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D3.4 - Report on new sensor developments

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Table of Contents

TABLE OF CONTENTS **3**

1. DOCUMENT DESCRIPTION **5**

2. EXECUTIVE SUMMARY **6**

3. INTRODUCTION **7**

4. MAIN REPORT **10**

4.1. Sensors for FerryBox **11**
4.1.1. Overview 11
4.1.2. Phytoplankton 12
4.1.2.1. Chlorophyll: Flow-through PSICAM 12
4.1.2.2. Phycocyanin fluorescence sensors for cyanobacteria biomass 16
4.1.3. pH 19
4.1.3.1. Scientific relevance 19
4.1.3.2. pH sensor (HZG) 20
4.1.3.3. pH sensor (NIVA) 22
4.1.3.4. pH sensor (SMHI) 25
4.1.3.5. pH sensor (ULPGC) 28
4.1.3.6. pH sensor (NERC) 30
4.1.4. Total Alkalinity (A_T) 32
4.1.5. pCO_2 35
4.1.5.1. Scientific relevance 35
4.1.5.2. pCO_2 sensor (NIVA) 36
4.1.5.3. pCO_2 sensor for water and air measurements (SMHI) 38
4.1.5.4. pCO_2 sensor (CEFAS) 40
4.1.6. Passive Sampler 45
4.1.6.1. Scientific relevance 45
4.1.6.2. Passive Sampler (CEFAS) 46
4.1.6.3. Passive sampler (NIVA) 49

4.2. Sensors for Gliders **52**

4.2.1. Overview 52

4.3. Sensors for Fixed Platforms 56
4.3.1. Overview 56
4.3.2. Wipers (CEFAS) 57
4.3.3. Fish detection echo sounder (AZTI) 59

5. CONCLUSIONS 63

ANNEXES AND REFERENCES 65

1. Document description

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2. Executive Summary

Ocean observing systems like FerryBoxes, Gliders and Fixed Platforms are ideal for testing new sensors under controlled conditions. The potential of existing systems to integrate new sensors for a period of time will be briefly identified, before an overview is given about developed sensors that are in non-observational mode on board of an ocean observing system.

Many of the partners already test new or prototype instruments on a non-operational basis, yet the results of tests are often not widely known. Here, the performance of new sensors will be assessed, as it is one of the main issues of sub-tasks 3.1.4 and 3.3.4 of JERICO WP3.
The range of instruments encompasses e.g. carbonate parameter sensors (i.e. pH, pCO_2), chlorophyll sensors, passive samplers and fish detection systems.

The mentioned sub-tasks of WP3 are tightly linked to WP10; however, this report will be focused on sensors that are already in pre-operational mode. WP10 addresses on (potential) development of new physico-chemical and biological sensors, which are in test phase.
The main issues of each sensor presentation in this report are applied methods, the implementation on a platform and data quality control. For gliders, we will give only a brief overview of existing new sensors deployed on gliders and refer to EU project GROOM (GROOM, 2014).

3. Introduction

In European coastal waters, a vast number of observation platform systems of different kinds have been installed in the last decades, mounted with a number of various sensors. The equipment chosen for each observation site depends on several factors, e.g. the surroundings, the energy supply, the accessibility and the scientific questions that are being answered. Much effort has been invested in the development of reliable platforms and in development of autonomous, robust and stable sensors which are mounted on the observation platforms. With the introduction of new technologies, new solutions to the main difficulties could be applied, i.e. to the challenges of miniaturization, low energy need and robustness.

Ocean observation platforms in European coastal waters can be classified in three groups:

- FerryBox
- Glider
- Fixed platform (e.g. buoy, pile)

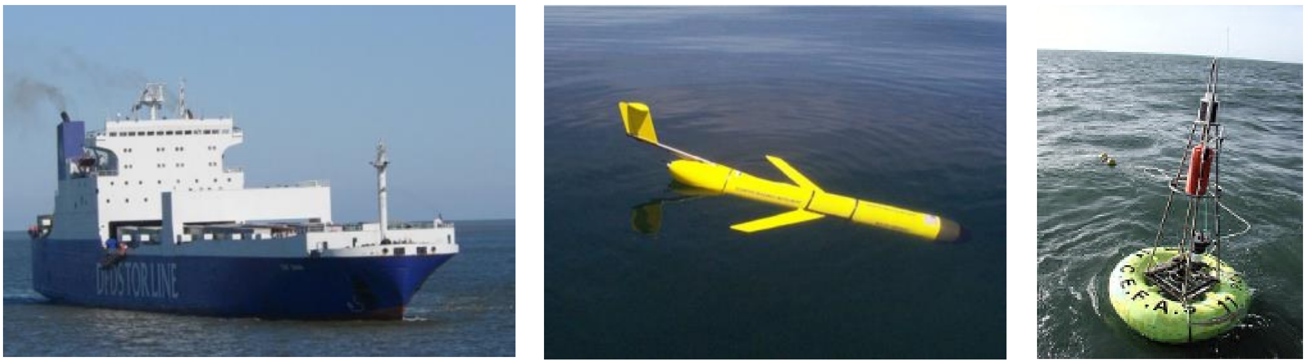


Figure 1 : Ocean observing systems : FerryBox on Ship of Opportunity (left), Slocum glider (middle) and SmartBuoy (CEFAS) (right).

Within JERICO, these three platform types (seen in Figure 1) are well described in previous deliverable reports in WP3 (D3.1 - Report on current status of FerryBox (Hydes et al., 2012); D3.2 – Report on current status of glider observatories within Europe (Tintore et al., 2013); D3.3 – Report on the current status of fixed platforms in Europe (Collingridge et al., 2013)). These reports provide information on the current status of existing systems in operational use within Europe and define the best technical practises for the operational use of these systems. They also describe the best procedures for harmonizing and merging quality-assessed high-frequency in situ data and they point out gaps in the present coverage of observation platforms.

Many solutions have been developed for placing unmanned logging sensors in the marine environment in order to collect high quality data for research and monitoring purposes. Sensors have been attached to anchored buoys, to seabed landers and to fixed platforms either onshore or offshore. Some locations have now been successfully collecting environmental data for well over a decade, and this type of continuous high resolution data is a highly valuable asset for understanding the marine environment and for fulfilling the requirements of policy such as the Marine Strategy Framework Directive.
These observation systems also serve as a indispensable platforms for testing newly developed sensors of different types. This approach offers many benefits; including those of existing infrastructure and maintenance regimes together with, in many cases, supporting ancillary data from other sensors. In JERICO, the goal has been to deliver heterogeneity of technological design, maintenance practices and quality control. This also includes the transfer of knowledge about new technologies and new sensor developments for ocean observing systems. Thus, we present in this report newly developed sensors that have been tested as prototypes or that have an operational or pre-operational status on different platforms.

The range of instruments presented includes those measuring carbonate parameters (e.g. pH and pCO_2) sensors that provide a role in measuring ocean acidification, fluorometers for the measurement of primary productivity using the variable fluorescence technique fluorescence, automated nutrient analysers, submersible flow cytometers and water samplers, spectroradiometers and absorption meters. Advances in existing sensors due to their miniaturisation or improved resolution are also assessed here.

The report is structured mainly according to the different platforms, i.e. FerryBoxes, Gliders and Fixed platforms. Beyond that, the report addresses different relevant parameters for each platform type.

For gliders, this report gives only a short overview of various sensor developments for biogeochemical and physical parameters, as well as profiling devices. This has been addressed in more detail in a project report for GROOM (GROOM, 2014).

4. Main Report

In the following sections, various sensor developments are presented with a focus on different observation platforms and the parameter which will be measured by the sensor. This chapter will be divided into three parts according to the different platforms. There, the listed sensor developments will be addressed in a manner adopted from GROOM (2014) as follows

- Scientific relevance
- Applied methods
- Implementation on platform
- Data quality control
- Outlook for possible improvements

So, beside the methods applied to each new sensor type, each sensor has also been classified according to the actual level of its implementation, i.e. if implementation on the platform is in a pre-operational or operational mode. New potential sensor developments will be addressed in WP 10 deliverable.

4.1. Sensors for FerryBox

4.1.1. Overview

FerryBox systems are cost-effective tools that support the collection of marine scientific and monitoring data. They are able to produce a high yield of reliable high-frequency and high-quality data that is gathered along repeated transects, this often greatly increases the data density over that obtained using conventional monitoring strategies based on infrequent sampling. Many of the technical problems that are typical for fixed and isolated marine measuring systems such as buoys do not pose a problem for FerryBoxes. These include constraints in the availability of power, installation and storage space, protection of components against harsh marine environments and longer-term fouling. FerryBox systems are normally installed on ships that service a constant route, so instrument servicing and calibration can often be done directly in a nearby home port. Compared to devices deployed off shore the operating costs of FerryBox systems are significantly lower.

Key oceanographic parameters such as the water temperature, salinity, chlorophyll-fluorescence, dissolved oxygen content and turbidity are easily and consistently observed. Additional instruments are relatively easily added and these can extend the basic measurements to provide information on a wider range of process. The instruments on board of a FerryBox system are stable and have low maintenance requirements once an appropriate installation has been developed.

The period from 2000 onwards has seen a steady growth in the number of FerryBoxes and related deep-sea systems in operation around the world. The potential for considerable further growth has been widely recognised (Borges and Co-Authors, 2009; Hydes et al., 2009). Key scientific research can be addressed with FerryBox data. For example, the deep sea measurements of air sea fluxes of carbon dioxide have been lately a focus of activity and this work has clearly demonstrated the power of the concept, when data from a number of routes can be merged together as was done by Watson et al. (2009).

The high resolution of FerryBox systems in space and time can provide deeper insights into marine processes that can be used to better assess the ecosystem and the underlying physical-biogeochemical processes in the marine environment. Special events like intense short-term algal blooms, rarely detected by standard monitoring methods, can be studied in detail and related to variations in influencing factors such as temperature, wind and nutrient load. This information can then be used for the further development of ecosystem models.

4.1.2. Phytoplankton

4.1.2.1. Chlorophyll: Flow-through PSICAM

- Scientific relevance

In the context of climate warming, knowledge of the global carbon cycle is of great interest and importance. In coastal areas, the carbon cycle plays an important role; the sources and sinks have to be evaluated. Besides the abiotic parameters the research of phytoplankton is important for complete understanding of the carbon cycle mechanisms. Phytoplankton acts as a primary producer, so they fix CO_2 in the water. They fuel the export of carbon into deeper waters, and also constitute the basis of the marine food web. Thus, the dynamics of phytoplankton biomass have to be evaluated, as well as the different types of phytoplankton species. The parameters have to be determined as reliably as possible and with high spacial and temporal resolution. Continuous measurements are beneficial as trends and relative changes are not adequately resolved by point measurements. With an automated continuous observation device, long-term measurements as well as detection of single events can be achieved (Wollschläger et al., 2013).

- Applied methods

Laboratory integrating cavity measurement systems like point-source integrating cavity absorption meter (PSICAM; e.g. Röttgers et al. (2005)) overcome the problem of particle scattering by introducing the sample in a diffuse light field set up in an integrating tube or sphere, respectively. Scattered photons cannot get lost, but are reflected from the cavity wall until they are absorbed or reach the detector. Additionally, the optical path length is increased drastically by the reflective walls allowing the measurement of very clear waters with a relatively small device. A concentration of the sample prior to the analysis can therefore be avoided.
The Flow-through PSICAM (ft-PSICAM) is similar to the previous developed conventional PSICAM, described and used by Röttgers et al. (2005). However, the cavity of ft-PSICAM is made from PTFE which has been equipped with water inlets and outlets to enable flow-through operation. It was installed into a setup of pumps, valves, and tubes for water supply, drainage, and supply of other fluids needed for the experiments. A detailed overview of the assembly is given in Figure 2.
For illumination of the cavity, a 150-W IT 3900 lamp (Illumination Technologies, USA) was used. Light leaving the cavity was detected by a Ramses UV/VIS-spectrometer (TriOs, Germany) in a range from 400 to 710 nm. Thus, the detector was different from the one used for the conventional PSICAM.

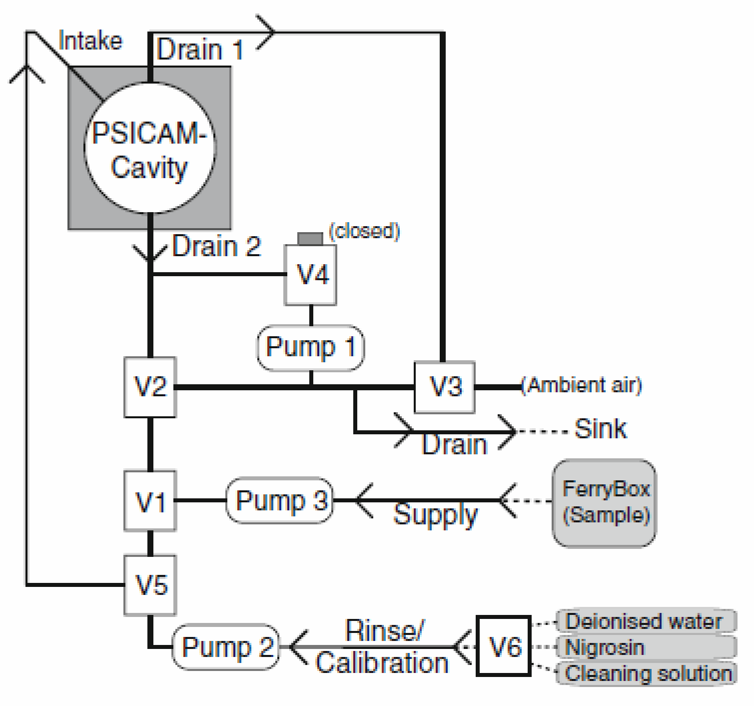


Figure 2: Flowchart of the ft-PSICAM. V stands for valve. From Wollschläger et al. (2013).

- Implementation on platform

The ft-PSICAM is designed to be connected to a FerryBox (Petersen et al., 2011) which collects other parameters important for the correction of the absorption coefficients like salt and temperature.

The sensor has been tested in the German Bight during two ship cruises with the R/V "Heincke" conducted in April and June 2011 (Wollschläger et al., 2013). The German Bight is affected by different water masses: (1) the southern and eastern part along the coasts is influenced by runoff from the major rivers Ems, Weser, and Elbe as well as by freshwater discharge from the hinterland via the Wadden Sea, while (2) the offshore areas have more open ocean characteristics. Therefore, the study area provided a broad spectrum with strong inshore–offshore gradients of relevant parameters like TSM and CDOM.

Results of ft-PSICAM measurements have been compared to conventional PSICAM observations and reveal good performance of the new sensor. Good linear correlation for all wavelengths has been found (Figure 3). See for more details in Wollschläger et al. (2013).

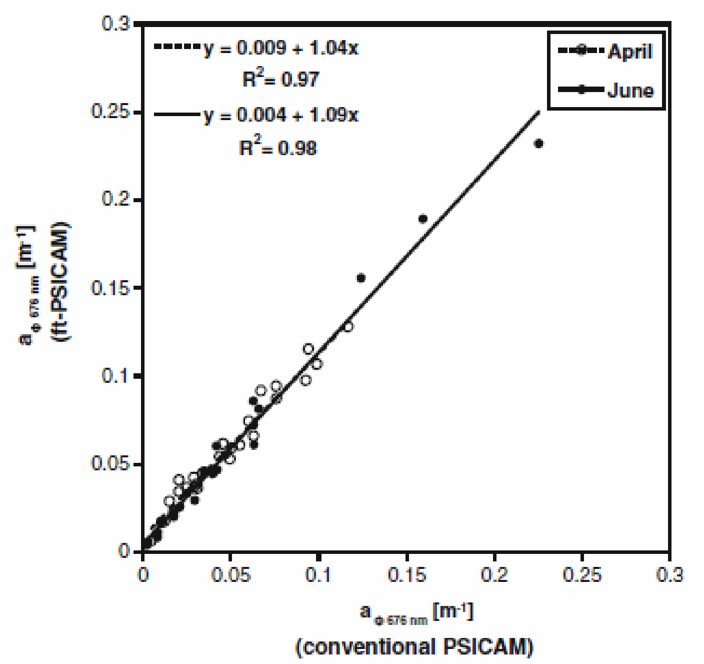


Figure 3: Correlations with linear fit between estimated phytoplankton spectral absorption coefficient a_{Φ} for from conventional and from ft-PSICAM. From Wollschläger et al. (2013).

❖ Data quality control

The principle of calibration and the equations for the calculation of spectral absorption coefficients are the same for both the ft-PSICAM and the conventional PSICAM. Calibration of the device was performed once a day in the same manner as for the conventional PSICAM, but with a modified cleaning step: In order to clean the system after each calibration measurement, first the cleaning solution was cycled from its container through the cavity for 2 min, afterwards the same was done with the bleaching solution for 5 min. Subsequently, the cavity was rinsed first with deionized water, then with purified water.

❖ Outlook for possible improvements

The ft-PSICAM has, since it is only a first attempt to use the PSICAM principle for continuous measurements, potential for further improvement in the future, namely achieving accuracy comparable to the high precision of conventional PSICAM measurements and a more convenient use by automation (Wollschläger et al., 2014). Moreover, devices like the PSICAM and the ft-PSICAM measure not only the absorption coefficients important for Chl-a and TSM determination, but those of the whole visible spectrum. Such data could be used for the discrimination and identification of phytoplankton groups, what would be an additional set of valuable information for a variety of ecological questions. Therefore, it is important to put further effort in the improvement and development of such systems for reliable, high frequency measurement of water constituent absorption coefficients in the whole visible light spectrum.

4.1.2.2. Phycocyanin fluorescence sensors for cyanobacteria biomass

❖ SMHI FerryBox overview

SMHI operates a FerryBox system on the ship TransPaper on the route Gothenburg-Kemi-Oulu-Lübeck-Gothenburg since 2009. Sampling of most parameters is every 20 seconds corresponding to approximately every 200 meters depending on the speed on the ship. To investigate ocean acidification high quality analyses of the carbonate system is needed. There are four interconnected parameters in the marine carbonate system, at least two are needed to describe the system. The SMHI approach to investigate the situation in the Baltic Sea and in the Kattegatt in JERICO is to analyse three parameters using the FerryBox system for automated analyses of pH and PCO2 and as a sampling platform for water samples for on land laboratory analysis of total alkalinity.

Cyanobacteria blooms occur in mainly in fresh water and in brackish water. In the Baltic Sea surface accumulations of cyanobacteria is a recurrent phenomenon in summertime. In the Southern North Sea (Frisian Islands) a cyanobacteria bloom was observed in 2011. Cyanobacteria blooms in river mouths are observed in several European countries.

❖ Experiences of phycocyanin fluorescence sensors

SMHI has evaluated the TriOS micro flu blue sensor as part of the FerryBox system on the ship TransPaper. It is illustrated together with other sensors in Fig. x. The sensor is cleaned manually every two weeks when the ship is in the harbour of Gothenburg. Automated cleaning is carried out whenever the ship is in harbour, i.e. four times per week. Calibration of the sensor was made in cooperation with SYKE, Finland, using a culture of the picoplanktonic cyanobacteria *Synechococcus*. The field data show that the observed fluorescence from cyanobacteria is often at the lower end of the range of the instrument.

In addition another phycocyanin sensor (ECO FL manufactured by Wetlabs Inc., USA) is being evaluated by SMHI on the Huvudskär E. mooring in the Baltic Sea. The sensor has been deployed on the mooring during two summers but due to technical problems no reliable data is available yet. The sensor uses a copper plate with a rubber wiper as an anti biofouling device. The plate covers the optical window when no measurements are made and open during measuring sessions.

Results will be presented in a report from work package 10.

Figure 4 : Sensors for chlorophyll fluorescence, turbidity, phycocyanin fluorescence and fluorescence of coloured dissolved organic matter on the ship TransPaper. All the sensors have flow through cells.

❖ Applicability to different platforms

Both sensors are applicable for use in FerryBox system, small and large moorings and other fixed platforms and on AUV's and gliders. Results from SYKE (Jukka Seppälä) based on experiments with algal cultures indicate that the wavelength windows for excitation and emission used in the Wetlabs instrument is not well suited to detect the cyanobacteria in the Baltic Sea. Fluorescence from other pigments may influence the results. The TriOS instrument is better suited for the cyanobacteria in the Baltic Sea. The use of anti biofouling devices and regular cleaning is necessary.

4.1.3. pH

4.1.3.1. Scientific relevance

The pH of seawater is one of the key parameters of the carbon cycle and the CO_2 system in ocean and atmosphere. In the context of climate change, it has been found that pH levels in the oceans are decreasing by 0.0019 pH units per year. This is due to an increased uptake of CO_2 in the ocean, the so-called ocean acidification (Doney et al., 2009) which is supposed to have great influence on marine ecosystems (Fabry et al., 2008). So, the monitoring of components of the CO_2 cycle is of major interest, especially in coastal areas, where rough environmental conditions and rapid changes of the composition of the water mass takes place (Aßmann et al., 2011).

For the measurement of seawater pH different approaches are described in the literature. The most promising approach for pH determination are spectrophotometric measurements employing an indicator dye, refined by Clayton and Byrne (1993). The use of glass electrodes for potentiometric pH determination of seawater cannot be recommended due to the limited accuracy of these sensors. However, another promising approach is the application of Durafets (ion sensitive field effect transistor based pH sensors) tested by Martz et al. (2010).

Many designs of pH sensors are not suitable for integration into an automated water measurement system like the FerryBox (Petersen et al., 2003). This system is commonly used in coastal regions which can have large changes in water temperature and a wide range of pH values due to e.g. high primary production.

The FerryBox devices are usually built into ships of opportunity operating under highly varying conditions without user interaction.

4.1.3.2. pH sensor (HZG)

❖ Applied methods

The sensor presented here is a bench-top system which consists of a syringe pump, a heat exchange system, a cuvette composed of polyethylene terephthalate (PET), a control and data logging unit, and the optical system (Figure 5). The liquid handling is performed by a peristaltic pump (ISMATEC, ISM597D, marked as PP) to ensure a continuous stable flow and a syringe pump (Hamilton, PSD/2) for accurate injection of the indicator.

A gas tight plastic bag with an aluminum coating (Calibrated Instruments, Cali5Bond) is used as the indicator reservoir (IR). The indicator stock solution consists of 2 mmol kg-soln^{-1} mCP sodium salt (Sigma Aldrich, 211761) in a 0.7 mol kg-soln^{-1} NaCl (Merck, 106404) solution (ionic strength I = 0.7) to keep the equilibrium constants of the carbon system nearly undisturbed. An injection of 112.5 µl indicator stock solution by the indicator pump (IP) into the continuous sample flow of around 10 ml min^{-1} results in an indicator concentration of up to 115 µmol kg-soln^{-1}. This equates to absorbance values up to 0.9 at the isosbestic point of the dye (487.6 nm) and to absorbance values up to 1.8 at the indicator maxima (434 nm, 578 nm). Mixing of indicator dye and sample is realized by injecting the indicator solution through a tight Y-piece (YP) followed by a static mixer (piece of tubing filled with glass balls).

The seawater sample is provided by the FerryBox. The seawater stream passes a T-piece and ends up in an open outflow to waste. The other end of the T-piece is connected to the peristaltic pump (PP).

After indicator aspiration and injection the sample flows through a stainless steel tube embedded in an aluminum body which is kept at 25 °C (heat exchanger). The sample then passes the static mixer and enters the cuvette.

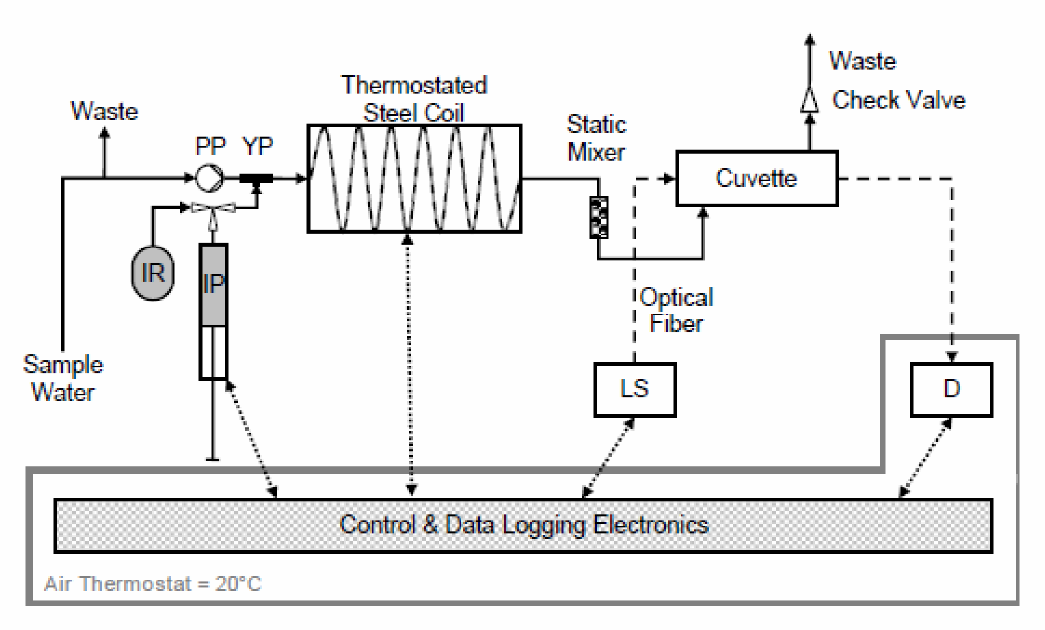


Figure 5: Scheme of the spectrophotometric pH system. IR: Indicator Reservoir, PP: Peristaltic Pump, YP: Y-piece, LS: Light source, D: Detector. From Aßmann et al. (2011).

❖ Implementation on platform

Underway measurements were performed during the R/V *Polarstern* cruises ANT-XXVI/1 (November 2009) and ANTXXVI/ 4 (May 2010) over periods of six weeks each as well as on several shorter cruises of approx. six to ten days in the North Sea (August 2009, July 2010, September 2010). During these cruises, the system was further optimized and tested.

The presented system is very portable and much smaller than comparable systems with similar features. No water bath is needed, which reduces all related problems like size and handling. The whole system consists of three units not including the computer. The fluid handling system has a volume of 13 l, the electronics box (including the spectrometer) is about 9 l, and the two programmable power supplies have a combined volume of 9 l. For integration into an automated water measurement system some simple size optimization would lead to a system about half that size.

The sensor is not yet implemented on a FerryBox, but it has been shown, that the implementation is possible (Aßmann et al., 2011). The device is ready to be used in combination with analysers for dissolved inorganic carbon (DIC) or total alkalinity (TA) for a comprehensive characterization of the seawater carbon system.

- Data quality control

For comparison purposes the pH data of this sensor system are plotted along with FerryBox data generated by a glass electrode. The glass electrode was chosen because it is a part of the flow-through system of the FerryBox. Up to now it is the only operational commercially available system suitable for FerryBox integration. The comparison is however limited to qualitative aspects as the accuracy and stability of these electrodes is very limited.

4.1.3.3. pH sensor (NIVA)

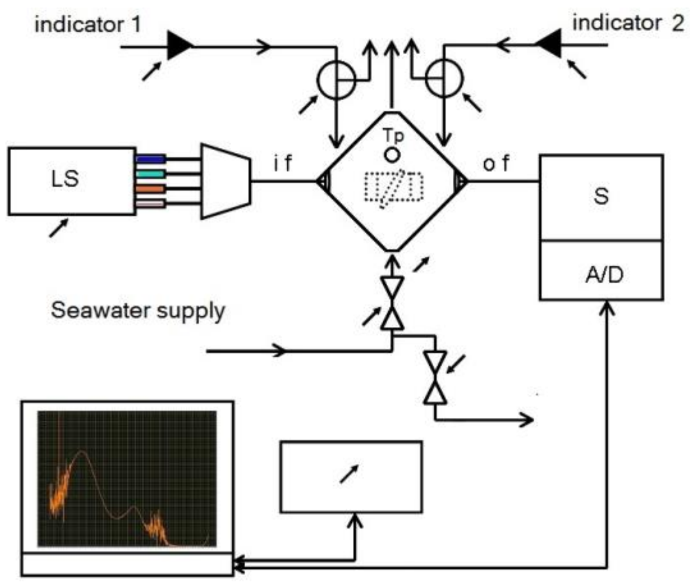
- Applied methods

The seawater pH detection system developed and currently adopted is based on spectrophotometric absorbance determination (Clayton and Byrne, 1993) in an automated flow-through system, natural evolution of what presented in Bellerby et al. (2002). A custom designed 8ml PTFE cuvette features bubble free optics achieving 40mm pathlength, valved water inlet/outlet and magnetic stirring, one or multiple indicator dye injection, calibrated sample's actual temperature probe, heating pad.
Further advanced design will include extended path-length (using a mirror) and a more compact design.
Light is provided by a combination of LED for minimal power consumption and high S/N ratio at investigation wavelengths. Light is fed by a PMMA optical combiner/guide to the cuvette.
Transmitted light is detected by a miniature spectrophotometer (STS, Ocean Optics). The system is supervised by a laptop interfaced with the spectrophotometer and a data acquisition/control board (LabJack).
The water is fed through a peristaltic pump or just opening the inlet/outlet valves if operating in a stream like a wave-glider. The detection sequence lasts around 15s. First a blank spectra is acquired (this is performed

every time to achieve the highest precision), then 60-80 µl of 2mM thymol blue, sodium salt/milliQ water solution from a gas tight aluminum bag is injected into the cuvette via a solenoid pump. Final concentration in the sample is below 20µM, with isosbestic absorbance around 0.4. Absorbance levels and S/N of detection achieve a precision as low as 0.0005 demonstrated on fast replicates (Reggiani et al., unpublished). Indicator perturbation should be assessed routinely (this can be performed automatically by the system itself). At present is estimated to be around 0.004 (±0.001).

500ml stock solution, at 10 minutes sampling interval, give up to 40 days autonomy. The reviewed design will achieve up to 3 months deployment without attendance or calibration.

At present the set-up is being reviewed, in order to run the system without the need of PC based software and enhance integration in existing platforms.



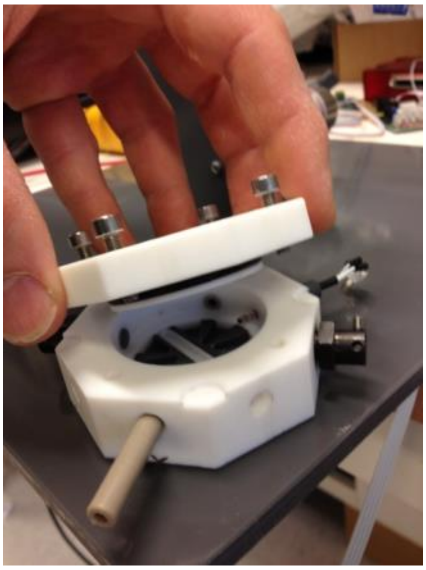


Figure 6 : System manifold (left) and cuvette close-up (right).

❖ Implementation on platform

Underway measurements with such a system have been already extensively performed and it turned out to be its optimal environment although it would be easily adapted to moorings or specific coastal surveying vessels. The system is regularly in operation aside the NIVA FerryBox onboard the Hurtigruten cruise line M/S Trollfjord, achieving continuous monitoring of Norwegian coast from Bergen to Kirkenes.
One more system is undergoing safety checks in order to be hosted by the FerryBox system running on board the Color Fantasy cruise line, for continuous monitoring of Skagerrak and Kattegat from Oslo to Kiel.

Figure 7 : pHaro (pH analyzer for oceanography) deployed on MS Trollfjord.

❖ Data quality control

Carbon system determination is achieved through parallel monitoring of pH and pCO_2 thanks to a flow through CO_2 detection system integrated in the FerryBox (Franatech). Water samples are routinely taken for over-determination and cross-check (seen e.g. in Figure 8).

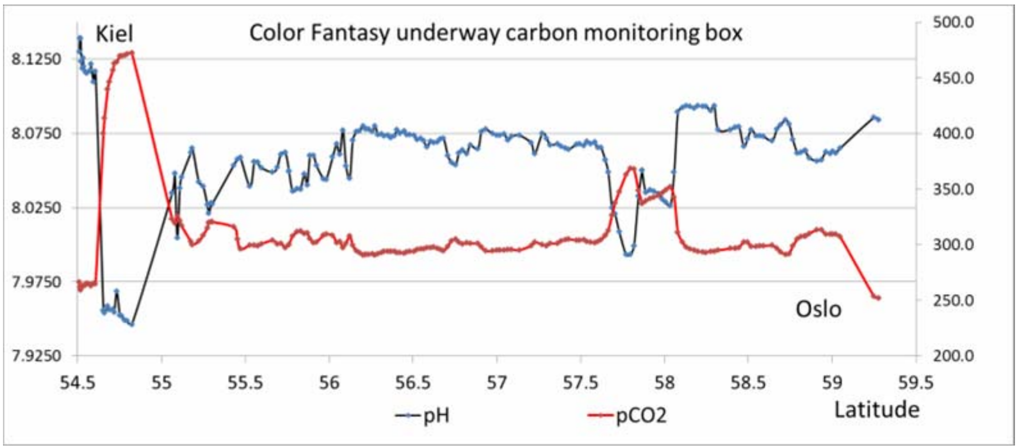


Figure 8 : Cross-check of pH and pCO_2 measurements on MS Color Fantasy.

4.1.3.4. pH sensor (SMHI)

❖ Applied methods

SMHI has together with the University of Gothenburg developed a novel sensor for pH. The system is based on a fluorescent probe DHPDS (Figure 9). The ratio between red and green fluorescence varies due to pH. An important advantage of the method is that it works in a large salinity range. SMHI is evaluating it in a range from 3-30 psu from. The method was published in 2013 (Hakonen et al., 2013) and the system is being evaluated further in the JERICO project. SMHI evaluates two systems, one is mounted on the ship TransPaper and the other one is evaluated during cruises with research vessels. The system is illustrated in Figure 9 (left). The measurement device, shown in Figure 10 (left) is mounted next to the General Oceanics CO_2 system on the ship TransPaper (see Figure 10 (right)).

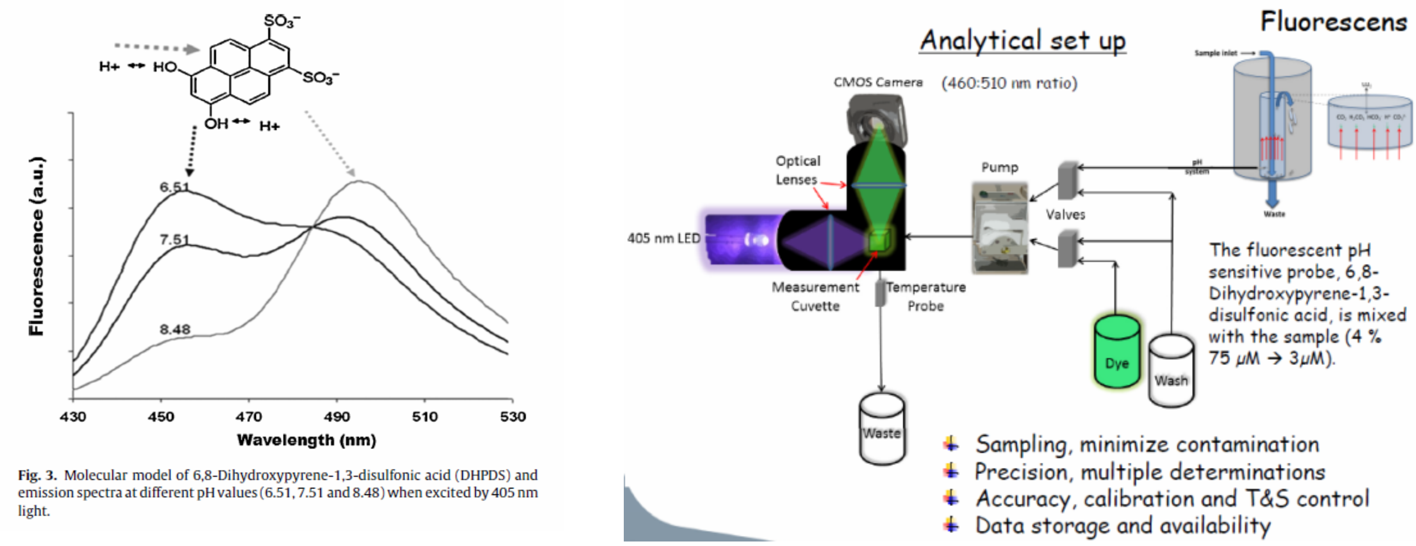


Figure 9 : Left: the fluorescent probe DHPDS and right: analytical setup (Hakonen et al., 2013).

Figure 10 : The pH measurement system (left) on the ship TransPaper (right).

❖ Results

An example of data on pH in the Kattegat is presented in Figure 11 together with salinity. pH varies naturally in the Baltic Sea due to differences in river flow into the different basins etc. Also primary production influences pH, high pH is associated with high primary production because of reduced CO_2.

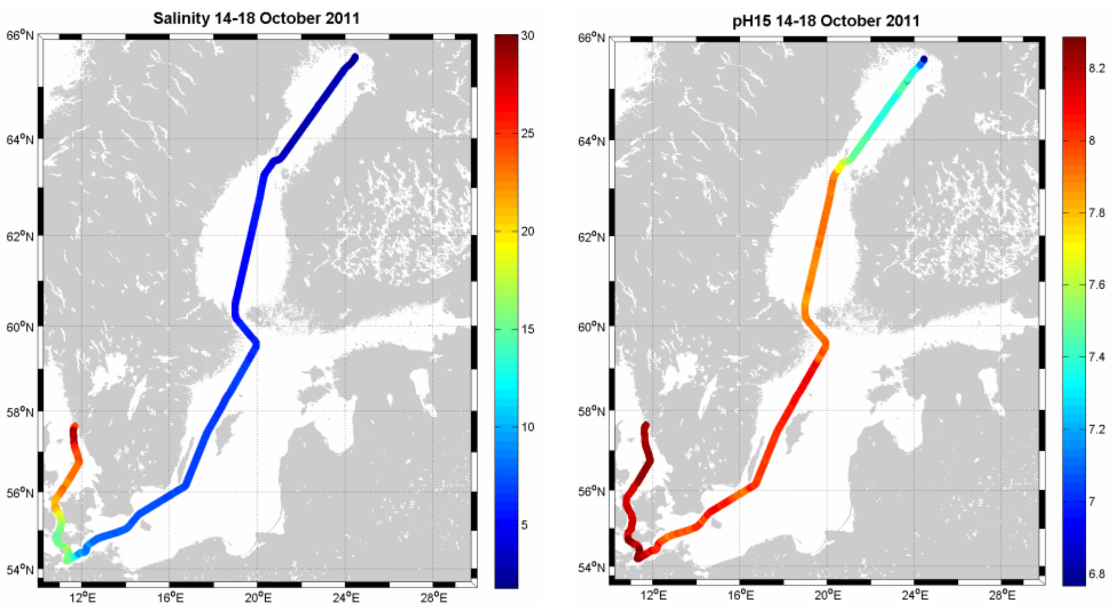


Figure 11 : An example of salinity and pH measured using the system on TransPaper from Oulu (Finland) via Lübeck (Germany) to Gothenburg (Sweden). Note the salinity range of approximately 3-30 psu.

❖ Applicability to different platforms.

In the present form the system needs electricity (230 volts), it includes a PC and the box for the system is relatively large. This is fine for use in FerryBox systems and on large moorings and other fixed platforms but not suitable for gliders and small moorings. However, the system lends itself to miniaturization which means that is should be possible to use it on small moorings, AUV,'s gliders etc.

4.1.3.5. pH sensor (ULPGC)

During the JERICO TNA's activities a new pH sensor for fixed platforms, based on the prototype developed by the QUIMA-ULPGC group, was deployed in one coastal buoy of the Poseidon sea monitoring network.

Coastal waters are badly sampled for carbon dioxide and only some CO2 sensors have being recently deployed along USA coastal waters and North of Europe. One pH sensor which has a 0.001 pH unit reproducibility deployed in an important region as it is the east coastal Mediterranean seawater will be a great added value for a) the pH development system, b) the monitoring of ocean acidification in the Mediterranean Sea and c) for the JERICO project.

The experimental method consisted in fixing the pH sensor to the underwater body of the buoy in the depth range from surface to 10 m and integrated to the stations power, data acquiring and the telemetry subsystem. The resolution for the pH reading was adjusted as indicated by the buoy provider (6 hours). The values of pH will be related to other parameters determined by sensors deployed together at the buoy.

The pH sensor developed by the QUIMA-ULPGC group, integrating a spectrophotometric pH system in a standalone submarine unit, can be deployed in any buoy/fixed platform with a power supply of 9 - 18 V and is able to transmit real time data of pH in total scale at in situ temperature, sea temperature and salinity to the central unit of the buoy. The system includes a real time clock allowing autonomous operation, as well as a high accuracy internal temperature sensor. It can be connected to an external conductivity / temperature sensor for deployments where high salinity variations occur.

The spectrophotometric light source used is a Sensorlab SL001, a compact, high stability, low settling time and low power LED, that does not degrade and do not require bulb replacements as traditional halogen lamps do. The development of the first lab-based pH sensor prototype was completed in 2007. The experience from this first prototype enabled the development of the first submarine pH sensor, completed in 2009.

Figure 12: Sensorlab pCO2 sensor. By courtesy of HCMR.

Figure 13: Sensorlab pCO2 sensor, deployed on HCMR coastal buoy. By courtesy of HCMR.

4.1.3.6. pH sensor (NERC)

❖ Applied methods

A simple micro-fluidic pH sensor integrated in a shipboard instrument featuring good precision (0.001 pH units) and accuracy (better than 0.004) is presented as a key step toward a targeted pH micro-sensor system. The system uses a simple micro-fluidic design integrated in a shipboard instrument with low sample (550 µL) and reagent (12 µL) consumption. A robust optical setup is achieved using a custom made polymeric flow cell coupled to a three wavelength Light Emitting Diode (LED). The system is adaptable for continuous underway measurements or discrete sample analysis.

The seawater sample and indicator solutions are pumped at a flow rate of 60 µL/min, in order to obtain an enhanced dispersion and homogenous mixing across the channel, by two different syringe pumps and mixed in the flow cell in a static mixer before entering the absorption cell.

A tri-coloured LED was used to transmit the light source with two wavelengths (435 nm and 596 nm) for the absorption maxima of the indicator forms (HI^- and I^{2-}) and 750 nm to monitor the sample turbidity. The light is transmitted through a 10mm long absorption cell and recorded by a spectrometer (Oceanoptics HR4000). The measurement is made close to the in-situ temperature (+0.2 °C) by placement of the microfluidic cell in the sampling chamber which has a continuous flow of the ship's underway seawater supply. The seawater sample and indicator solution are pumped by two different syringe pumps and mixed in the flow cell in a static mixer before entering the absorption cell, as shown in Figure 14A.

Figure 14B shows the microfluidic flow cell which was milled in tinted PMMA (polymethylmethacrylate). The channel width is 250 x 250 µm except for the absorption cell which is 700 x 700 µm. Figure 14C shows an image (left hand side) of the pH system on board the RSS Discovery showing the sampling chamber with the two syringe pumps on top. Next to this are the electronic control box, light source and detector situated.

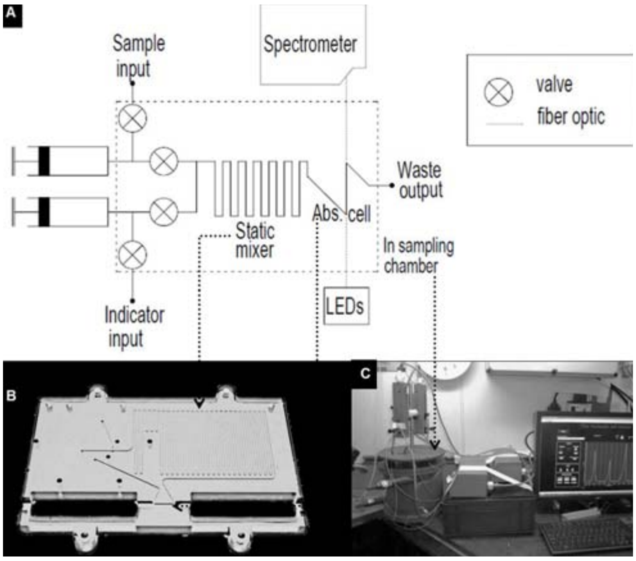


Figure 14 : The pH system showing (A) schematic of the sensor and (B) the chip and (C) the complete system on board the RSS Discovery. From Rerolle et al. (2012).

❖ Implementation on platform

The underway pH sensor was deployed on RRS Discovery cruise D366 (between 06/06/22011 and 07/07/2011) round the coast of Ireland. The automated pH system was operated continuously over a period of a month on an underway seawater supply. Measurements were only interrupted for system performance checks and maintenance. The pH observed during the first week of the cruise ranged between pH 7.974 and 8.118. The highest pH values were observed northwest of Ireland due to high phytoplankton biomass and primary productivity resulting in the uptake of DIC. Lowest pH values were observed in the north Irish Sea as a result of DIC production through remineralisation of organic matter.

❖ Data quality control

Comparison of cruise pH data with pH calculated from carbonate parameters DIC, TA and pCO_2 showed a discrepancy between 0.005 and 0.013 pH units.

4.1.4. Total Alkalinity (A_T)

❖ Scientific relevance

Due to the rapid influx of anthropogenic CO2, the marine carbon cycle and thus the marine ecosystem is affected. There is a substantial need for autonomous sensors which are able to measure continuously parameters of biogeochemical cycles, especially for the carbonate system. So, the monitoring of ocean acidification and the understanding of its principles is not only restricted to measuring of pH and pCO_2, but should also expanded to monitoring of Total Alkalinity (A_T). It is one of the four key measurement variables for characterizing the carbonate chemistry in seawater. Here a newly developed alkalinity sensor is described which gives the opportunity for monitoring the carbon system as a whole.

Until lately, automated measurements of A_T have not been available because of technical limitations.

❖ Applied methods

The measurement of Total Alkalinity can also be done with an autonomous flow-through system as for pH. Also the scheme is similar; so, including into a pH measurement system is possible. However, the accurate dose of liquids is even more crucial than for pH. There are two different methods for determining A_T, i.e. the open-cell and the closed-cell titration method.

The most restricting step for an open-cell titration is the required quantitative outgassing of CO_2. This takes at least 6 min for a complete equilibration to the gas phase and is thus connected to the environment (Aßmann, 2012). Nevertheless, Roche and Millero (1998) developed such a measurement system with high accuracy which is characterized, however, by a high complexity which makes maintenance difficult.

Closed-cell titration does not need outgassing which makes the method potentially fast. Mostly closed-cell titration systems are used due to the advantages of this method. The equilibration of the carbonate chemistry after an abrupt acidification to pH = 4.5 of the sample takes at most 2 s at 25 °C. The sample solution is separated from the environment and provides a clear material balance envelope. All masses going into the system are present during the measurement procedure without further alteration of the solution.

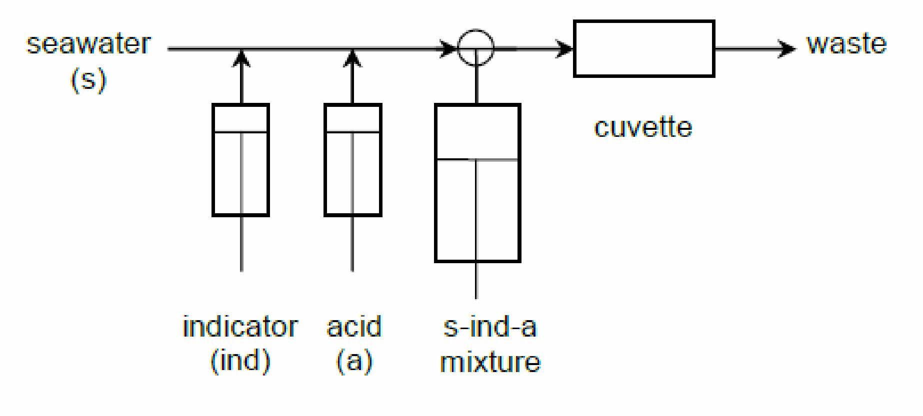


Figure 15 : Scheme for A_T determination by closed-cell titration (Aßmann, 2012).

For determination of A_T a closed-cell titration with hydrochloric acid is performed (see Figure 15). Monitoring of the titration curve in the pH range of 3.5 to 5.5 is done by an acid-base indicator dye (Bromocresol green, see Figure 16). The sample syringe (s-ind-a mixture) aspirates simultaneously sample water, indicator dye, and hydrochloric acid. The homogeneous solution is then led through the cuvette for spectrophotometric determination of the pH value. Calculation of A_T is done by a least-squares procedure based on a non-linear curve fitting approach.

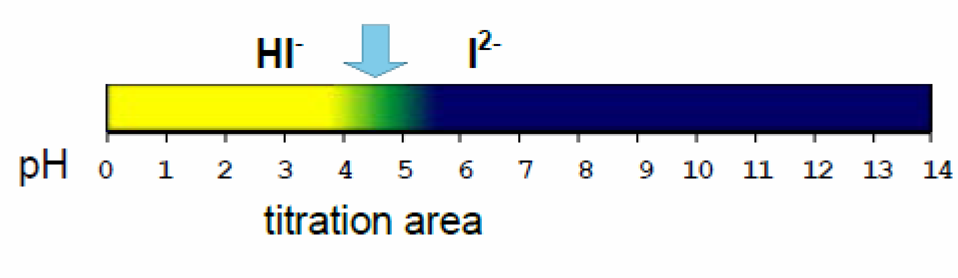


Figure 16 : Titration scheme of an indicator dye (Bromocresol green) (Aßmann, 2012).

❖ Implementation on platform

The application of A_T measurement systems is currently restricted to *laboratory-like* platforms where operator supervision and maintenance can be provided. The autonomous application on e.g. VOS or buoys for surface ocean measurements demands specific performance characteristics. The development of a fully-autonomous device is on the way.

❖ Data quality control

When measuring A_T in critical matrices it is highly recommended to cross validate this parameter by measuring the C_T – pH or C_T – *p*CO2 combination. C_T denotes the anorganic carbon. A combination of pH – *p*CO2 is not recommended due to its strong anti-correlation and unfortunate error propagation leading to high uncertainties of the calculated values. Currently only pH (e.g. Sunburst) and *p*CO2 (e.g. Contros, General Oceanics, Sunburst) are commercially available measurement systems providing high quality measurements of carbonate parameters.

For both A_T and C_T a more sophisticated approach is needed to carry out automated measurements. The accurate handling of sample water/reagents and the accurate measurement of the pH value are the most determining parts. An overview of the errors which are associated to the A_T titration procedures was described by Hydes et al. (2010).

4.1.5. pCO_2

4.1.5.1. Scientific relevance

The accurate determination of the inorganic carbon system is a key requirement for ocean acidification studies, as it forms the basis for assessments of biogeochemical responses to changes in ocean carbonate chemistry as a result of rising atmospheric CO_2 concentrations. It is also essential for the determination of the air–sea fluxes of CO_2, calculation of carbon budgets and estimation of anthropogenic CO_2 concentrations in different water masses (Ribas-Ribas et al., 2014). Therefore, there is a large interest to include CO_2 system parameters as standard parameters during ship cruises and on monitoring stations. Especially in coastal areas these monitoring devices have to be very robust to withstand rough environmental conditions as well as rapid changes in the composition of the water body.

CO_2 is only one species of the carbonate system, and changes in the chemical equilibrium may change the pCO_2. When the carbonate system is overdetermined, it is possible to test if the different variables are consistent with one another. This requires that more than two of the analytical variables (total dissolved inorganic carbon (C_T), total alkalinity (A_T), pH_T, or partial pressure or fugacity of CO_2 are determined.

A combination of pH – pCO_2 is not recommended due to its strong anti-correlation and unfortunate error propagation leading to high uncertainties of the calculated values. Currently only pH (e.g. Sunburst) and pCO_2 (e.g. Contros, General Oceanics, Sunburst) are commercially available measurement systems providing high quality measurements of carbonate parameters (Aßmann, 2012).

4.1.5.2. *pCO_2 sensor (NIVA)*

❖ Applied methods

The seawater dissolved CO_2 measurement system developed by Franatech in collaboration with NIVA and currently adopted, is based on gas separation from the water phase and successive detection by high temperature ceramic solid state, selective piezoelectric element.

Gas separation occur in a flow-through chamber at a rate of 2 l/m via a peristaltic pump, CO_2 diffuses through a silicon membrane and enter a gas loop constantly monitored against temperature and pressure. Calibration of the gas phase has to be performed prior to deployment and after recovery. Data are logged internally and the system can be interfaced via serial port to a PC.

Due to the relatively high power consumption to maintain the sensing unit at the working temperature, this system is ideally suited for FerryBox operations, achieving +/- 2 vpm CO_2 precision.

❖ Implementation on platform

Underway measurements with such a system have been already extensively performed and it turned out to be its natural environment. The system is regularly in operation aside the NIVA FerryBox onboard the Hurtigruten cruise line M/S Trollfjord, achieving continuous monitoring of Norwegian coast from Bergen to Kirkenes.

One more system is undergoing laboratory calibration in order to be hosted by the FerryBox system running onboard the Color Fantasy cruise line, for continuous monitoring of Skagerrak and Kattegat from Oslo to Kiel.

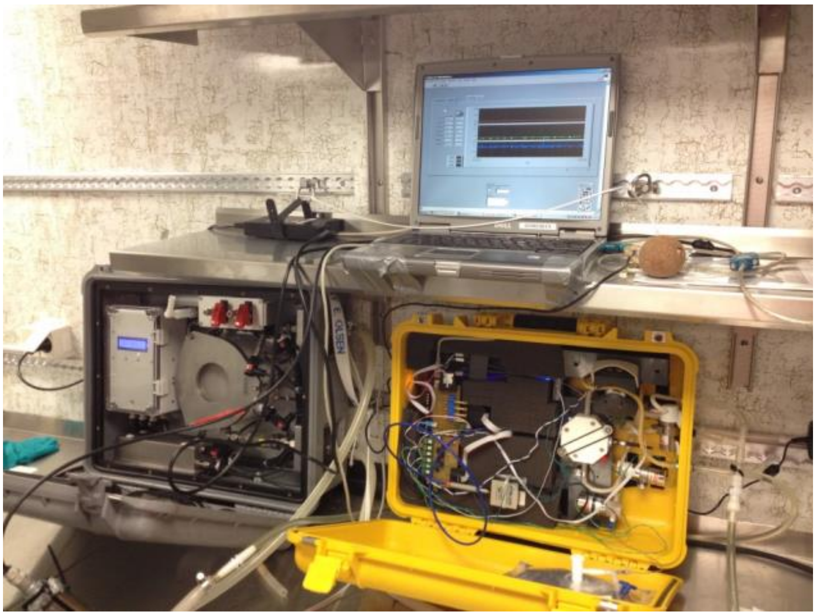


Figure 17 : pCO_2 and pH detection systems onboard M/S *Lance* during arctic cruise in March 2014.

❖ Data quality control

Carbon system determination is achieved through parallel monitoring of pH and pCO_2 thanks to a flow through pH detection system integrated in the FerryBox (pHaro). High precision makes it possible in an effective manner, limiting uncertainty propagation due to the anti-correlation of this pairing (see plot of raw data reported below, provisional results). Water samples are routinely taken for over-determination and cross-check.

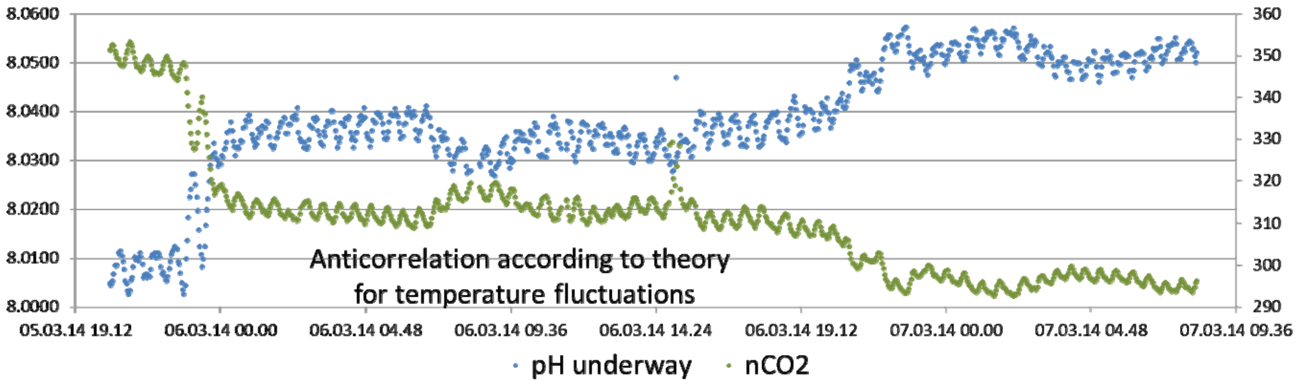


Figure 18 : Sensitivity of pH/pCO_2 conjugate detection for CO_2 system determination during arctic cruise north of Svalbard, March 2014.

4.1.5.3. pCO_2 sensor for water and air measurements (SMHI)

A CO_2 analyser produced by General Oceanics Inc. (model 8050) is being used and for analyses of pCO_2 in water and CO_2 in air. Water is pumped from approximately 3 m depth into the FerryBox-system. The water flow is split into two paths; one goes to the general FerryBox sensors (salinity, temperature, chlorophyll fluorescence, phycocyanin fluorescence, CDOM fluorescence, oxygen and water sampling. The other path goes to the sensors for pH and pCO_2. Air is collected at the bow of the ship with a tube connecting the sampling inlet with the sensor located near the FerryBox.

❖ Applicability of sensor to different platforms.

The GO8050 instrument Figure 19 is relatively large with a pump, a wet box with the analyser, and a dry box with computer etc. In addition reference gases are used for automated calibrations of the instrument. The use of the reference gases is very important for the high quality of the results. However, it adds bulk and weight to the system.

Figure 19 : CO_2 analyses system on ship TransPaper, left: wet box with analyses instrument, middle: dry box with computer and right: tubes with reference gases. By courtesy of SMHI.

The weight and bulk of the system means that the GO8050 system is not useful on gliders or on small moorings. The system also requires electricity and regular maintenance. As part of a FerryBox system that can be regularly serviced the system is very good. SMHI oceanographic unit in Gothenburg is conveniently located close to the harbour where the ships are available six hours every week for service, collection of samples etc.

❖ **Results**

A data set on pCO_2 in water is presented in Figure 20. pCO_2 is affected by temperature; in cold water pCO_2 are at higher levels due to higher solvability than at higher temperatures. Another factor is primary production of phytoplankton. High production results in a reduction of pCO_2 due to photosynthesis. An example is the spring bloom in the Kattegatt (area A in Figure 20) in February and first part of March.

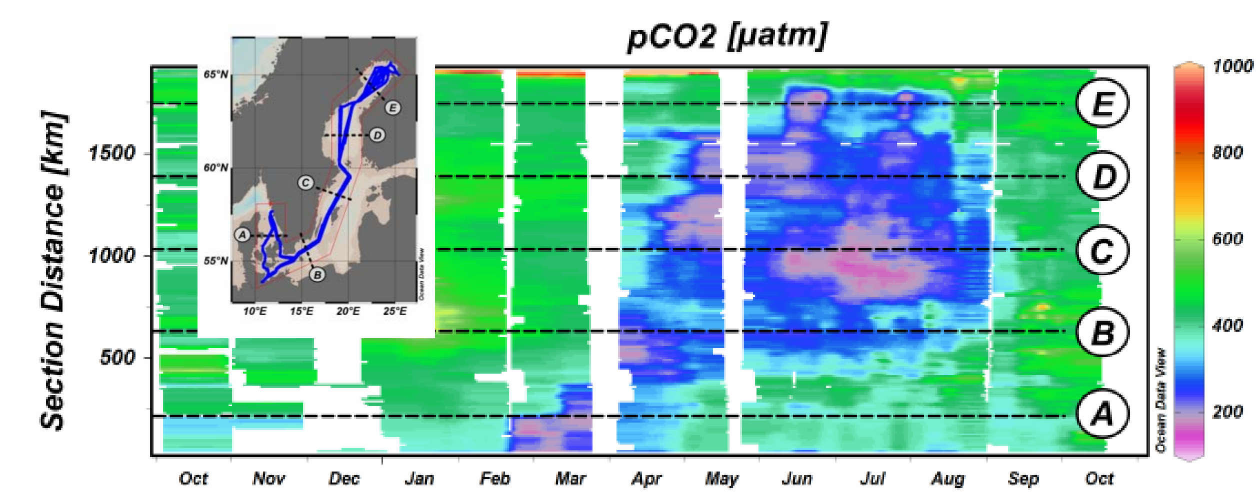


Figure 20 : pCO_2 measured in a strong salinity gradient from the Kattegat to the Northern part of the Baltic Sea. Data was collected twice every week. Gaps in data are due to problems with water flow (pump problems) or to other practical issues (Fransson et al., in prep).

4.1.5.4. pCO_2 sensor (CEFAS)

❖ Applied method

The here described sensor is an underway pCO_2 instrument (PML-Dartcom Live pCO2), described in detail by Hartman-Mountford et al. (2008); Ribas-Ribas et al. (2014), with the modified “vented” equilibrator introduced by Kitidis et al. (2012). The system uses a vented-showerhead equilibrator, with ambient light blocked out, to equilibrate seawater CO_2 with a headspace. In order to maintain atmospheric pressure in the equilibrator headspace, the unit is vented to a second equilibrator, which in turn was vented to the atmosphere.

The equilibrator was fitted with 2 platinum resistance thermometers (Pico Technology, model PT100) and a water-jacket supplied with seawater from the ship’s underway seawater system.

Atmospheric measurements of CO_2 are taken from an intake located in front of the ship’s bridge. Both gas streams from the equilibrator headspace and the air inlet are dried in a Peltier cooler (−20 °C). Mixing ratios of

CO_2 and water in the marine air and equilibrator headspace are determined by infrared detection (LI-840, LI-COR).

Sea surface pCO_2 data are corrected to sea surface temperature to account for the warming between the seawater intake and the equilibrators (Takahashi et al., 1993). Continuous conductivity data are obtained from the Sea-Bird Electronics SBE45 thermosalinograph (TSG) installed on the ship's underway supply and temperature is measured with a PT100 on the water intake. Discrete surface water samples for salinity (*S*) are collected in order to calibrate the conductivity measurements and analysed using a salinometer (Guildline Autosal 8400B).

❖ Implementation on platform

A Dartcom Live-pCO_2 system has been operational on RV Cefas Endeavour since January 2011. CO_2 is analysed in surface water (from 4m depth) and in air (inlet in front of bridge). The system is comprised of a wet system, a dry box and calibration gases – see Figure 22 and Figure 25 below.

Figure 21 : Wet system installed in CTD garage on RV Cefas Endeavour.

Figure 22 : Dry box installed in CTD annexe on RV Cefas Endeavour.

- Data quality control

There is reasonable agreement between measured pCO_2 and calculated pCO_2 (from measured TA and DIC) for two cruises in September 2012 and October 2012 (Fig. 2 and Fig. 3). The comparison is summarised in Table 1.

Figure 23 : Calibration gases installed in outside CTD garage on RV Cefas Endeavour.

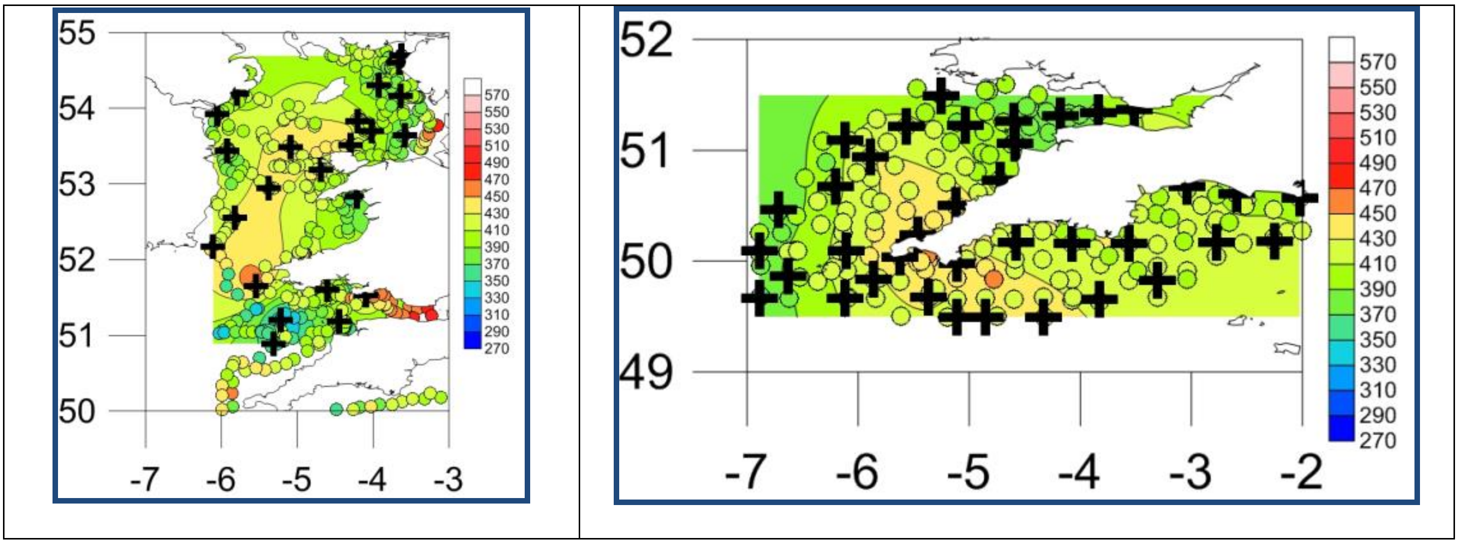


Figure 24 : *p*CO_2 measurements onboard of RV Cefas Endeavour in September 2012 (left) and October 2012 (right).

cruise	n	RMSE (μatm)	bias (μatm)	r^2
September 2012	23	15.2	-6.76	0.81
October 2012	37	10.6	-0.10	0.76

Table 1 : Comparison between measured and calculated pCO_2 on two cruises in September and October 2012.

4.1.6. *Passive Sampler*

4.1.6.1. Scientific relevance

Measurements of organic micropollutants in marine surface waters are challenging and expensive. For many priority contaminants such as organochlorine pesticides, flame retardants and PAHs, they require collection and treatment of large volumes of water under “clean” conditions, by qualified personnel, utilising a dedicated sampling campaign and a considerable amount of ship time. Contaminant concentrations fluctuate and are close to or below limits of detection of current techniques.

Silicon or low density polyethylene based passive sampling has received much attention in recent years as a technique that may help meet such challenges concerning time resolution and spatial resolution.

It has been recently suggested (Allan and Harman, 2011) that monitoring may take advantage of existing mobile platforms such as commercial shipping vessels and line ferries. This would allow a major step change concerning cost effectiveness of monitoring. However, the use of vessels requires further development in passive deployment procedures which will allow exposing them in water while the ship is moving, and handling/preserving the adequately to avoid interference in the environmental pollutant signal.

The complex water bulk matrix is required to be analysed for chemical pollutants. This means passive samplers (targeting only the dissolved phase) alone cannot provide a full answer to both regulatory and scientific demands.

There clearly is a demand for technological advances which will allow a better exploitation and integration of available resources. Active sampling or semi-passive sampling approaches may represent the way on to achieve such integration. NIVA strategy was to develop a versatile system (Automatic-on-board-laboratory) capable of handling different type of sampling and sample handling. Initially we set for testing functionality with passive sampling deployment.

4.1.6.2. *Passive Sampler (CEFAS)*

- Applied Methods

Silicone rubber passive samplers have been used for determining concentrations of organic contaminants in water for several years. Typically samplers are exposed in the environment for approximately 6 weeks and the uptake of contaminants can be calculated as a function of the loss of pre-spiked performance reference compounds (PRCs) from the silicone rubber sheets. The technique is relatively well understood, and the main problem preventing its widespread implementation is the shortage of appropriate mooring platforms from which samplers can be deployed. Additionally, two visits are required to deploy and collect the samplers, which can be prohibitively expensive for offshore stations in a climate of rising fuel costs and contracting monitoring budgets.

A strategy that could overcome the problems of deployment on offshore platforms is to use a research vessel as a mobile platform, providing that sampling duration can be scaled down successfully. With this in mind, a purpose built flow-through system was engineered and installed on the RV Cefas Endeavour. The apparatus was added to the dedicated seawater line delivered from 4m below the waterline, on which a FerryBox monitoring platform (providing oceanographic data) and pCO_2 analyser was already installed. The new apparatus has 6 chambers (Figure 25), each of which contains a rack designed to hold 6 double-length silicone rubber sheets, and which are designed to provide high turbulent flow.

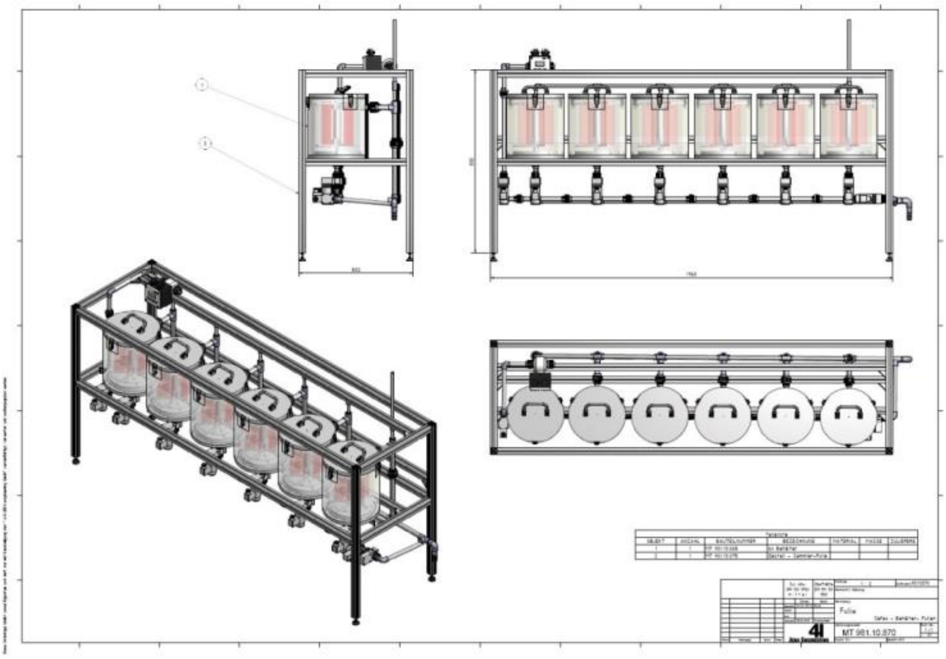


Figure 25 : Scheme of passive sampler. By courtesy of CEFAS.

- ❖ Implementation on platform

The RV Cefas Endeavour was surveying the western English Channel and the Celtic Sea from 23rd of October to 9th of November 2012 and this survey was used to test the newly installed system. During this trial deployment, the amount of time required to measure changes in the concentration of PRCs within the samplers, and to detect dissolved contaminants was investigated. Samples were exposed for 1, 2, 4, 8 and 16 days and the relevant area plotted. The volume of seawater that passed through each chamber was electronically recorded and the position of the ship logged every minute. After the deployment was complete, each sampler was left sitting in the seawater that they had been sampling until the ship returned to harbour (D. Sivyer (2014), pers. comm.).

Figure 26 : Silicone rubber sheets mounted in a rack (by courtesy of CEFAS).

- Data quality control

A comparison of storage conditions was also undertaken and it was shown that is better to drain the samples and store silicone sheets dry, rather leaving them in the last of the seawater.

Some recommendations were made for the next deployments, including; to investigate the loss of PRCs at higher flow rates, adding lower KOW PRCs to shorten time to measure loss and leave field blank in a trap for the whole deployment.

The system has recently been upgraded with its own high volume pump and an increased bore of internal pipe work to bring flow rates up approximately 50l per minute.

4.1.6.3. *Passive sampler (NIVA)*

❖ Applied methods

A fully automatic system here after named (Chem Mariner) for chemical pollution monitoring is under development to take advantage of existing ferry box infrastructures. The aim is to provide a device to allow fully automatic collection, pre-concentration and preservation of a range of organic micropollutants present in water at trace concentrations. The device has been installed on board of the ferry MS Color Fantasy in service between Oslo (Norway) and Kiel (Germany).

Similar to the CEFAS approach the present configuration (devoted to test functionality for passive sampler deployment) allowed deployment of Low Density Polyethylene (LDPE) passive samplers in flow-through chambers inside the ship. The sampler encompasses a pump delivering a calibrated flow of seawater from the ship inlet to a system of programmable valves which distribute it to the different chambers. After flowing through the exposure chamber the water is addressed to the outlet line and discharged back to the environment. The system is designed to produce enhanced flow conditions and turbulence around the LDPE in order to increase the uptake rate.

NIVA system has peculiar characteristics distinguishing it from the CEFAS approach. Each chamber is thermostatically insulated and inner temperature can be controlled. Each sampling chamber is dedicated to an individual sample. Sampling on a given chamber can be triggered by remote communication, or by ship positioning (e.g. when the ship enters a preset area defined by geographical coordinates) or again by some specific condition observed by one of the FerryBox sensor.

The sampling can be suspended (e.g. when the ship leaves the preset geographical sampling area). This activates a procedure which introduces a preservative gas in the chamber. The gas pushes the water outside the chamber, cool the samplers and kill most of the organisms which may adhere to the LDPE.

If a single sampling section is not sufficient to achieve detection of the target compounds, the sampling in a given chamber can be reactivated in any moment (e.g. when the ship returns in the preset area).

The sampler is therefore designed to allow fulfilment of both spatial and temporal integration requirements, simultaneously solving the problem of handling and preserving samples.

The environment in which the sampling media are deployed is isolated (physically and terminally) from the onboard atmosphere. This is an important feature given that on board contamination of a range of semivolatile organic chemicals, is a major problem for ship based sampling.

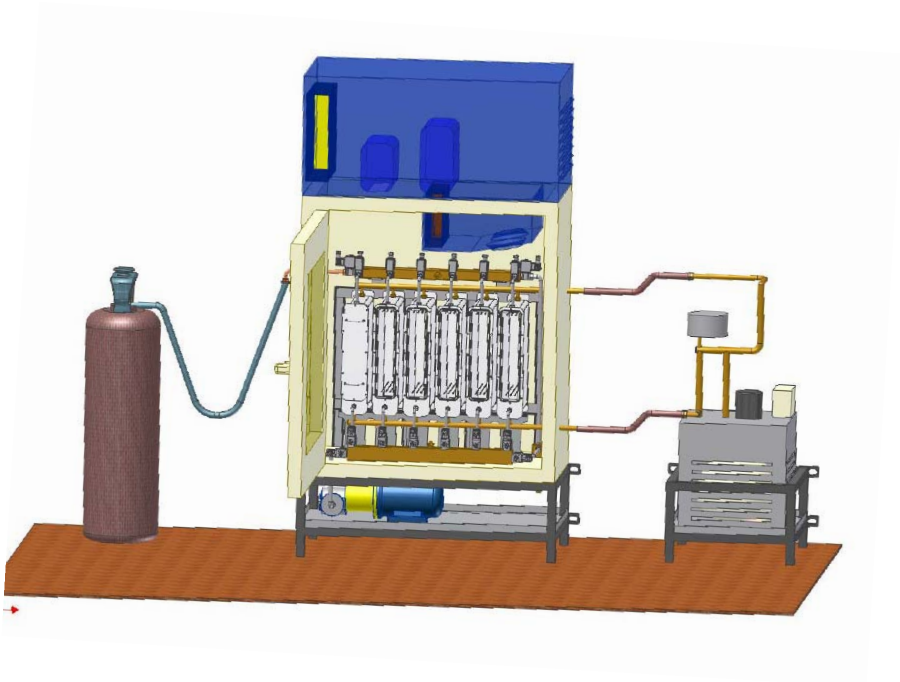


Figure 27 : Scheme of Chem Mariner. By courtesy of NIVA.

❖ Implementation on platform

The Chem Mariner system was implemented on board the MS Color Fantasy in service between Oslo and Kiel and coupled to the communication system of the FerryBox unit. A full text of functionality was conducted where the system was successfully operated in autonomous mode during two entire cruise legs. Sampling programme was predefined based on a set of geographic coordinates. Passive samplers were deployed inside the chamber and were exposed for preliminary testing purposes for a period of about 8 hours each in their respective locations. All the system components worked efficiently. Results of chemical analysis of this preliminary test suggested longer exposure time are required to achieve detection of targeted contaminants (in this case PAHs).

Figure 28 : Chem Mariner installed at MS Color Fantasy (left) and one of the chamber opened to illustrate the membranes (right). By courtesy of NIVA.

4.2. Sensors for Gliders

4.2.1. Overview

The concept of oceanographic underwater gliders emerged from the need for an enhanced oceanographic sampling of the core parameters in the oceans and for easier and cheaper observations. Gliders, as fixed platforms providing observations at high resolution and in real time, can fill the gaps on the spatio-temporal scales covered by the existing oceanographic platforms. Gliders not only enhance the spatio-temporal sampling of the core parameters, but they also offer a unique possibility to carry any kind of sensors provided these can be miniaturized. As often argued (i.e. Testor and Co-Authors (2009)), the gliders component already occupies a critical position in the future ocean observing systems (GROOM, 2014).

Gliders were initially restricted to physical parameters (Temperature and Salinity), but soon started to be equipped with optical sensors delivering biogeochemical proxies. Fluorescence and oxygen sensors were the first to be implemented (Körtzinger et al., 2005; Riser and Johnson, 2008), and now a large set of other sensors are already successfully tested (e.g. Johnson and Coletti (2002); Rusello et al. (2011)).

Miniaturization and energy cost were and are still (and will probably remain) the main limiting factors for implementation of new sensors, in particular biological and chemical. A less important factor, although crucial for long deployments, is the volume of collected data, which could prevent massive on board computation and, consequently, critically affects transmission time and costs. Last but not least, sensor price and the cost for implementation, which could rapidly grow if only few prototypes are developed. However, most of these factors are counter-balanced by the good performances of the technology and its high potential for “new science” (extreme environments, “new vision” of the marine system, etc.) (GROOM, 2014).

One must also consider that miniaturization of sensors (i.e. the other limiting factor for gliders) is strongly progressing in environmental studies, as this is also required for other platforms such as buoys or floats.

To get an overview of the state-of-the-art, we here show a few aspects out of the GROOM report on existing sensors for gliders (GROOM, 2014) in Table 2 (implemented sensors) and Table 3 (new developed sensors). More details about every sensor can be found in the report we refer to (GROOM, 2014).

Parameter	Sensor	Methods	Implementation	Quality Control (QC)
Chlorophyll-a	Fluorescence based methods		Implemented on gliders	QC protocols from Bio-Argo usable (additional water samples), calibration routine before and after deployment
	Radiometric inversion of light measurement		Seldom equipped on gliders	
Animal biomass	Echosounder 853	Receiver, piezoelectric principle	Designed for gliders	-
	VEMCO	transmitter/receiver, piezoelectric principle	mission-proved	-
	High Tech Inc. Hydrophone	Receiver, piezoelectric principle	mission-proved	-
CDOM	ECO CDOM WET labs	Optical scattering, fluorescence	Implemented on Darwin glider, comparison with Cyclops in progress	Subtraction of nominal offset, correction by linear scale factor, calibration before and after deployment, sensor inside cause high calibration effort
Current	Aquadopp (Nortek)	Integration of Doppler velocity	mission-proved	Low maintenance, no zero-point drift, at surface, GPS calibration possible at start, and stop dead reckoning problematic
	Signature 75 (Nortek)	ADCP hardware platform, multiple measurement modes	mission-proved	
	Explorer Doppler Verlocity Log (Teledyne RD Instru.)	Compact and versatile version. Same method as Aquadopp	mission-proved	
Nitrate	SUNA (Satlantic)	Spectrophotometer, based on UV absorption	Tested on profiling floats, implemented on SLOCUM glider, commercially available	Reprocessing on land; offset and bias evaluated by in situ samples at deployment
Oxygen	Optode (Aanderaa)	optical measurement principle, lifetime-based luminescence quenching principle	Mission-proved	Long-term drift, Winkler titration samples
	SBE 43 (SeaBird Electronics)	Clark polarographic membrane type		Calibration drift from membrane fouling, in-situ calibration using Winkler titration samples
	Rinko (JFE ALEC Co. Ltd)	optical measurement principle, sub-meter resolution		Winkler titration samples
Phycobilin	ECO phycobilin fluorometer (WET Labs)	Detection of either blue-green (phycocyanin) or brown (phycoerythrin) algae. Range detection: 0-230 ppb;	Mission-proved	Calibrated by cell counts for particular water mass
Turbidity backscatter	ECO BB (WET Labs)	Minimum convergence point for variation in volume scattering function (470, 532, 650 nm)	Mission-proved	Intercomparison of two sensors on same glider possible
	Beam Attenuation Meter (ABM) (WET Labs)	Collimated source, reflective sample cell with diffuser in front of wide area detector (470, 532, 650 nm)		
	Turbidity Meter (Seapoint Sensors)	light scattered by particles suspended in water, Sensitivity is selected by two digital lines that can be hardwired or microprocessor controlled		
CTD	Glider Payload CTD , GPCTD (Seabird)	Established measurement system for conductivity, temperature, pressure.	Structure originating from Argo float principle, mission-proved	-
	Fin-cell GCTD (WHOI)	Specific designed for gliders, four-electrode conductivity cell with internal temperature sensor, no pump needed	Mission-proved	Thermal lag error methodology proposition
Radiance	OCR 500 (Satlantic)	Four customer-defined discrete optical wavelengths (400-865 nm)	Mission-proved	QC algorithms are available for optic sensors
	QSP-2000 (Biospherical Instruemtns)	PAR-sensor with spherical receiver, quantum scalar irradiance measured, 400-700 nm	Deployed on seaglider, implementation possible	
Turbulence	MicroRider (Rockland Scientific)	Instrument package of six sensors	Mission-proved	-

Table 2: Implemented sensor features for glider measurements. Adopted from GROOM (2014).

Parameter	Sensor	Methods	Implementation	Quality control
Bioluminiscence	UBAT (WetLabs)	Controlled-stimulation imaging sensor, pump impeller for turbulent passage of sample organisms	Designed for ship-board profilers, AUV and moorings, glider implementation possible	Measurement of stimulation efficiency, intercomparison with independent sensor. Calibration know-how not yet available in glider community
Carbon Dioxide	HydroC (CONTROS)	Thin-film composite membrane, IR absorption spectrometry	Implementation on glider possible (inside or on hull)	-
	SAMI-CO2	Colorimetric reagent method		
Dinoflagellate	AMG (NOC)	Ribonucleic Acid amplification with nucleic-acid-sequence-based amplification (NASBA)	Implementation on glider possible	-
Sulphur	ISUS (MBARI)	Bisulfide (HS^-) concentration measured by absorption spectrum of seawater in UV	Not yet tested on glider, but implementation possible	-
	H2S underwater probe (AMT GmbH)	Permeation separation through a membrane of gaseous H_2S	Adaptable to glider installation	-
Hydrocarbons	Triplet sensor (WET Labs)	Special-order, three-optical-sensor, use of broad absorption and emission spectra of crude oil	Compace dimensions, so possible implementation	Ancillary measurements are needed to decrease false positive results.
Nutrients	APNA (SubChem Syst. Inc)	autonomous, submersible chemical analyzer utilizing spectrophometric and fluorometric analytical methods, use wet chemical techniques and micro-fluidics	Not yet	-
	ChemFIN (SubChem Syst. Inc)	single channel analyzer, specifically designed for low-power underwater measurements, use wet chemical techniques and micro-fluidics		
	MarChem (SubChem Syst. Inc)	low-power autonomous single or multi-channel submersible chemical analyzer, utilizes spectrophometric and fluorometric analytical methods, specifically designed for AUVs		
Ozone	Amperometric ozone micro-sensor (AMT GmbH)	permeation membrane, electrolyte with a redox catalyst and 3 electrodes, rapid decrease of the analyte inside the sensor resulting in very fast response times	Implementation possible, max depth 100m.	-
pH	SAMI-pH (Sunburnst Sensor)	Colorimetric reagent method	Implementation possible	measure of two parameters of the carbonate system (Alk, DIC, pCO2) provides a method to estimate independently pH
	SeaFET (Satlantic)	ion selective field effect transistor (ISFET) type sensor for accurate long-term pH measurements		
Radioactivity	GAMMA-RAD5 (AMPTEK Inc)	integrated wide range γ-ray spectrometer, scintillator and Photo-Multiplier Tube, a charge sensitive preamplifier, a digital pulse processor and Multi-Channel Analyzer	Implementation possible	-

Table 3: New developed sensor features for possible installation on gliders. Adopted from GROOM (2014).

Gliders have been designed as a multi-function, multi-parameter platform. All the present-day commercially available gliders enable the integration of sensors measuring physical, chemical and biological parameters of seawater. Additionally, the possibility to pilot gliders in real-time during a specific mission makes gliders today's "perfect" tool for multi-disciplinary process studies, which often require rapid adaptation of sampling to environmental conditions. Consequently, recent years have seen an exponentially growing interest in new sensors for biological and biogeochemical applications on gliders.

4.3. Sensors for Fixed Platforms

4.3.1. Overview

Fixed platforms are fixed with respect to their position on or above the seafloor and they are a part of a coastal network, or they may be located offshore. The resolution of processes at time scales from seconds to years gives fixed platforms a unique role in the global ocean observing network, providing an unparalleled ability to detect processes which otherwise may be missed.

These platforms host different types of sensors for making measurements of the water, marine life or contaminants. The location of sensors on the seabed or throughout the water column provides an important capability to sense large parts of the ocean which are not detectable from the surface. The greatest number of measurements is for physical oceanography, with sea level being the commonest instrument type.

The observing systems are predominantly located in the shallow coastal zone where the seabed is less than 50 m deep.

A number of stations were recorded as holding multiple sensors, and there are even examples of stations which simultaneously record biological, chemical and physical parameters. If observations at these stations could be sustained, then they will make a very important contribution to the global marine observing network.

Moored and fixed systems are usually unmanned and compared to drifting platforms such as Argo floats or gliders can carry a greater range of sensors. Power to the platform can be derived from renewable sources such as solar panels, or from large battery packs. Newly developed cabled observatories will have additional capability to transmit high volumes of data in real time, as well as the ability to support more powerful instruments. So, these platforms are an ideal base for the testing of new developed sensors.

4.3.2. *Wipers (CEFAS)*

- Overview

On SmartBuoy, ZebraTech wipers have been installed for the Aanderaa optode, Seapoint Chl and OBS and Licor PAR. This is not a sensor development but allows using data from sensors which would normally be bio-fouled within 4-6 weeks. Now it is expected to receive data for up to 12 weeks even in the bloom periods.

- Implementation on platform

During the Warp chlorophyll fluorometer trial a separate buoy for double length and two "normal" deployment in-between have been in service (see Figure 29). Each of the two normal duration deployments collected 20 and 13 days good data out of a total of 68 days collected by the wiped double length buoy. Approximately 30% and 20% of the total from each of the "normal" deployments was good data whereas all the wiped fluorometer data was acceptable.

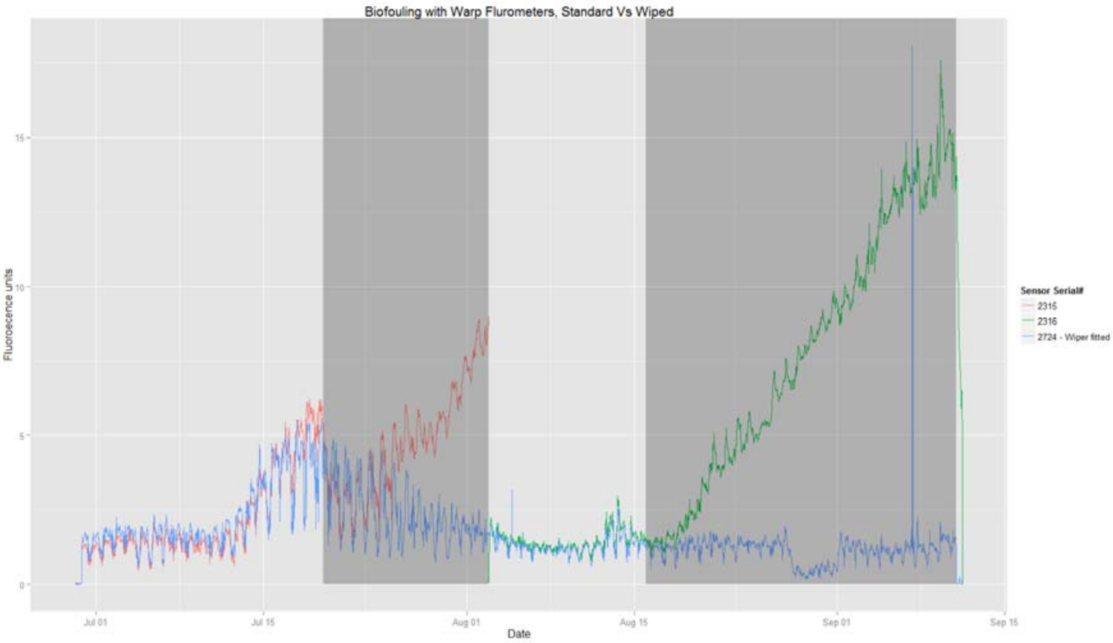


Figure 29 : Effect of wipers installed on fluorometers during Warp trial. By courtesy of CEFAS.

With the Dowsing site two consecutive SmartBuoys both fitted with a wiped and non-wiped OBS have been used. With the first deployment the non-wiped sensor collected 15 days out of 70 (22%) (see Figure 30). The second collected 34 days out of 106 days total (32%). The bio-fouling seen in the second deployment would probably not have been detected easily without contrasting with the wiped sensor.

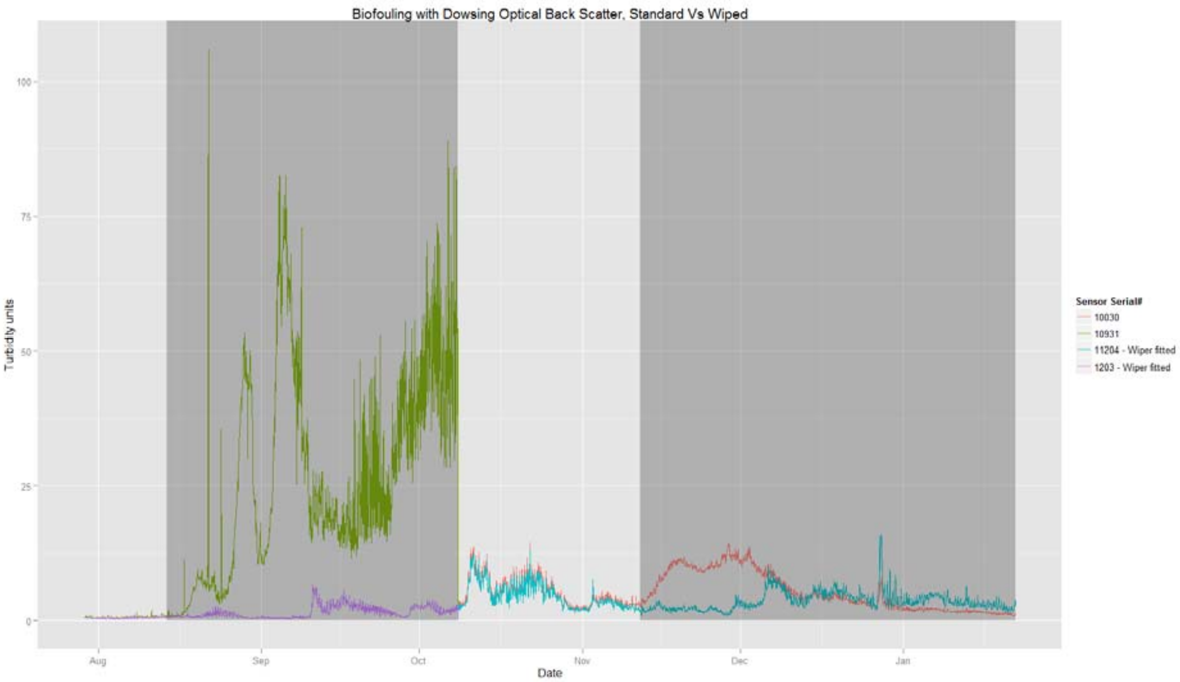


Figure 30 : Comparison of wiped and non-wiped OBS, deployed on SmartBuoys. By courtesy of CEFAS.

It's fair to say there is a 70% increase in good data collection making 3 month deployments possible and thereby significantly reducing ship and servicing costs. As a result, 5 out of 6 SmartBuoy sites now have wipers.

4.3.3. Fish detection echo sounder (AZTI)

❖ Background

- AZTI has several projects related with FADs (Fish Aggregating Device) and tuna fishing fleet in the Indian Ocean
- Both recreational and commercial fishing fleet are using the deep water buoys in the Bay of Biscay as FADs
- Close relation with main FAD related fishing echo-sounder manufacturers
- At present these biomass buoys are been successfully used to study the effect of WEC (Wave Energy Converters) over fish schools

The main objective is the establishment of a procedure for the integration of biomass echo sounders on fixed platforms.

❖ Scientific relevance

As the Basque network deep water buoys have 200m long CT string and a 150kHz current profiler, it is possible to correlate fish presence with water physical conditions under a kind of fish aggregating device. By the other hand it permits to have near real time information about presence of fish at a known position and then study the fish school with scientific echo-sounders (grain size, density, school volume, etc.).

❖ Implementation on platform

The size differences between both buoys makes possible the installation of the fish detection buoy onboard the big Metocean buoy.
The characteristics of the fish detection buoy are:

- Model: Marine Instruments M3i
- Echo sounder frequency: 50 kHz@42º

- Communications: Iridium
- Power: 500 W
- Weight: 6,9 kg
- Resolution per layer: 3 m
- Blind area: 6 m
- Range: 6 to 150 m

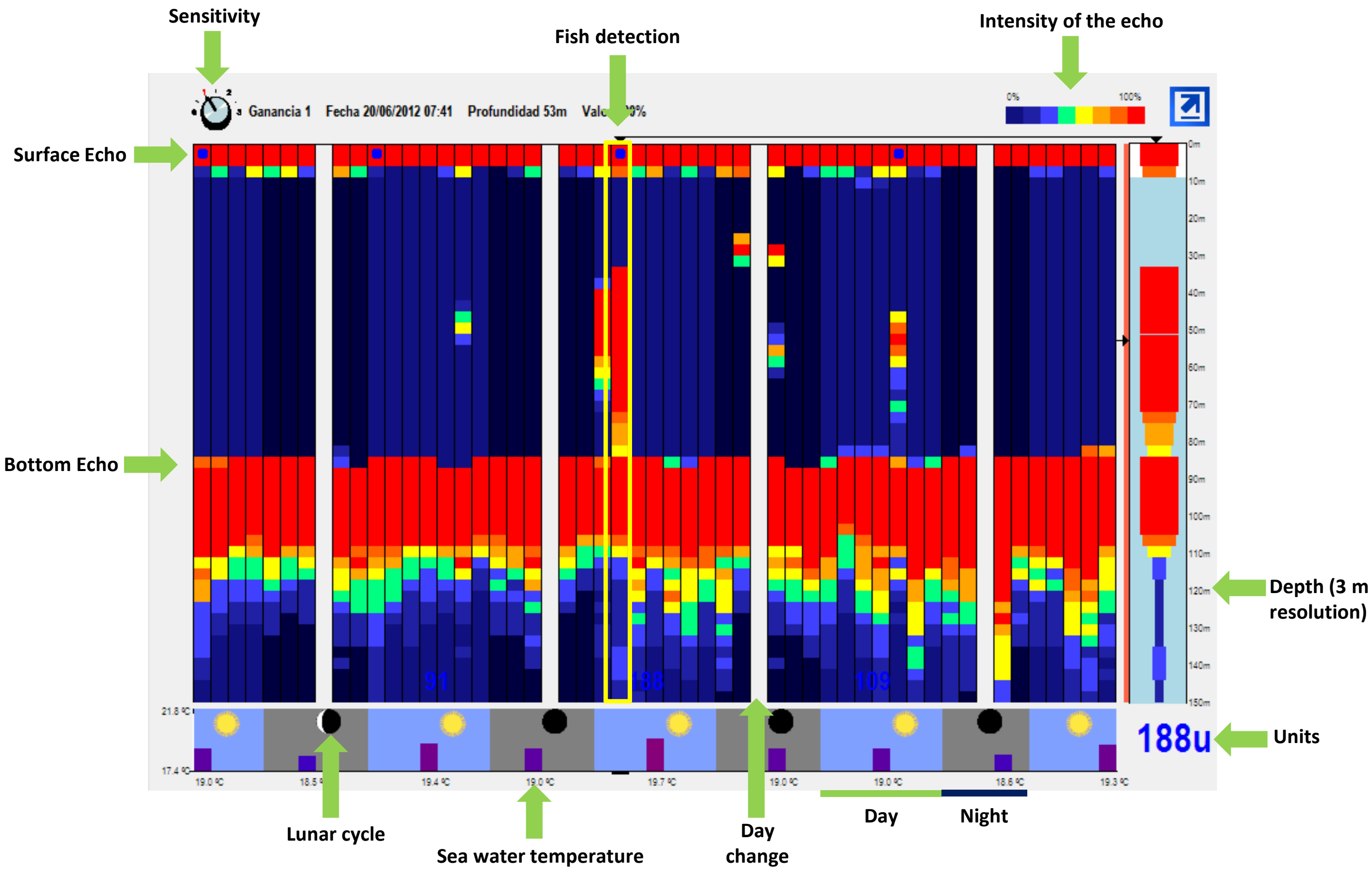
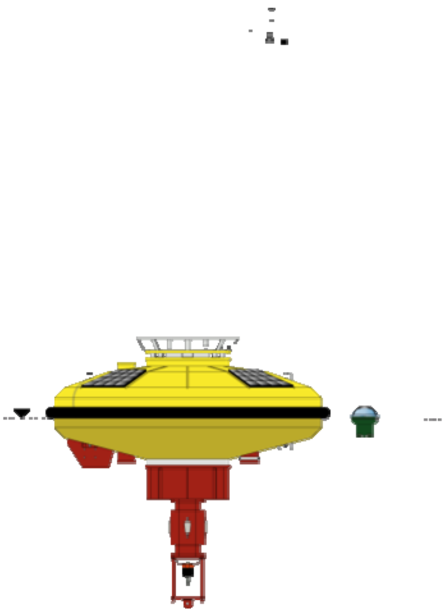


Figure 31 : Marine Instruments M3i fish-detection buoy data reception example. From 2012/06/18 to 2013/06/22.

The fish detection buoy small size allows its installation and fixation to the Wavescan buoy using the tracker spare hole at the upper part of the hull. The fish detection buoys maintains its own power supply and communication system. The fish detection transducer or the lower part of the fish detection buoy should be in contact with water which is not the case with the onboard installation. In order to resolve this issue, the transducer is led out of the fish detection buoy hull using a through-hull plastic device. The transducer is attached to the Wavescan buoy hull using the spare mast hole and is installed inside a protection case.



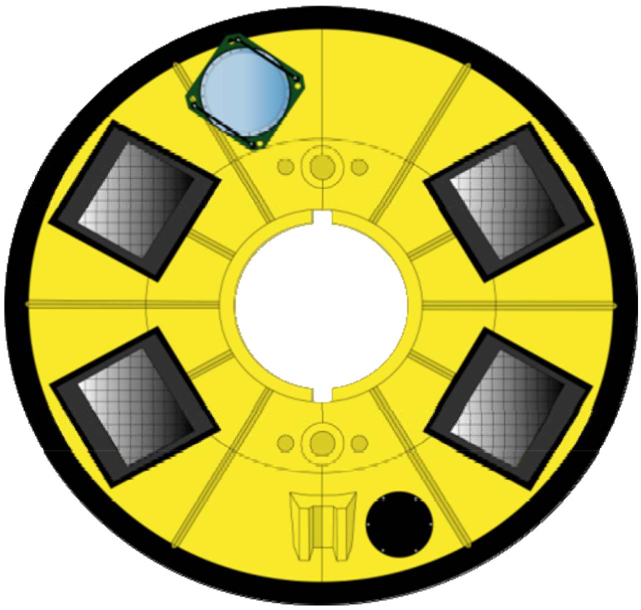


Figure 32 : Size differences between fish detection buoy and metocean buoy (left) and implementation onboard Wavescan buoy (right).

Figure 33 : Integration onboard the Wavescan buoy (left) and transducer close view (right).

- Outlook for possible improvements

The use of multi-frequency echo sounders will permit the implementation of algorithms to identify other organisms apart from fishes as zooplankton or gelatinous organisms.

5. Conclusions

In this report, an overview is given about the status of sensor developments for offshore observing platforms. Several new promising developments are deployed on platforms in a test mode; some sensors are already in pre-operational mode.

FerryBoxes are a valuable tool for testing new developed sensors, as conditions are easy to handle for new developed devices: only minor energy and space restrictions, shelter from the elements and easy integration in data processing tools. There has been considerable development of new sensors that measure components of the carbonate system, thus research addressing ocean acidification and eutrophication will benefit from this progress. Especially, new sensors for pH monitoring are established on FerryBox routes. They provide better accuracy, higher salinity range (important for Baltic Sea monitoring) and more compact designs for easier installation on autonomous systems. Also, a new generation of pCO_2 sensors has been described.

Until lately, the Total Alkalinity has not been measured autonomously but more often has been calculated from other components of the carbonate cycle. It will be soon possible to measure the Total Alkalinity directly with the described device which can be easily combined with pH measurement devices.

Gliders, on the other hand, are much more restrictive concerning energy and space availability. However, with new technologies, these restrictions have been overcome. So, a variety of new sensors have been developed and already tested in recent years. A short overview is given in this report, as more details can be found in GROOM (2014). Here, the sensor developments for gliders have been divided in two groups, i.e. sensors in pre-operational mode which are mainly mission-proved. The other group consists of developments which are not yet tested on gliders. In the second group, however, all requirements for a successful deployment are fulfilled.

Fixed platforms provide an important contribution to the monitoring coastal oceans. Due to their eulerian form of observation, they provide a high temporal resolution of measurements for coastal positions and they are able to carry a higher load of sensors than e.g. floats. Thus, they are capable of accommodating spacious observing systems such as passive samplers, which also can be deployed on FerryBox systems.

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