, parity, none) or Ethernet (batch download). The instrument allows for external control of the system, via a FerryBox for example. Commands for the serial communication protocol are provided in the manual.

A state-of-the-art total alkalinity (TA) analyser, the CONTROS HydroFIA TA (Kongsberg Maritime Contros GmbH, Kiel, Germany), was developed by Steffen Aßmann, within the research group of Wilhelm Petersen. It was first made commercially available at the end of 2014, beginning of 2015.

Features of the HydroFIA@TA

- Power supply: 100-240 V AC for the 15V DC, 13.4A power supply; no battery option available.
- Sensing principle: wet chemical flow-through measuring system for total alkalinity determination. A known amount of seawater is acidified using dilute hydrochloric acid, after which the sample is degassed in an open-cell titration principle. The change in pH is measured using an indicator dye (bromocresol green (BCG)) and VIS absorption spectrometry (Hamamatsu spectrometer, cuvette, degassing unit & heat exchanger in one unit). While temperature of the sample is kept constant at 25°C, external input of salinity is necessary for TA calculation in a flow-through system.
- Latest specifications (based on manufacturer and verified by laboratory tests):
 - range: TA 2000-2400, salinity 20-37 psu
 - accuracy: $\pm 25 \mu\text{mol/kg}$ (successfully tested in the lab)
 - precision: $\pm 5 \mu\text{mol/kg}$ (we found varying precision, up to $\pm 20 \mu\text{mol/kg}$)
 - stability: instrument was stable over a period of about 1.5 months after several tests in the lab; this was due to a considerable improvement in system design between 2015 and 2017. The improvements were implemented based on extensive tests in the laboratory and field at HZG, in close cooperation and exchange of experience with the instrument manufacturer.
- Fouling issues: no fouling studies; we found it useful to clean the instrument with 0.2M HCl regularly.
- Electronics: Data interface is RS-232 (live data, baud rate 115200, data bits 8, parity, none) or Ethernet (batch download). The instrument allows for external control of the system, via a FerryBox for example. Commands for the serial communication protocol are provided in the manual.





Testing (field and lab)

The HydroFIA TA was extensively tested in the laboratory in 2015-2016. During this time, substantial improvements in the instrument design were made by the manufacturer, based on our measurements regarding stability and system control. Once the system produced stable measurements in the lab, field tests were started in 2016 on a stationary FerryBox station in Cuxhaven, Germany. At the same time, serial port communications to the FerryBox were established.

In 2017, the HydroFIA-TA was first deployed on a moving platform in a flow-through setup aboard the Hafnia Seaways. In 2017, the Hafnia travelled between Cuxhaven, Germany and Immingham, UK (**Fig. 3.3a**). For the most part, the ship travelled along the north route (**Fig. 3.3b**).

Sample water, diverted from the main flow, was filtered through a 0.2 μm cross-flow filter. The filtered sample water was collected in a reservoir (~ 200 mL long tube), connected to the TA system intake (**Fig. 3.3c**). Timing of the sample intake and measurement frequency were tested during the first two months of deployment; following these tests, it was decided that sampling every 10-15 min (the sample measurement routine lasted for less than 10 min) was sufficient to capture the TA patterns along this route. Reagents made in the laboratory (0.1N HCl and bromocresol green (BCG) indicator dye) were replaced every 6 weeks. After each reagent change, the instrument was calibrated using certified reference material (CRM) provided by Andrew G. Dickson's laboratory. On two occasions (15.05.2017 and 22.08.2017) the calibration on board the Hafnia Seaways was not successful. The TA record was corrected by adding 105 $\mu\text{mol kg}^{-1}$, to all samples between 15.05 and 07.06.2017 and 84 $\mu\text{mol kg}^{-1}$ to all samples between 22.08 and 25.09.2017, based on the calibration offsets. The offsets were calculated using the difference between expected and measured value of CRM before the next calibration.

The results from the 2017 deployment have helped to characterize seasonal and regional characteristics in TA in the southern North Sea (**Fig. 3.4**) and are analysed in detail in Voynova et al. (in review). In 2017, the Hafnia FerryBox measured continuously (every 10 seconds) a number of oceanographic parameters: temperature and salinity (Falmouth Scientific Inc. (FSI), Cataumet, MA and Teledyne Instruments, Poway, CA, USA), dissolved oxygen (DO; Aanderaa optode, Xylem Analytics, Germany), pH (Meinsberg pH glass electrode, Xylem Analytics, Germany), and partial pressure of carbon dioxide (pCO_2 , CONTROS HydroC CO2 FT, Kongsberg Maritime Contros GmbH, Kiel, Germany). The high-frequency measurements revealed that in coastal systems, where carbon fluxes are dynamic, total alkalinity can differ significantly (by up to 100 $\mu\text{mol kg}^{-1}$) between the nearshore and adjacent coastal regions. Even though this study could not account for the net yearly total alkalinity production in the coastal region, it demonstrated that there was a seasonal increase in total alkalinity of 100-150 $\mu\text{mol kg}^{-1}$ in coastal waters of the North Sea, equivalent to total alkalinity production of 11.7-26.8 $\text{mmol m}^{-2} \text{d}^{-1}$ during the spring and summer months. This seasonal change could not be accounted for by riverine contributions, but instead was probably related to seasonal organic matter production and distribution in coastal and nearshore regions. Bottom sediments and the tidally-coupled biogeochemical reactor between coastal (North Sea) and nearshore (Wadden Sea) regions are mediating this total alkalinity change, and the ~4 months lag between the seasonal increase in alkalinity and the peak organic matter production could be explained by the temperature-dependent remineralisation of organic matter via both aerobic and anaerobic pathways.



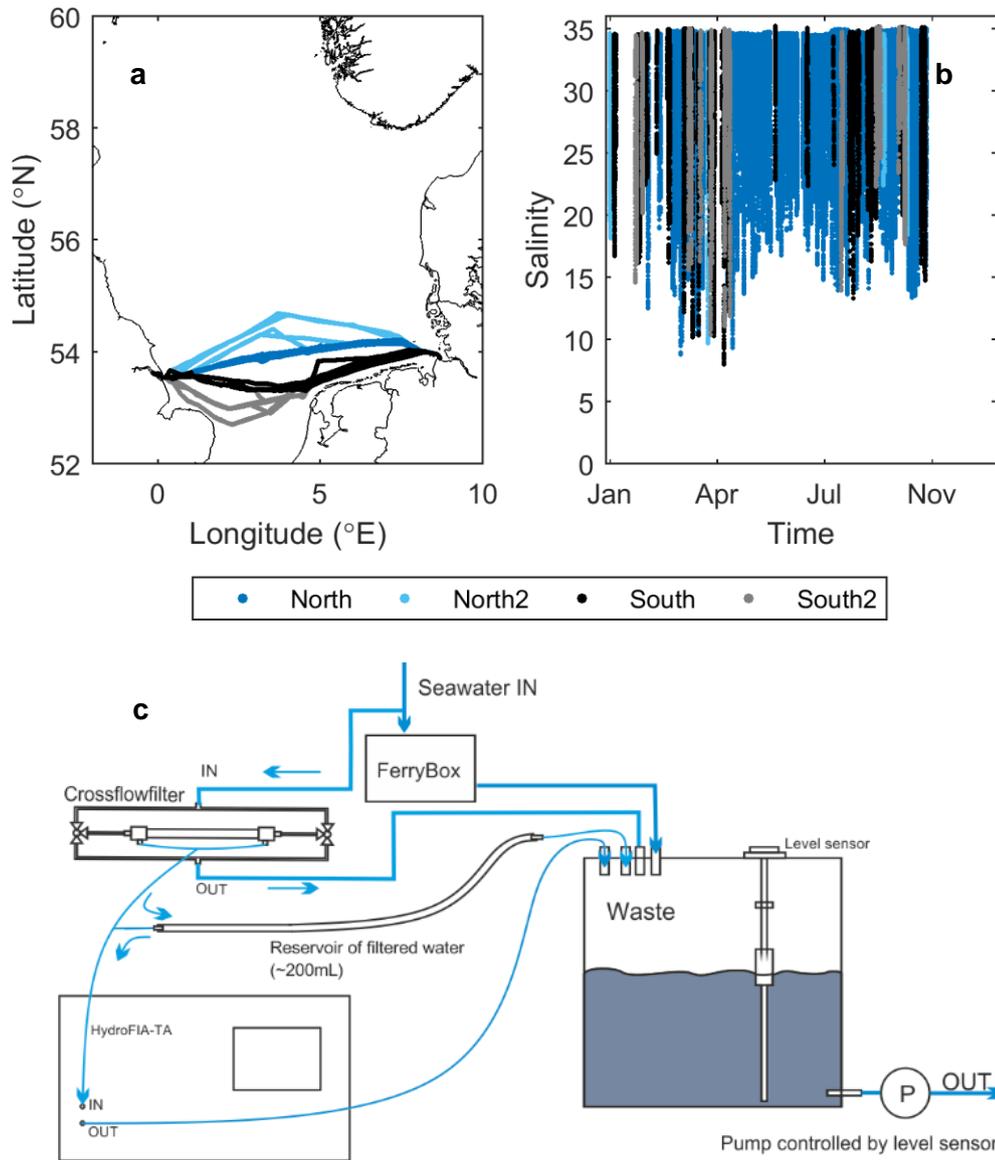


Figure 3.3. a) Hafnia Seaways routes in 2017 (1.1 - 31.10.2017), divided in North (light and dark blue) and South (black and gray) transects. The gray and light blue transects indicate slight deviations from the typical North and South routes. b) Salinity distribution during 2017. c) Flow-through setup of FerryBox and HydroFIA TA. Figure reproduced from Voynova et al. (in revision).

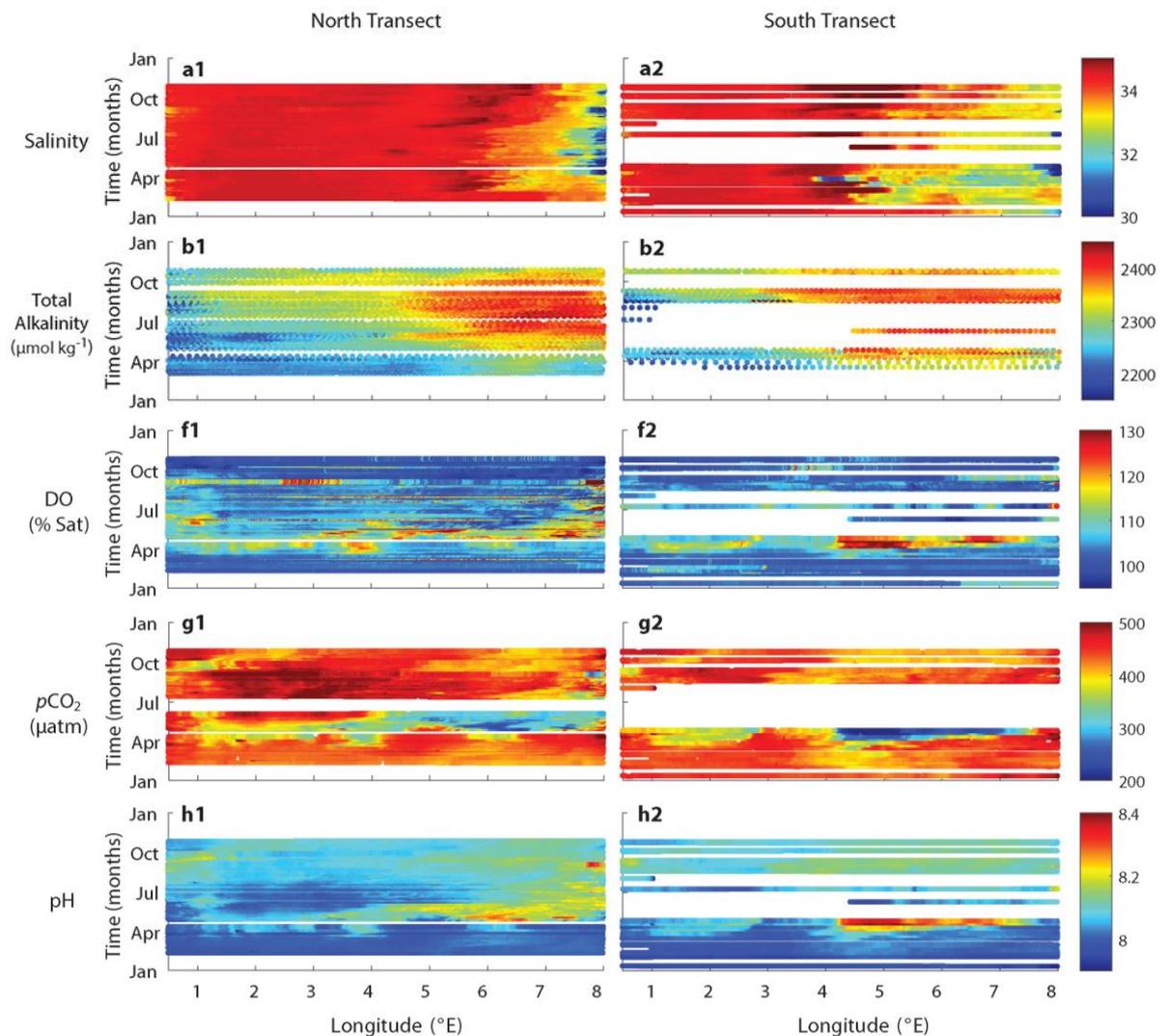


Figure 3.4. a) Salinity, b) total alkalinity (TA, $\mu\text{mol kg}^{-1}$), f) dissolved oxygen (DO, % saturation), g) partial pressure of carbon dioxide ($p\text{CO}_2$, μatm), h) pH measured along the North (marked with 1) and South (marked with 2) routes (Fig. 2a) in 2017. The port regions (up to 50 from both shores) are not shown. Figure reproduced from Voynova et al. (in review).

Currently, the HydroFIA TA is being deployed on the Lysbris Seaways, a ship equipped with a FerryBox, which travels over a larger area in the North Sea, between England, Norway and Belgium. Another ship, the Color Fantasy, travelling between Germany and Norway in the Baltic Sea was also equipped with a HydroFIA TA over a short-term experiment, along with several carbonate system sensors from NIVA, and a different FerryBox setup. In addition, the HydroFIA TA has been successfully deployed onboard the RV Heincke, during 4 research cruises in 2017-2018. With every setup, and a different moving platform, care has to be taken for the best application of the flow-through setup described in Fig. 3.3. More recommendations will be given in the following section.

In November 2018, a TNA experiment is planned on the NIVA stationary FerryBox research station. Both the HydroFIA TA, and the HydroFIA pH analysers will be deployed during this experiment, along with a number of other carbonate system sensors from different partners.



Recommendations

- Temperature controls

The measurements of the HydroFIA systems are highly sensitive to temperature changes, and the instruments are suited for environments between 5 and 30°C. On moving vessels, FerryBoxes are usually deployed in or near the engine rooms, where temperatures can get higher, especially during the summer months. We recommend temperature measurements of the deployment environment to determine their influence on the instrument stability. In addition, we recommend that the manufacturer is aware of the deployment requirements, and that the system is adapted for deployment in a larger temperature range. Currently we are working with the manufacturer to test whether changes to the system design regarding these recommendations is possible.

- Flow-through setup

We recommend that the HydroFIA instruments are deployed in a flow-through setup that includes a cross-flow filter, and a flow cell, similar to **Fig. 3.3c**. This will reduce the amount of suspended matter, and sources of fouling to the system, and prolong its deployment in the field. This is particularly important in coastal systems influenced by high or moderate suspended sediment loading. It is recommended that the flow to the cross-flow filter is monitored, to ensure that enough water is being supplied to the instrument. The flow-cells can vary in size and shape, depending on the instruments attached to the cell. We have deployed the HydroFIA TA together with nutrient analysers, sampling continuously, or at an interval of 15-20 minutes.

- Reagent preparation and deployment

It is recommended that the reagents are prepared with degassed deionized water (preferably MillQ), and that the dye is filtered. These can be carefully made in the laboratory, and placed in light- and gas-tight bags, or ordered from the manufacturer. It is recommended that each batch of reagents is carefully labelled, so that it is known if changes in the reagents influence the calibrations. For long-term deployments, it is recommended that the amount of reagents is increased, which requires the manufacturer's help for the instrument setup for such a deployment. We are in the process of testing this in 2018, and have so far had good experiences with placing reagents outside of the instrument. Studies of indicator dye purity from different suppliers are underway, and the manufacturer should come out with recommendations of the best sources in the near future.

- Calibration and reference sea water samples

It is recommended that calibration is done every time the reagents are replaced, after a reagent flush, and a seawater flush. Prior to calibration, the stability of the instrument should be checked with filtered seawater, preferably of known TA, and a suitable salinity. Once the instrument is stable (within expected precision), 2-3 samples of CRM should be measured, after which calibration can be done. Following calibration, 2-3 samples of CRM, and several seawater samples are measured to check for the change before and after calibration. Even though it is recommended that the filtered seawater is treated with mercuric chloride for larger stability, we have successfully used it as a reference after only filtering it with a 0.2 µm filter, and storing it in the dark at 4°C in large Nalgene canisters over a prolonged time (several months).

- Discrete sampling

It is recommended that discrete samples for dissolved inorganic carbon (DIC) and TA are collected alongside the instrument, either manually or autonomously via an autosampler. The autosampler samples should be collected less than 24, and preferably less than 14 hours before fixing them with mercuric chloride. From our experiences on two moving platforms, the Hafnia Seaways, and Color Fantasy, we have found minimal influences on the DIC content of these samples when they were stored in the dark and cold, in 1 L ISCO sampler bottles, with no caps. Care should be taken when subsampling the collected ISCO samples, so that they are gently shaken and poured in the storage containers where they are fixed. While air-sea gas exchange has no direct influence on TA, DIC is



sensitive to changes in CO₂, and thus prolonged sample storage without preservation, or vigorous shaking can affect the DIC sample content (Dickson et al., 2007).

- Drift correction and elimination

The HydroFIA TA drifts every time the instrument is idle for >6 hours. Therefore, it is recommended that a small flush of the reagents and sample is introduced prior to the next sampling cruise or period. At the moment, we are working with the manufacturer to introduce a command that will allow us to do this without resetting the reagent levels.

Subtask 3.5.3: Combined electrode and spectrophotometric technology for high-accuracy, high-resolution pH determination (Fluidion/IFREMER)

Development - The Ferrybox prototype combined pH sensor is complete (**Fig. 3.5**).

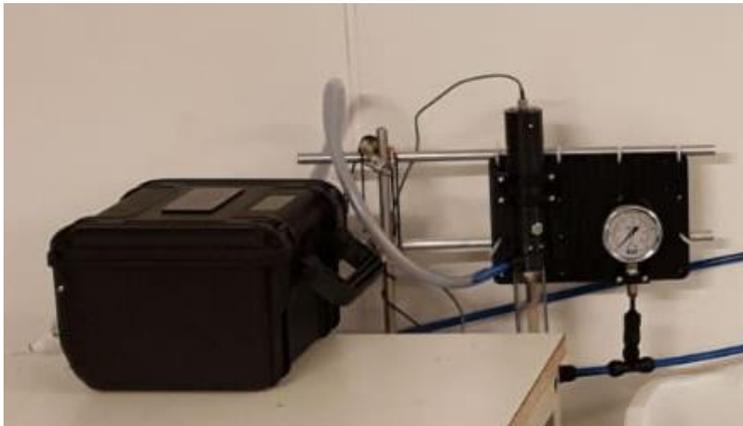


Figure 3.5. Fluidion hybrid pH sensor set up on the Oden Swedish research ship, August 2018. The box on the left is the colorimetric analyser and the potentiometric electrode is on the right with the pressure gauge.

The colorimetric analyser's optics have been improved for better stability of the measurements. A flow-through set up has been designed for FerryBox installation (see **Fig. 3.6**): the seawater flows through a first flow-cell for measurements with the potentiometric sensor (pH electrode), a small sample is filtered after the pH electrode for colorimetric measurement. A manual pressure gauge is used to monitor the pressure of the flow (7-30 PSI). Temperature is recorded both at the electrode flow cell and the colorimetric analyser optical cell. The instrument is a stand-alone unit: it can be controlled via the integrated LCD screen and two buttons and all data are logged in the electrode. A Java interface is used for live data observation, data retrieval and electrode calibration. Communication is performed via USB cable. pH electrode data points are recorded every 10 s whereas colorimetric analyser can be set to perform an analysis from every 5 minutes to several hours depending on deployment requirements. Colorimetric measurements are performed using purified meta-cresol purple indicator.

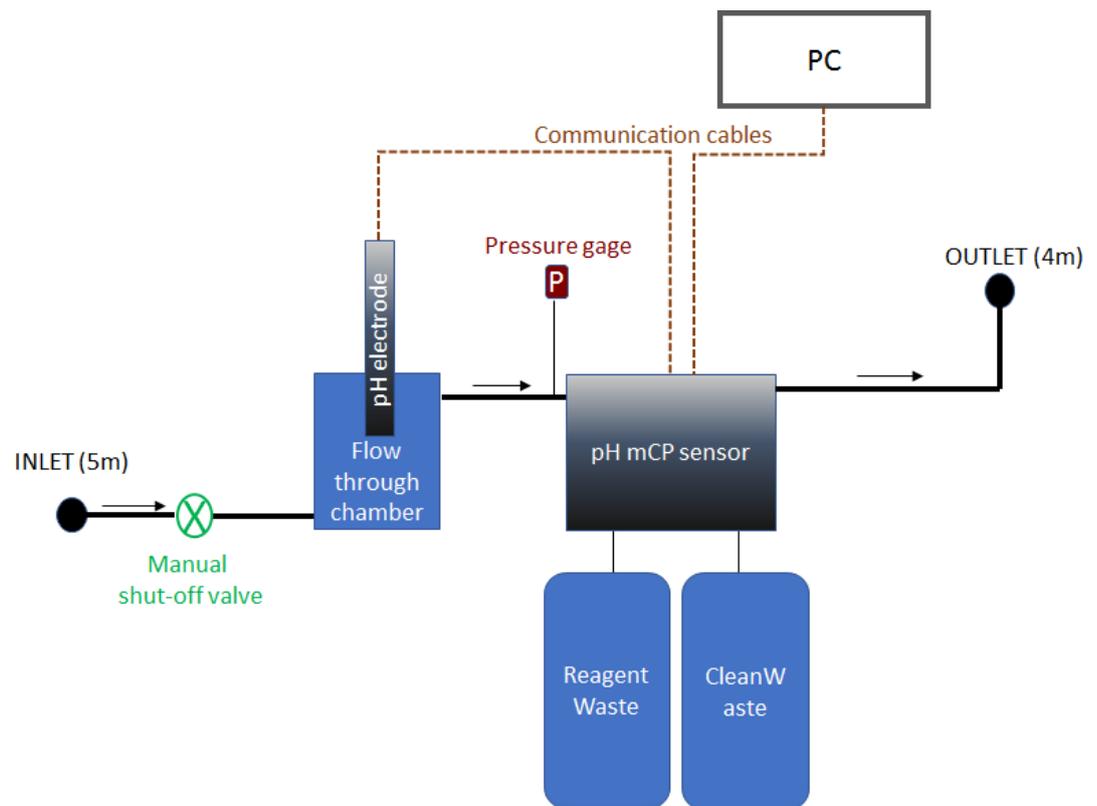


Figure 3.6. Fluidion hybrid pH analyser and electrode FerryBox set up.

Testing (field and lab) - The system was tested for several weeks (April-July 2018) in the laboratory with seawater and Tris buffer solutions (see **Fig. 3.7**) enabling characterization of the instrument and improvements of the software for automatic control and user handling. The hybrid pH sensor was calibrated at 20-21°C, by running large batch of Tris buffers (pH around 7.5, 8.0, 8.4). The temperature was controlled using the temperature-controlled bath and the thermostated chamber. The exact Tris pH values are analysed manually just after instruments' calibration using Standard Operating Procedure (SOP, Dickson et al., 2007). The quality of the bench top protocol was checked by analysing Tris buffer certified reference material from Dickson's Scripps laboratory (pH_{ref}=8.093 at 25.0 °C): pH_{measured}= 8.271 ± 0.002 (n=3) at 19.2 °C -> 8.094 ± 0.002 (n=3) at 25.0 °C .

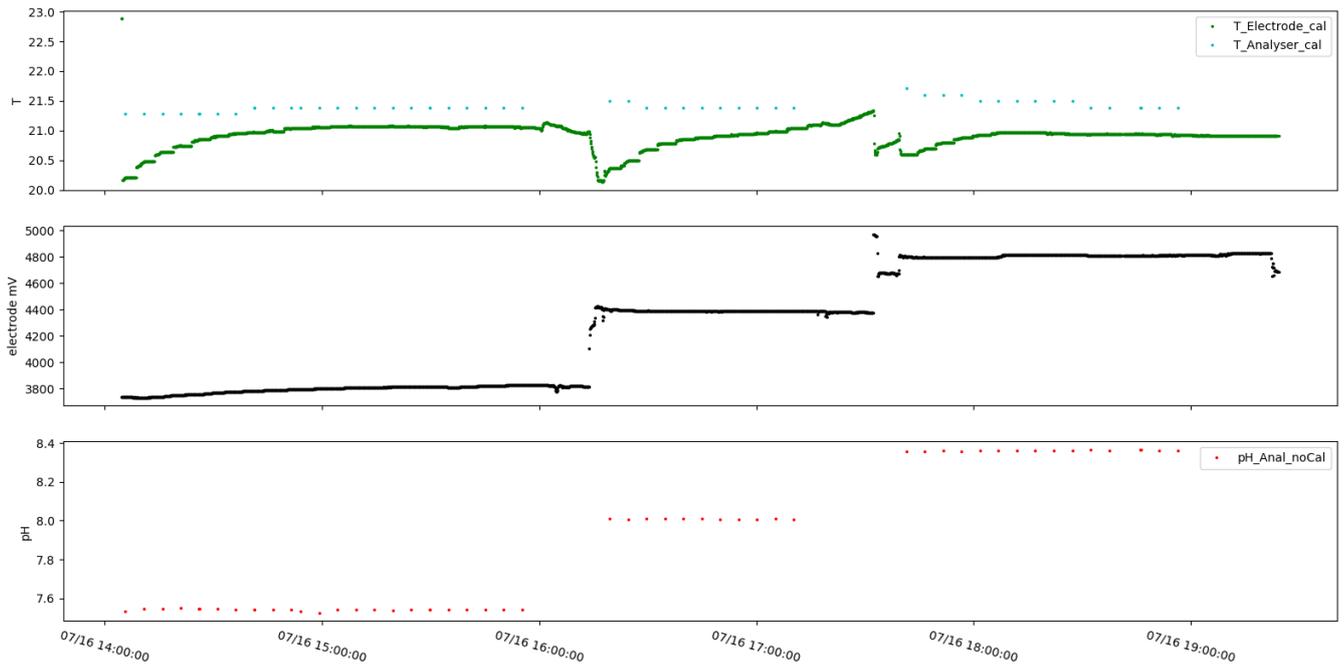


Figure 3.7. Fluidion Hybrid pH sensor data during calibration experiment (July 2018). Top panel: Colorimetric and electrode temperatures. Middle: Electrode output (mV). Bottom: Colorimetric analyser pH data.

A comparison between the pH electrode and the analyzer was performed in seawater at 21 °C. Seawater pH was adjusted by adding 0.1 M HCl and then 0.1 M NaOH by steps (**Fig. 3.8**). Electrode and analyzer datasets are following the same pattern but a large offset of 0.2 pH units is observed (probably due to change of media and electrostatic interference). The electrode is re-calibrated using analyzer’s seawater data-points.



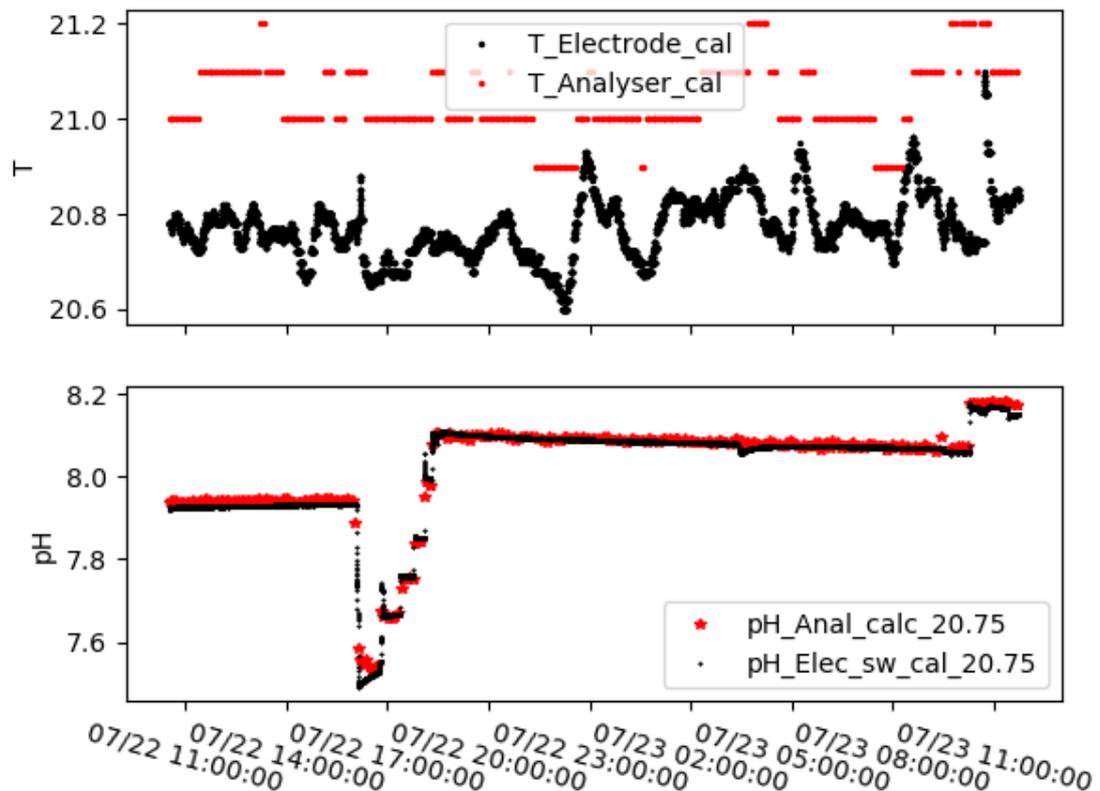


Figure 3.8. pH electrode (black) and analyzer (red) seawater inter-comparison after electrode re-calibration from analyzer seawater data (July 2018).

Temperature characteristics: To test the performances of the system at different temperatures, the system was left to run with a large batch of Tris buffer at several temperatures (bath at 5, 10, 15 and 20 °C). To know the exact value of the Tris buffer solution during the experiment, a sample of Tris solution was taken during each temperature period and stored overnight in the fridge. The Tris samples were then analyzed manually following the SOP protocol. Analyzer results compare well to manual measurement: residuals between -0.004 and 0.006. Electrode results show a much larger discrepancy at low temperature (residuals up to 0.039). This highlights the need to characterize the electrode temperature dependency and not use directly the temperature relationship supplied by the manufacturer. The analyzer can be used to re-calibrate the pH electrode.

Field tests - The system was sent end of July 2018 for an 8 weeks test on the Arctic Ocean 2018 Swedish-US research cruise. Unfortunately, the system was flooded after a miss-handling while setting up the system, it was impossible to recover the system while on the ship. The instruments will be shipped back for repair at Fluidion's laboratories at the end of September 2018.

Recommendations

-The colorimetric analyser is performing well with comparisons between reference manual measurements of Tris and seawater within 0.01 pH units (=accuracy). Precision was found between





0.001 and 0.004 (n=3) with an average precision of 0.003 pH units over several datasets of Tris and seawater data.

-pH electrode was found difficult to calibrate with interferences from the environment. A new housing in stainless-steel has been designed and has shown to remove electrostatic interferences. Further tests are required to check electrode stability with the new housing.

-pH electrode temperature's response needs to be characterized for better accuracy

-Long term tests are required to develop an automatic electrode recalibration algorithm using colorimetric analyser's high quality data.

-The flow-through design is being reviewed to avoid the risk of flooding for next deployments.

-Pontoon/buoy tests are planned for November 2018.

4. Outreach, dissemination and communication activities

Please describe all outreach and communication activities carried out to promote the deliverable results and products to stakeholder user groups. Specify individual activities and targeted groups as appropriate.

2018 July: Voynova, Y.G, Petersen, W., Gehrung, M., Aßmann, S. King, A.L. 2018 (in revision). Intertidal regions changing coastal alkalinity: the Wadden Sea-North Sea tidally-coupled bioreactor. *Limnology and Oceanography*.

2018 June: Geesthacht, Germany; Regional Coastal Research Meeting with the Lower Saxony Water Management, Coastal Defense and Nature Conservation Assembly (NLWKN)

2018 May: Brussels, Belgium; EuroGOOS General Assembly

2018 April: Vienna, Austria; EGU General Assembly 2018

2018 March: Oceanology International

2018 March: Bergen, Norway; 1st ICOS OTC Instrumentation Workshop

2018 February: Portland, OR, USA; Ocean Sciences Meeting 2018

2017 December: Oslo, Norway; NIVA Ocean Acidification SIS workshop

2017 November: Providence, RI, USA; 24th Biennial CERF conference

2017 October: Oslo, Norway & Kiel, Germany; 8th FerryBox Workshop

2017 October: Bergen, Norway; 8th EuroGOOS International Conference

2017 September: Oslo, Norway; NIVA Strategic Initiative Science Day

2016 December: Clean Gulf Conference & Exhibition

2016 November: Pollutec International trade show for environmental equipment, technologies and services

2016 June: Clean Pacific Conference & Exhibition

2016 April: Heraklion, Crete; 7th FerryBox Workshop

2016 March: Oslo Norway; Ocean acidification workshop, Norwegian Environment Agency

2016 March: Oceanology International

5. Conclusions

Carbonate system observations are crucial for understanding present day processes and future change due to fossil fuel emissions. Developing sensors for these types of observations, and in the case of this task developing combined sensors for measuring two carbonate system variables at the same time, is an important step towards improving observations and hence bettering our understanding of the





coastal carbon cycle. While each task encountered issues during the development and testing of these combined sensors, promising progress has been made, and work and collaboration beyond the funded subtasks is continuing. There is also the intention that sensors from subtask 2 and 3 will be further developed for wider distribution and use through SMEs.

6. Annexes and references

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Voynova, Y.G, Petersen, W., Gehrung, M., Aßmann, S. King, A.L. 2018. Intertidal regions changing coastal alkalinity: the Wadden Sea-North Sea tidally-coupled bioreactor. *Limnology and Oceanography*, in review.

