SenseOCEAN: Marine Sensors for the 21st Century

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1. Introduction[1]

The oceans play a crucial role in the prosperity and future of civilization; providing natural resources, food, recreation and a route for the global transport of goods and services. The oceans play a key role in climate regulation, arguably the most important environmental issue facing mankind. The sustainable use of the oceans is vital for mankind. However, our understanding of ocean processes is limited by a paucity of information around the key biogeochemical cycles operating in marine systems. To understand, predict, protect and manage ocean processes and resources requires a step change in the available data from this environment.

In 2008, the European Union established the Marine Strategy Framework Directive (MSFD) with a goal to protect the marine environment in Europe. Many aspects of the MSFD are common to the Sustainable Development Goal 14 (SDG 14) from the United Nations which aims to 'Conserve and sustainably use the oceans, seas and marine resources for sustainable development'. In 2008 the EU also adopted the 'European Strategy for Marine and Maritime Research' to provide a framework for marine and maritime research in Europe. To support all of this the European Commission developed a key initiative, the Ocean of Tomorrow, to 'foster multidisciplinary approaches and cross-fertilisation between various scientific disciplines and economic sectors on key cross cutting marine and maritime challenges'. The aim of the final call OCEAN-2013.2 for proposals in 2013 was to develop innovative marine technologies for a wide range of applications. The developments outlined in this document are the results of the final topic area – marine sensing technologies (including biosensors) to monitor the marine environment.

The four projects selected from the OCEAN-2013.2 call were: COMMON SENSE – Cost-effective sensors, interoperable with international existing ocean observing systems, to meet EU policies requirements; NeXOS – Next generation, cost effective, compact, multifunctional web enabled ocean sensor systems empowering marine, maritime and fisheries management; SCHeMA – Integrated in situ chemical mapping probes and SenseOCEAN – Marine sensors for the 21st Century.

The projects address key aspects of the MSFD and SDG14, by developing novel sensor systems for the determination of important aspects of the oceans' health. Macronutrients that are important causative agents in both the development of harmful algal blooms and the increase of oxygen minimum zones in the oceans are measured using a number of different technical approaches. Trace metals (lead, cadmium, copper, mercury etc.) that are essential (micronutrients) or toxic (micropollutants) elements (depending on their concentrations, chemical speciation and the nature of the organisms) are detected in real-time using on-chip microsensor arrays. The increasing concerns around microplastics in the oceans, a global problem, are addressed. There are a range of approaches for the determination of carbonate system parameters to understand ocean acidification and the ability of the oceans to ameliorate climate change through CO_2 absorption. Some of the projects have taken the approach of measuring the complete ecosystem in order to determine community shifts in plants and/or animals. Such community shifts can be an indicator of natural or anthropogenic effects.

The projects all combine academic researchers with small to medium enterprises (SME's) involved in aspects of the commercialization of marine technology and sensors. There is a key drive in the Ocean of Tomorrow projects to place Europe at the cutting edge of sensor technology for marine applications, and to allow the exploitation of the developments from the projects.

[1] Please note, the COMMON SENSE project finished several months prior to the production of this document, hence their sensor developments are not included in the 'State of the art developments' section, However, despite the project ending, they made significant contribution to the 'Data Management and Standards' section.

2. State of the art developments

The following sections highlight the major sensor developments and specific innovations from the NeXOS, SCHeMA and SenseOCEAN projects in order to give decision makers a realistic overview of what can be achieved in terms of the parameters that can be measured, monitored and assessed.

The NeXOS project has implemented six main scientific and technical innovations: three innovations specific to the chosen observation frameworks (optics, acoustics, EAF) and three that are transversal and will increase reliability, sensor and data interoperability for integration with GOOS, GEOSS and other initiatives.

SenseOCEAN took a holistic approach to environmental challenges such as climate change, eutrophication and biological community structure, and used several technological approaches (often for the same parameter, e.g. pH, phosphate etc.), to develop sensors suitable for deployment in a range of marine environments (estuarine, coastal and open ocean). Individual sensors have been combined into an integrated multifunctional sensor package.

SCHeMA, using innovative analytical approaches and integrating enOcean technology, developed a suite of multichannel submersible sensing probes incorporating miniature solid state sensors and analytical platforms. The interfacing of the individual probes, via a dedicated Network Controller, provide an open and modular sensing solution for gathering spatial and temporal information on a range of chemicals and organisms that may have an adverse effect on marine ecosystem functioning.

The sections are presented according to the types of parameters measured by the sensors/technologies, e.g. nutrients, carbon cycle related, pollutants etc. rather than by project.

2.1. Optodes for marine measurements

Highlights:

- **a palette of novel optical sensing materials for O_2, pH, CO_2 and NH_3**
- **two types of read-out devices with opto-electronics shared for all the analytes**
- **no analyte consumption, low power demand, small size and weight**
- **multi-parameter sensing with screw fit sensor caps**

Optode technology relies on the ability of a sensing material to change its optical properties (absorption, luminescence etc.) depending on the concentration of the chemical being measured. Over the last few decades optodes have successfully replaced other analytical methods for most measurements of O_2, and optode technology is highly promising for several other chemical species. Unfortunately, application of the optodes in practice was hindered by a lack of high-performance sensing materials and the necessity to have dedicated devices for signal read-out.

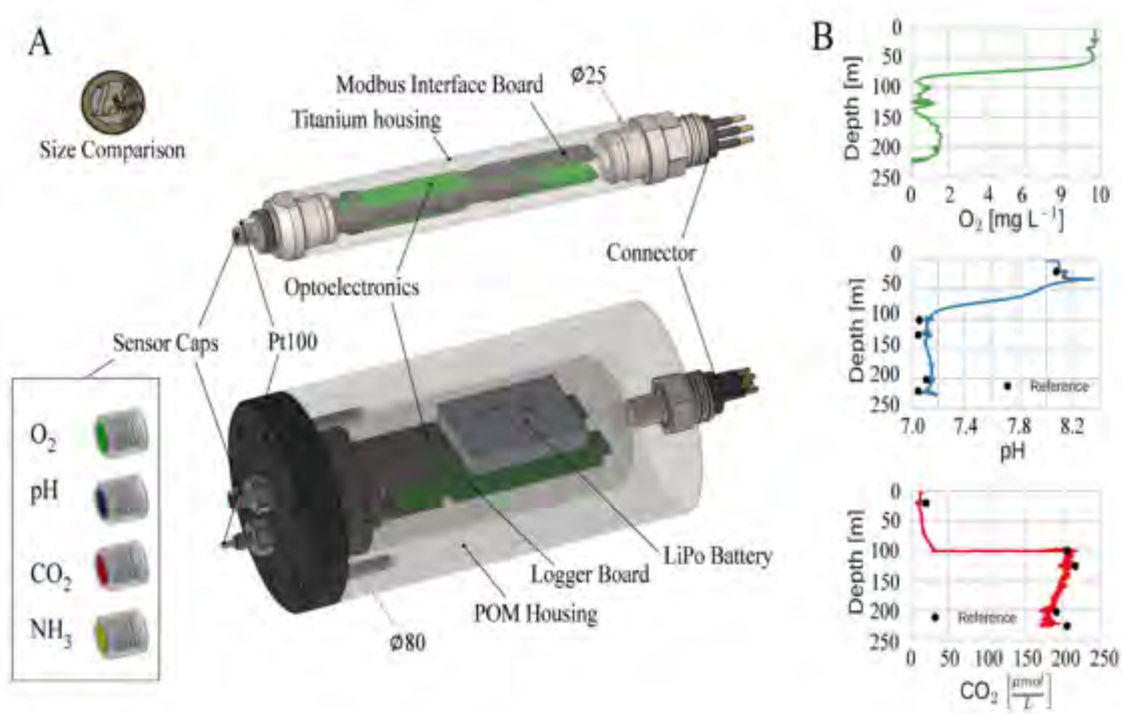


Figure 1 A: Deep water optode with MODBUS interface (top), shallow water stand-alone optode (bottom) and exchangeable sensor caps for different analytes (left). B: Experimental results for profiles measured at the Gotland basin in the Baltic Sea

Within the SenseOCEAN project, the TU Graz and Pyro Science GmbH teams combined their expertise to create a new generation of optodes for monitoring of O_2, pH, CO_2 and NH_3 in seawater. Novel luminescent indicator dyes have been synthesized and immobilized in various polymeric matrices to obtain 'sensing chemistries' with optimal dynamic range, high long-term stability and fast response (known as 'sensor foils').

Two types of compact read-out unit have been produced. The first type relies on an opto-electronic unit in a pressure-resistant titanium housing and is equipped with a deep-sea connector and a Modbus board allowing for shared data logging along with other units developed by SenseOCEAN partners.

The second type is a stand-alone version that includes a logger and a battery. It can be operated to a depth of 500 m. Maximum optimisation of the optode and logger power consumption means that the battery capacity is sufficient for approximately 1.4 million single measurement points. This equates to a deployment time of over a year with a measurement interval of 30 s. The devices are equipped with an additional temperature sensor for temperature compensation.

The spectral properties of the sensing materials have been engineered to enable read-out with a standardized opto-electronics unit, which greatly simplifies handling and minimizes the manufacturing costs.

Screw fit sensor caps with different sensor foils can be exchanged easily to modify individual devices according to the experimental demands, enabling simultaneous monitoring of several parameters without changing the optoelectronics. The chemistry of the oxygen foil is optimised for the dynamic range of 0.2-500 µM O_2, however materials with detection limits down to several nmol/l can also be used. The pH optode shows response from pH 6 to pH 9, with highest sensitivity between pH 7 and 8. The pH and oxygen optodes show fast response times of 1-10 s. The carbon dioxide optode shows the dynamics from about 2 to 1000 $\mu mol \cdot l^{1}$ of CO_2 but is significantly slower than the other optodes. The response is particularly slow at low temperatures (~ 5°C, > 1h time) therefore the optode is yet not suitable for profiling applications. The ammonia optode responds from 0.5 to 200 µg/l of NH_3 with the optimal sensitivity around 25 µg/l which is the toxicity limit for many marine organisms. The response is similarly slow to that of the CO_2 sensor. Much faster carbon dioxide and ammonia sensors have been prepared as well with the trade-off of significantly lower operational stability.

2.2. Species relevant to the Carbon Cycle Sensing Module: CSM

Highlights:

- **Accurate and rapid measurements**
- **Direct detection of pH, carbonate and calcium in seawater**
- **Suitable for long-term monitoring**
- **Easy maintenance**

The accurate measurement of the carbonate system in seawater is of critical importance to study ocean acidification caused by the absorption of anthropogenically emitted CO_2. As the concentrations of the associated chemical species (CO_2, pH, carbonate and bicarbonate) are interconnected by thermodynamic constants, the carbonate system can be described from the measurement of just any two species among the four (i.e. pH and carbonate). Additionally, the quantification of dissolved calcium is related to the carbon cycle as it is involved in carbonate precipitation/dissolution processes and its monitoring may contribute to a more complete description of the marine system. Thus, CSM is based on the simultaneous potentiometric detection of pH, carbonate and calcium in seawater using membrane electrodes.

Essentially, in potentiometric sensors the analytical information is obtained through an ion recognition event translated into a voltage signal. Thus, a local equilibrium is established at an ion-selective membrane and the activity change of the ion analyte in the aqueous solution results in a change in membrane potential. The potentiometric readout is the difference between this potential and that provided by a reference electrode. CSM incorporates a flow cell (25 × 25 × 25 mm) containing three miniaturized electrodes of all-solid-state type (2 mm of diameter and 20 mm long) based on nanomaterials and selective membranes[2] for pH, carbonate and calcium together with a reference electrode (Figure 2 a-c).

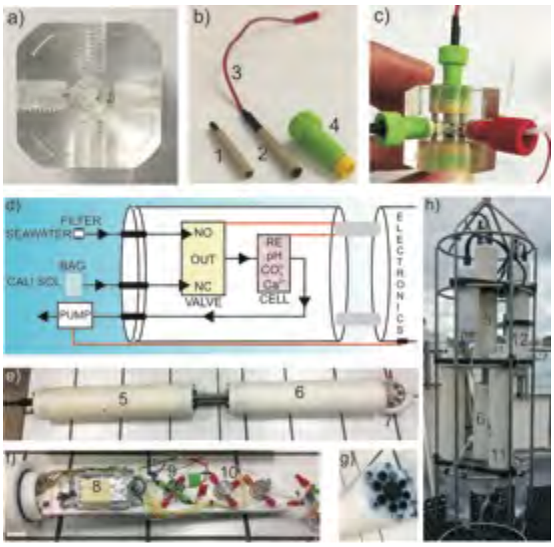


Figure 2.[3] *(a) Flow cell. (b) Electrode set-up. (c) Detection cell. (d) Fluidics design. (e) View from outside of the CSM probe. (f) View from inside of the CSM probe. (g) Cap to close the submersible housing allowing the coupling between internal and external connections. (h) SCHeMA probe. 1: miniaturized electrode, 2: modified electrode, 3: electrical connection, 4: fittings, 5: electronics housing, 6: housing for the fluidics system, 7: cap, 8: valve, 9: potentiometric flow cell, 10: algae module, 11: pump, 12: CTD multiparametric probe.*

The flow configuration of the detection cell allows for its implementation into a fluidics system driven by a submersible pump and mainly based on a two-position valve to select the pass of either a calibration solution or the seawater from the aquatic system (Figure 2d). The detection cell is placed together with the algae module into a water- and pressure-proof cylindrical housing (Figure 2 e-g), which is connected to the electronics part (hardware for pump and valve control, potentiometric

[2] Anal. Chem. 87 (2015) 8640-8645
[3] Environ. Sci. Technol. Let. (2017) Submitted

measurements, the adjustment of the experimental protocol, data acquisition, storage and management). After fixing the fluidic system containing the potentiometric sensors, closing the submersible housing and calibrating the CSM, this is incorporated into the titanium cage together with the rest of the SCHeMA probes (Figure 2h).

CSM is capable of measuring pH, carbonate and calcium directly in seawater with limits of detection of 3, 10^{-5} M and 10^{-5} M respectively. The probe operates in an autonomous manner with rapid data acquisition. The flow mode adopted for the potentiometric measurements allows the correction of electrode drift thus providing more trustable data. The use of nanomaterials in the electrode configuration provides improved lifetime for the sensors. Thus, the CSM has demonstrated appropriate and validated operation during three weeks continuously measuring in the Genoa Harbour (Italy) deployed at 4.3 m.

The environmental application of the system has been demonstrated in different aquatic areas of significance, i.e. in the Mediterranean Sea and the Atlantic Ocean.[2] As a result, interesting biochemical trends have been found, such as day/night cycles and temperature dependence of carbonate and calcium levels in Genoa Harbour (Italy) as well as tidal-dependence in Arcachon Bay (France), shown in figure 3.

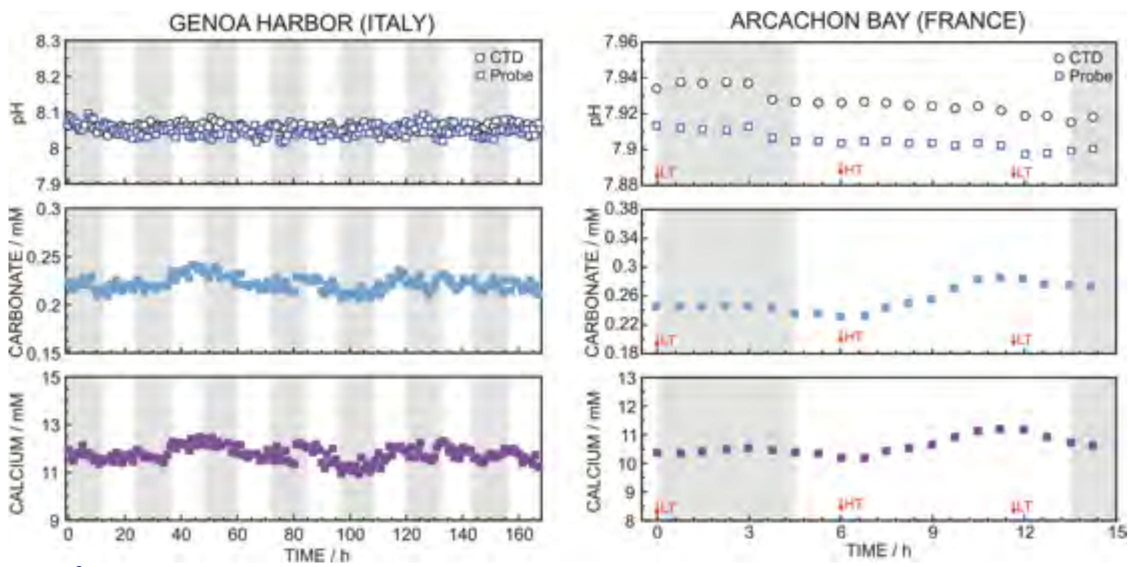


Figure 3.[2] *In situ temporal variation of pH, carbonate and calcium during a deployment in Genoa Harbour (from April 3rd, 2017 at 07:00 to April 10th, 2017 at 12:00) and in Arcachon Bay (from May 17th, 2017 at 17:00 to May 18th, 2017 at 09:00). Light hours are indicated with gray squares. HT=high tide and LT=low tide.*

2.3. Optical Sensor O3 – Carbon sensor system

Highlights:

- **Measure Carbon cycle relevant parameters such as pH, CO2, and alkalinity, depending on configuration, using photochemical reactions.**
- **Automated embedded spectrophotometry unit based on a miniaturized flow-through arrangement and absorbance detection at 435 and 596 nm**
- **Three sensor configurations for measurements on ferrybox and sailbuoy vessels**
- **OGC Sensor Web Enablement (SWE) enabled**

OSCAR-G2 (fig. 22.) uses 12 LEDs providing a continuous light spectrum from 370 to 730 nm. The light is guided by a collecting lens to the point light source within the cavity and light absorption is measured by a Zeiss MMS VIS spectrometer (Zeiss, Germany). OSCAR-G2 has an internal data storage capacity of 2 GB and a computational module which can calculate the absorption coefficients based on the measured raw light spectra and previously measured and saved calibration and reference data. The measurement process can be controlled via computer via a conventional web browser, thus no additional software has to be installed. It can also be timer-controlled, which allows for automated operation. OSCAR-G2 supports several types of protocols such as Modbus RTU, TriOS-protocol, ASCII and interfaces such as RS232, RS485, Ethernet.

The second cavity absorption spectrometer, HyAbS, is a prototype of the Helmholtz-Zentrum Geesthacht (HZG) completely automated absorption sensor dedicated for long-term usage as monitoring instrument in locations such as ships with no restrictions regarding power consumption (Fig. 6). In the HyAbS, the complete measurement protocol can be customized by the user and carried out automatically. Furthermore, also the calibration procedure has been simplified by replacing the need of measuring a liquid dye of known absorption by the measurement of a solid standard.

The ultimate goal of the NeXOS O3 carbon sensor is monitoring the calcium carbonate saturation state with enough accuracy to provide trends of threats to some marine organisms and their role in the ecosystem. This is observing some of the ecosystem impacts of ocean acidification. Fully understanding the carbonate system demands not only measuring temperature and salinity, but also knowledge of at least two of four measurable carbonate chemistry parameters: pH; dissolved inorganic carbon (DIC) which is the sum of all inorganic carbon sources (carbon dioxide (CO2), carbonic acid (H2CO3), bicarbonate ions (HCO3-) and carbonate ions (CO3--) in solution); total alkalinity (TA, the buffering capacity of seawater); and pCO2. If two of these parameters are known, then the calcium carbonate saturation state can be estimated.

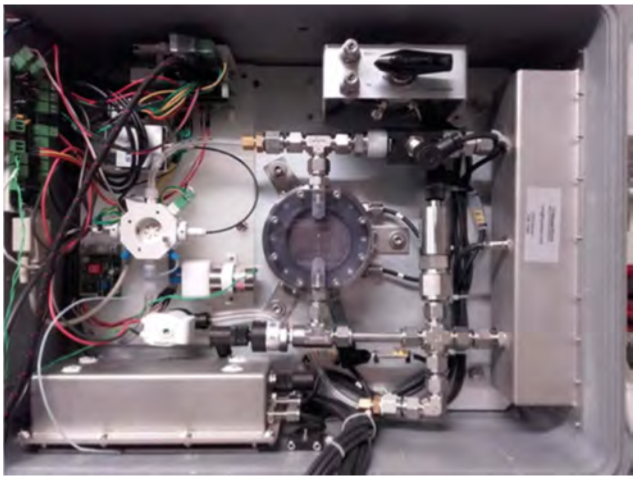


Figure 4. O3 sensor – Cbon2-fb

The NeXOS Cbon2 is the system produced for combined pH and pCO2 analysis and it has been built in two version, for Sailbuoy platforms (Cbon2-sv) and for ferrybox applications (Cbon2-fb). The Automated Flow-through Embedded Spectrophotometry (AFtES) unit is based on a miniaturized flow-through arrangement. Absorbance detection is supervised by a Debian based, versatile ARM architecture with custom electronics for signal conditioning, acquisition and controlling electromechanical parts. Water line is derived from the main water loop and is in parallel with the CO2 extraction branch. The light source is based on commercial LEDs controlled by custom electronics and D/A converters that accurately set light levels. In the Cbon2-fb version for ferries (fig. 4), pCO2 is measured by extraction from liquid phase in a continuous flow, followed by detection in the gas phase by a novel, selective, solid electrolyte sensor. The sensor needs high temperature to operate and provide enough current to be detected, resulting in limiting the application where continuously powered systems can operate, as onboard ships of opportunity. The system measures chemical-physical parameters of seawater. In the Cbon2-sv version designed for operation on a SailBuoy (fig. 5), the AFtES is coupled to a submersible device located below the keel of the hosting vessel. Extraction of gas phase from water phase is still accomplished by a semipermeable membrane supported by a titanium disc. The CO2 detection in the gas phase is then performed by a miniature near-infrared spectrometer, compensated for pressure and temperature, providing a milliAmpere output to be conditioned and acquired by the system. Here, power constraints are strict, due to the limited power supply of the hosting vessel.

The Cbon3, available only for ferrybox applications, is basically a Cbon2-fb coupled with a total alkalinity analyser based on flow injection analysis. The procedure is an alternative to the standard operating procedure, where a titration of the sample with HCl in a cell occurs and a pH electrode is essential to determine the amount of hydrogen ions needed to balance the excess of anions of the sample. Here, the electrode is replaced with a dye suited for the pH range during the analysis and pH is measured spectrophotometrically. The whole system takes 5 minutes to carry out a single alkalinity measurement, 30 seconds for a pH analysis and 1 second for pCO2. Precision is down to 3 µmol/kgSW, yet at present accuracy is not at the level of analytical laboratory systems. Nevertheless, the possibility of measuring three quantities provides an outstanding advantage to refine calculations and apply correction factors.

Figure 5. O3 sensor – Cbon2-sv is the upper box in the sailbuoy hull. The vehicle controller is the lower box

The O3 systems are web-enabled using the OGC PUCK and Sensor Web Enablement (SWE) standard protocols. The settings and sampling strategy of the systems can be modified remotely, according to weather conditions and power availability. For the SailBuoy application, data transfer is achieved by compact, low data flow satellite communication and data are visible real-time by a NeXOS client application. These ensembles implement, for the first time, novel solutions for providing researchers with monitoring ocean surface CO2 system with unprecedented resolution in time and space with high reliability and maintenance/attendance costs negligible compared to those needed for running conventional systems. The deployment of these systems is providing valuable information about the dynamics of CO2 fluxes in the ocean, fundamental to understand trends of ocean acidification on a local and global scale.

2.4. Lab on chip chemical sensors

Highlights:

- **Common design for all sensors**
- **Proven long term deployment**
- **6000m depth rating**
- **Able to measure pH, nitrate, nitrite, silicate, phosphate, ammonia, iron, total alkalinity and dissolved inorganic carbon**

These miniaturised analysers are all based on microfluidic lab on chip technology. The chip takes in a small sample of seawater through a filter, the sample is then mixed with chemical reagents (stored separately in plastic bags). The fluids are pumped round the chip using a custom designed three or four-barrel syringe pump, and controlled using multiple solenoid valves. The system is controlled and data is logged using a custom electronics package. The sensors are housed in an air-filled water-tight housing for shallow deployments, but a pressure compensating bladder can be fitted and the housing filled with oil for deep sea deployments.

The phosphate sensor uses the classic colourimetric assay 'phosphate blue' and is based on a low cost optical detection method, together with an automated microfluidic delivery system that is able to detect phosphate with a Limit of Detection (LOD) of 100nM. The silicate sensor performs in a very similar way, still using colourimetric analysis but with the ammonium molybdate assay. Silicate is at TRL 5 although components and previous versions have operated in coastal waters, the current version remains unproven in an operational environment (though we expect to do this in the next few months).

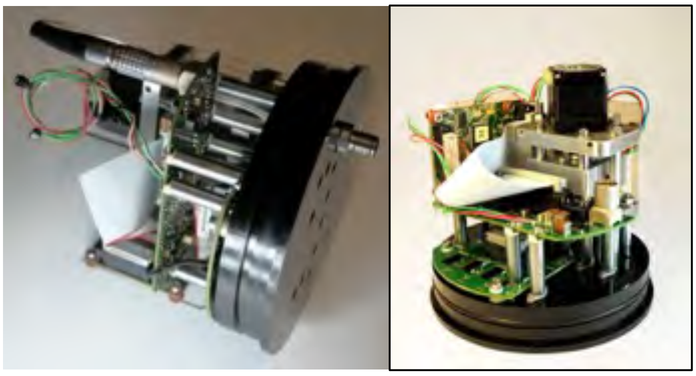


Figure 6 Common lab on chip sensor design

The iron sensor performs colourimetric analysis of Iron (II) and labile iron (III). Iron (III) is reduced to iron (II) using ascorbic acid, and iron (II) is measured using the ferrozine method. The sensor can alternate between iron(II) and iron(III) measurements, or just measure one of these parameters as desired by the user. Colourimetric analysis using the Griess assay is used for the nitrate sensor. Nitrate is reduced to nitrite using a cadmium tube. The sensor can be configured to measure just nitrite by removing the cadmium reduction tube.

The lab on chip ammonia sensor performs a high-resolution fluorometric NH_4^+ analysis using the o-pthaldialdehyde (OPA) assay. The methodology of ammonia detection is based on the fluorescent product formed between OPA and NH_4^+ in the presence of sulphite, after NH_4^+ is passed from the sample to the receiving fluid (OPA) in a gas exchange chip which incorporates a membrane developed in house.

Specifications of the sensors are detailed in the table below (total alkalinity and dissolved inorganic carbon sensors are at a lower TRL so specifications are not detailed).

Table 1. Current performance specifications of the lab on chip sensors

	Phosphate	**Silicate**	**Ammonia**	**Nitrate / Nitrite**	**Iron**	**pH**
Sample rate (mins)	7 (U) 21 (C)	7 (U) 25 (C)	100 (U) 160 (C)	5 (U) 15 (C)	25 (C)	15 (S)
Limit of detection	100 nM	100 nM	<5 nM	20 nM	1.9 nM	
Measurement *σ*	<2.0 % for conc^{n}s ≥ 3 µM	<2.0 % for conc^{n}s ≥ 3 µM	n/a	n/a	n/a	**Accuracy**: Better than 0.003 pH units
Range of linearity	0.1-100 µM	0.1-300 µM	0.005-1.1 µM	0.025-1000 µM	0.002-20 µM	**Precision**: 0.001 pH units
Sample volume per measurement	80-280 µL	80-280 µL	280 µL	280 µL	2.5 mL	550 µL
TRL	7	5	4	8	8	7
Environment demonstrated	Laboratory, estuaries, rivers, coastal	Laboratory	Laboratory, estuaries, rivers, CTD, glider, benthic landers.	Laboratory, estuaries, rivers, glacial, CTD, glider, benthic landers, Arctic	Laboratory, estuaries, rivers.	Laboratory, coastal, deep sea, arctic, AUV
U = uncalibrated; C = calibrated; S = self-calibrating						

2.5. Trace Metal Sensing Module: TMSM

Highlights:

- **High sensitivity, accuracy and reliability**
- **Integrated antifouling membrane**
- **Direct, simultaneous detection of the bioavailable fraction of a range of trace metals**
- **Wide range of application: surface freshwater to open sea**

The growing necessity to continuously monitor the level of trace metals lies with the critical roles they play in ecosystem function. Some metals (e.g. Hg, Cd, Pb) and metalloids (e.g. As) exhibit high toxicity even at low concentrations, while others are either essential or toxic (e.g. Fe, Cu, Zn), depending on their concentrations and the nature of the organisms. Assessing the risk of metal contaminations on ecosystem and ultimately human health is difficult. Trace metals are persistent and distributed under various chemical species (speciation). [4] Only some specific metal species are bioavailable[1]. Bioavailability is therefore of primary concern when considering if a metal serves as nutrient or toxicant. While the global regulatory environmental quality standards (EQS) for metals in water bodies are still mainly based on total (dissolved) concentrations, the revised Priority Substances Directive (2013/39/EU) suggests measurement of the bioavailability of some trace metals (Cd, Pb, Hg, Ni) either indirectly by modelling of their speciation or directly by applying specific measurement methodology.

The TMSM is a new generation of submersible multichannel voltammetric probe[5] allowing direct, simultaneous measurements of the bioavailable fraction of a range of trace metals (cadmium, lead, copper, zinc, arsenite, mercury) with sensitivity at sub-nanomolar (ng/L) level using antifouling Gel Integrated MicroElectrode arrays (GIME).

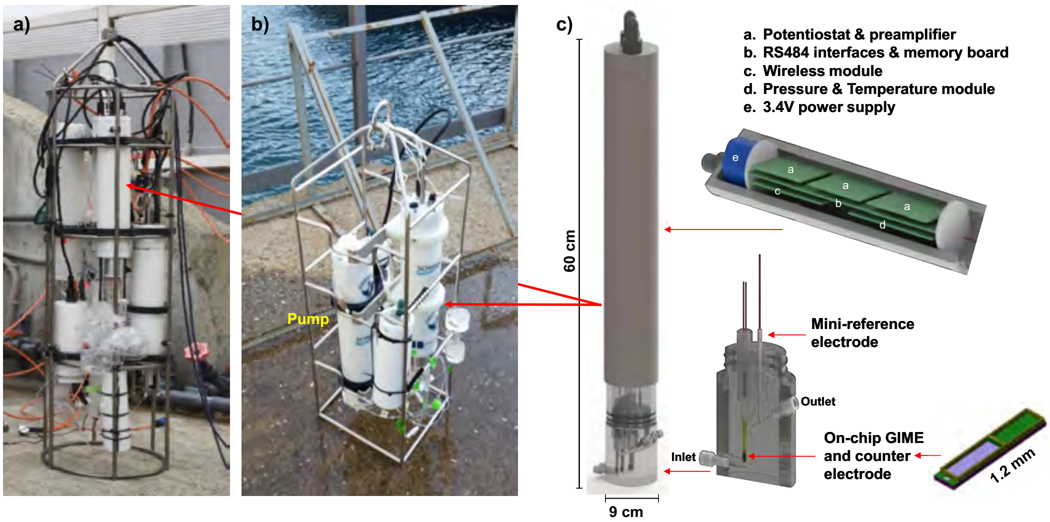


Figure 7 TMSM ready for operational deployment as part of the SCHeMA integrated mapping sensor probes (a) or individually (b). Details of the key components of the TMSM (c).

GIME are based on new designed on-chip 190 to 500 interconnected iridium microdisk arrays electrochemically plated with appropriate transducing element and covered by an antifouling membrane[6]. When a GIME sensor is interrogated using anodic stripping voltammetry, the metal flux (or current) during the electrochemical pre-concentration step selectively represents the dynamic metal species (sum of free metal ions and small labile complexes) which are potentially bioavailable[7].

[4] Arch. Sci. 65 (2012) 119-142
[5] Env. Sci. Tech., in prep.
[6] Sensors & Actuators, Submitted
[7] TrAC 24 (2005) 172-191

The whole system is comprised on an electronic housing, a three-channel flow-through cell and an external multi-channel pump. Each individual channel of the flow-through cell incorporates an on-chip GIME and counter electrode and a mini-reference electrode. The electronic housing incorporates three potentiostats and pre-amplifiers, a 3.4V power supply as well as all required hardware and firmware for trace metal, pressure and temperature measurements; background subtraction; automatic peak current measurements and their conversion into concentrations; data storing; and data transmission via wired or wireless interface. The TMSM can be used individually or interfaced with the other SCHeMA sensing modules (CSM, NSM, ASM) via a dedicated Buoy Controller developed in the project. The Buoy Controller also acts as a gateway between the deployed SCHeMA integrated mapping probes and the SCHeMA web information system gathering and storing the sensor data and providing open access to those data.

The TMSM was deployed for three months from the CNR platform of the Genoa Harbour (Italy) during the period January to April 2017. Simultaneous measurements of the Cd, Pb,Cu and Zn bioavailable fraction were performed at 2 hour time intervals. A life time of typically one month were observed for the GIMEs used. During their month operational deployment, up to 350 simultaneous measurements of the four metals were successfully achieved. The TMSM were also deployed in the Arcachon Bay and the Gironde Estuary representative of the southwest European Atlantic Coast hosting major coastal protected areas and economic activities (seafood production areas). Hg(II) levels were lower than the limit of detection of the developed GIME (< 20 pM/5ng/L). The results recorded for the other targeted trace metals revealed that, in dynamic tidal coastal ecosystems, the concentration of the bioavailable fraction of trace metals may double in a few hours (Arcachon Bay) and varies, under different trends depending on their complexation properties, in a range up to one order of magnitude in the salinity / turbidity gradients of the Gironde estuary (e.g. fig. 8)

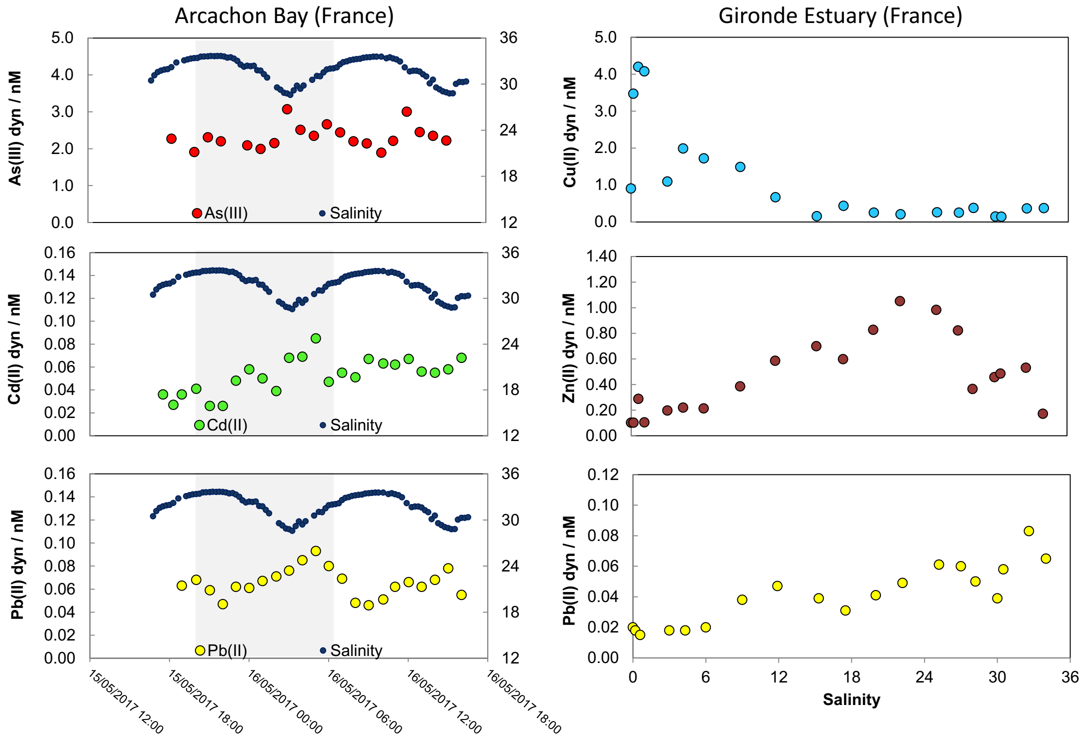


Figure 8: In situ recorded temporal As(III), Cd(II) and Pb(II) bioavailable concentrations and longitudinal profiles of Cu(II), Zn(II) and Pb(II) bioavailable concentrations monitored during a TMSM deployment in respectively the Arcachon Bay (May 2017) and Gironde Estuary (June 2017).

2.6. Nutrients Sensors Module: NSM

Highlights:

- **Accurate detection of nitrate in seawater**
- **Inline coupling of needed pre-treatments**
- **Can be used for the additional detection of chloride/salinity**

The importance of the reliable long-term monitoring of nutrients in seawater lies in their significant role as indicators of anthropogenic activities that perturb aquatic ecosystems. Currently established approaches for nutrient detection involve sample extraction using power intensive pumps, followed by analysis using expensive centralized laboratory instrumentation. The sampling procedures are likely to result in undesired alterations of the samples implying the loss of useful information and therefore the concept of decentralized sensors for the in situ monitoring of nutrients has reinforced its interest for environmentalists in the last years. Importantly, potentiometric sensors are especially suitable for this purpose[8] but it is necessary to reduce the amount of certain major ions in seawater, i.e. chloride and hydroxyl, prior to the potentiometric detection.

The developed NSM is based on the same potentiometric flow cell as in CSM but containing pH, nitrate and nitrite membrane potentiometric sensors. NSM and CSM are interchangeable modules sharing the same electronics. In the case of NSM, electrochemical desalination[9] and passive acidification modules[10] are coupled to the detection cell (fig. 9). Thus, the desalination module reduces the amount of chloride in seawater down to millimolar levels and then the acidification module lows the pH down to 5.5. In these conditions, potentiometric detection of nitrate and nitrite in seawater is affordable with limits of detection of 0.9 µM and 0.6 µM respectively. The incorporation of a calibration solution allows to compensate any electrode drift.

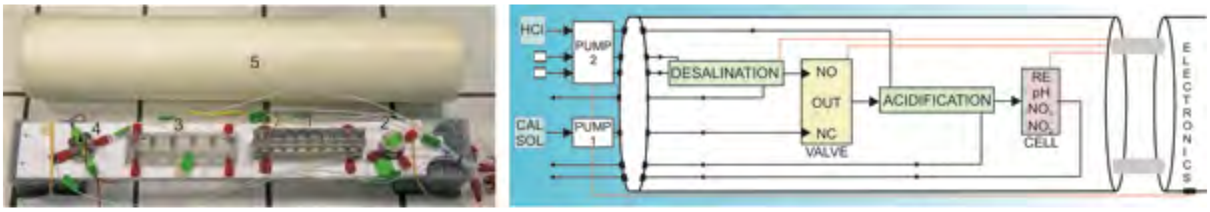
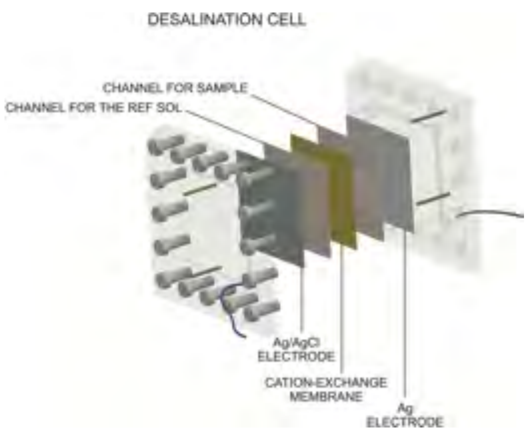


Figure 9. NSM image and fluidics design. 1: desalination unit, 2: valve, 3: acidification unit, 4: potentiometric flow cell, 5: submersible housing.

The Desalination unit[9]



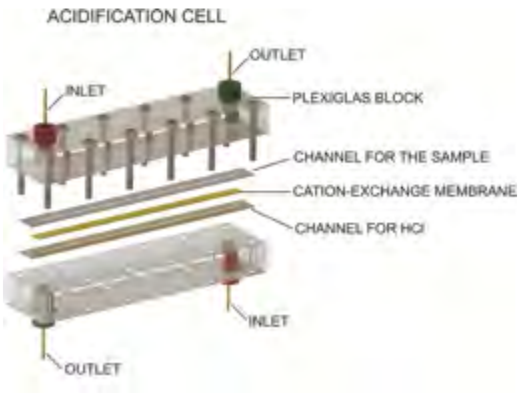
A microfluidic custom-fabricated thin layer flat cell allows one to electrochemically reduce the chloride concentration of seawater more than 100-fold, from 600 mM down to ~5 mM. The desalinator operates by the exhaustive electrochemical plating of the halides from the thin layer sample onto a silver element as silver chloride (Eapp= 800 mV, t=300 s), which is coupled to the transfer of the counter cations across a permselective ionexchange membrane to an outer solution. If the desalination cell is interrogated using cyclic voltammetry instead, the obtained peaks are chloride concentration-dependent and therefore it can be additionally used as chloride detector in the range of 0.5 µM-600 mM. Moreover, the linear correlation chloride-salinity permits the indirect

[8] Curr. Opin. Electrochem. (2017) DOI : 10.1016/j.coelec.2017.06.010
[9] Anal. Chem. 87 (2015) 8084
[10] Anal. Chem. 89 (2017) 571

detection of salinity without the need of changing the probe, as in the case of conductivity measurements.

The Acidification unit[9]

The working principle of the developed acidification unite relies on the cation-exchange process between the sample and an ion-exchange Donnan exclusion membrane in its protonated form. The resulting in-line acidification of natural waters with millimolar sodium chloride level (freshwater, drinking water, and aquarium water, as well as dechloridized seawater) decreases the pH down to ~5. The originality of the proposed flow cell lies in the possibility to adjust the pH of the sample by modifying its exposure time with the membrane by varying the volumetric flow rate.



The NSM was satisfactorily applied for chloride and nitrate detection in Arcachon Bay (France). Nitrite levels were lower than the limit of detection of the potentiometric sensor. The pH sensor serves to control the obtained pH after the desalination + acidification procedures. In the NSM, seawater passes first through the desalination unit for chloride detection and then desalination, thereafter through the acidification module and finally through the detection cell. The observed temporal trends (fig. 10) clearly show tidal-dependence of chloride and nitrate levels.

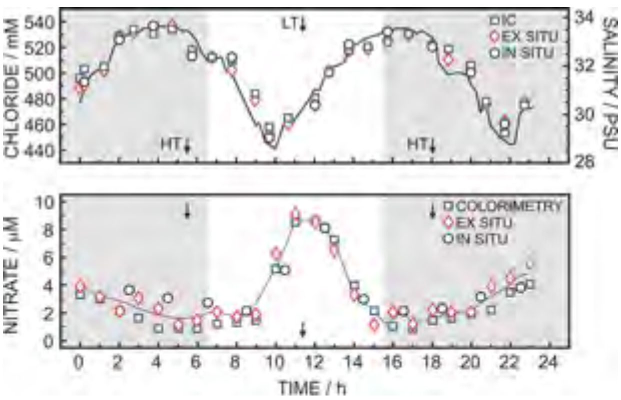


Figure 10. Temporal variation recorded for salinity (CTD), chloride and nitrate (in situ, ex situ) during a 24-h deployment in the Arcachon bay (from May 15th, 2017 at 15:00 to May 16th, 2017 at 15:00). Light hours are indicated with gray squares. HT=High tide. LT=Low tide.

2.7. ANESIS: Autonomous Nutrient Electrochemical Sensor In Situ

Highlights:

- **No liquid reagents**
- **Measure silicate and phosphate**
- **600m depth rating**
- **Adaptable to a range of platforms including profiling floats**

Nutrients are key players in the oceanic primary productivity. When delivered in excess to the coastal ocean, they may lead to eutrophication and harmful algal blooms. Observations of marine water quality and biogeochemistry are currently poor, especially for parameters that cannot be measured by remote sensing. ANES*IS* measures two important nutrients, silicate and phosphate.

Essentially, electrochemical sensors work by reacting with the nutrient (silicate or phosphate) and producing an electrical signal proportional to the concentration of the nutrient. In fact the nutrient must first be converted into a complex that will react with an electrode. The SenseOCEAN silicate and phosphate electrochemical sensors have been adapted from the laboratory prototype, which uses two separate cells: the first one for *in situ* formation of the complexes and the second for the detection of silico- and phosphomolybdic complexes on a gold electrode (see box below for technical details). The mechanical designs and the set-up of the electrodes are crucial steps to ensure effective mixing of the solution.

The electronics board (for silicate and phosphate) has been developed in close collaboration between CNRS-LEGOS and nke Instrumentation to miniaturise it as far as possible, while still maintaining performance.

Instruments lowered into the ocean need to be protected from the effects of pressure so are placed in 'housings'. The housings of the silicate and phosphate sensors are identical, which will reduce the cost of mass production. The sensors are 25 cm long (without connector) and 9 cm in diameter, weighing 2.2 kg in air.

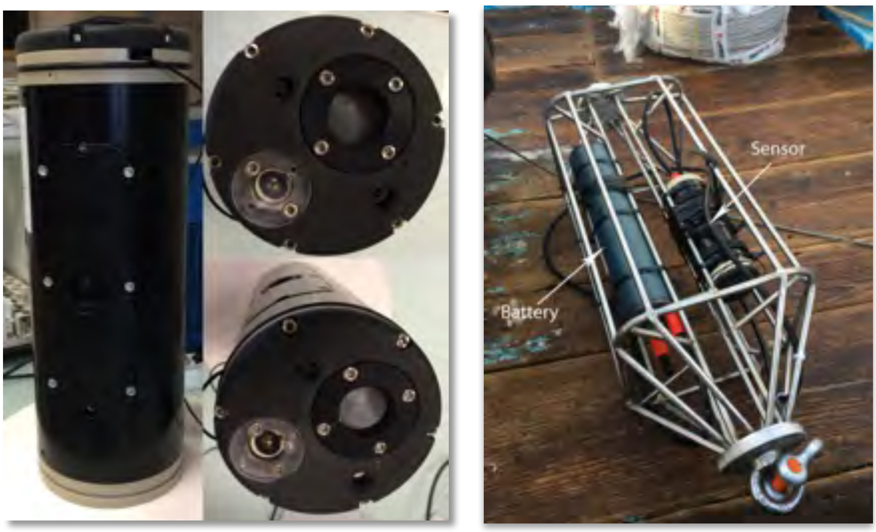


Figure 11. Sensor shown in pressure housing (left). Sensor and power supply mounted on a frame ready for deployment on mooring off the coast of Chile (right)

The silicate sensor was deployed for two weeks on a mooring at 55 meters depth in the upwelling zone off Chile at Talcaruca Point in April 2017. The silicate concentration was measured every hour and ~140 data files were successfully recorded. Separate water samples were taken to enable measurement by another method in order to verify the sensor results.

The silicate sensor has also been implemented on a PROVOR profiling float together with pH and oxygen optode sensors and a nitrate lab on chip sensor. The float was successfully deployed offshore Villefranche-sur-Mer in the Mediterranean Sea in Spring 2017. The deployment was very successful with ~40 measurements obtained and sent back to the lab by satellite for later analysis.

As silicate and phosphate are non-electroactive species, their conversion to electroactive molybdate complexes in acidic medium is required [a-c].

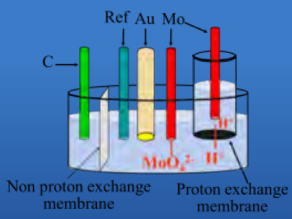
$$Si(OH)_4 + 12\ MoO_4^{2-} + 24\ H^+ \rightarrow H_4Si(Mo_{12}O_{40}) + 12\ H_2O$$

$$PO_4^{3-} + 12\ MoO_4^{2-} + 27\ H^+ \rightarrow H_3PMo_{12}O_{40} + 12\ H_2O$$

All the reagents needed are formed *in situ* by a simple oxidation of metallic molybdenum

$$Mo + 4\ H_2O \rightarrow MoO_4^{2-} + 8\ H^+ + 6\ e^-$$

In order to reach the needed acidic pH, the reduction of H^+ on the counter-electrode is prevented by isolating the counter-electrode behind a membrane limiting the protons diffusion.



Because silicate is an interference to phosphate detection, a ratio of H^+/MoO_4^{2-} equal to 70 is required. To reach this ratio another compartment with a second molybdenum electrode connected with a proton-exchange membrane is added.

[a]Lacombe *et al.,* Talanta 77 **(2008)** 744-75
[b]Jonca *et al.,* Electr. Acta88**(2013)**165-169
[c]Barus&Romanytsia *et al.*,Talanta,160 **(2016),**417-424

2.8. Electrochemical microsensors

Highlights:

- **Accurate and rapid measurements**
- **Non-destructive**
- **Can be used for sediment-water interface measurements**
- **Wide range of applications – waste water plants through to open ocean**

Electrochemical microsensors are needle-shaped probes with a tiny active tip area that allows the direct measurement of specific chemicals in the environment. The size of the microsensor tips, often thinner than a human hair, makes them ideally suited to studying the micro-distribution of chemicals inside soft material such as tissue, sediment or biofilms. The tips can penetrate the material without disturbance or destruction. The performance of the electrochemical microsensors is not affected by external motion. Combined with their accurate and rapid response, this makes them versatile tools for measuring chemicals of interest in the oceans.

In SenseOCEAN, Aarhus University in collaboration with Unisense A/S successfully developed state-of-the-art microsensors for two globally important greenhouse gases: carbon dioxide (CO_2) and nitrous oxide (N_2O). Greenhouse gases (GHGs) trap heat in the atmosphere (hence their name) contributing to global warming and climate change. CO_2, the most widely recognized GHG is released into the atmosphere from burning fossil fuels, waste and trees as well as from the manufacture of cement and steel. N_2O is also released via fossil fuel burning and during agricultural and industrial processes. Although smaller quantities of N_2O than CO_2 are released to the atmosphere, N_2O has a potential global warming effect of >260 times that of CO_2. At the moment, these large industrial inputs of CO_2 and N_2O to the atmosphere are balanced by absorption into the oceans. However, the capacity of the oceans is finite, hence the need to monitor these gases.

The CO_2 microsensor

This microsensor works by a reductive conversion of CO_2 on a silver cathode. The sensor signal consists of an amplification of the resulting current. It is necessary to apply a very negative potential to reduce CO_2. This means that other compounds such as H_2O and O_2 (that can be present in high concentrations) will give a signal. The challenge in constructing a functional CO_2 sensor was to avoid these compounds reaching and reacting on the cathode surface. This was solved by adding an oxygen scavenging compartment and a water-binding electrolyte.

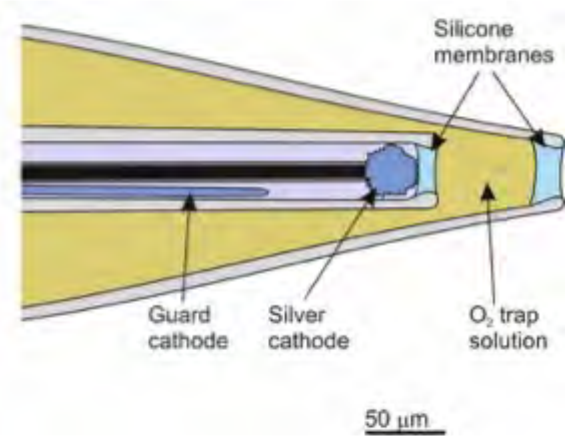


Figure 12 Structure of the CO_2 microsensor

The N_2O microsensor

The N_2O microsensor has the same schematic appearance as shown for the CO_2 sensor. These sensors respond linearly across a huge concentration range, from nanomolar to millimolar concentrations! The sensors have operational lifetimes of several months even when analysing continuously in a wastewater treatment plant. About 100 wastewater treatment plants world-wide are now equipped with Unisense N_2O sensors.

High-sensitivity N_2O microsensor (STOX-N_2O)

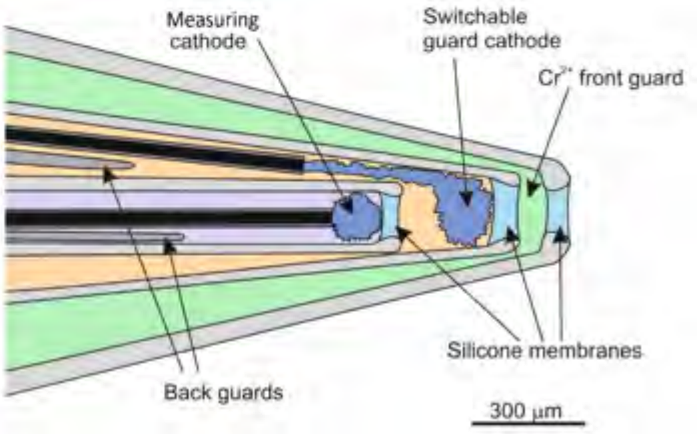


Figure13 Structure of the N_2O microsensor

At very low concentrations, it can be difficult to distinguish the N_2O signal from the background signal. The STOX-N_2O performs an internal referencing by use of an extra cathode to periodically remove all N_2O and thus reveal a precise zero current. As for the normal N_2O sensor there is also an oxygen scavenging compartment based on O_2 reduction by chromium (II) ions or ascorbate.

2.9. Multiparameter optical sensor

Highlights:

- **One design, several variants**
- **Measures CDOM, Chlorophyll A, PAHs**
- **Pollution detection for oil, sewage, agricultural run-off**
- **Detects onset of harmful algal blooms**

Fluorescence is a very sensitive technique for monitoring various compounds in the environment. Some compounds absorb light at very specific wavelengths and then re-emit the energy absorbed as fluorescence at a longer wavelength. Fluorescence is directly proportional to concentration and is typically 1000x more sensitive than more conventional absorbance measurements. In addition, fluorescence offers better selectivity, as not all compounds fluoresce.

UV fluorescence typically targets aromatic hydrocarbons, heterocyclic compounds and larger conjugated aromatics associated with Coloured Dissolved Organic Matter (CDOM). Visible fluorescence is typically used for dye tracing and chlorophyll detection.

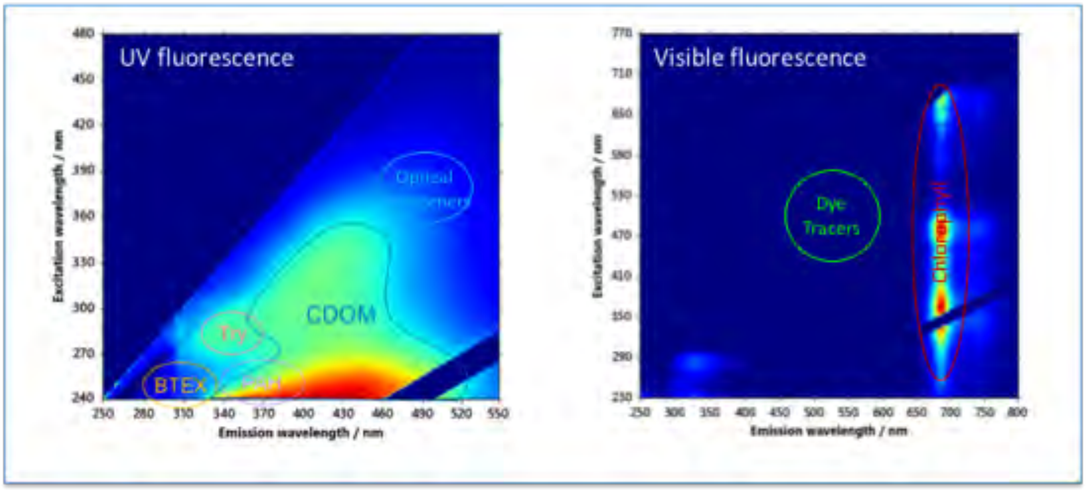


Figure 14 UV and visible fluorescence properties of different compounds

To date, fluorometers have combined a single excitation and emission wavelength to target specific compound groups. However, as can be seen in fig.14, there can be significant overlap in the spectral characteristics of different fluorescence compounds, making it difficult unambiguously to select for one type of compound. Further, environmental interferences, e.g. turbidity or 'colour' in the sample, can attenuate the excitation light leading to under-reporting of the fluorescence signal.

To overcome the problems outlined above, a multi-parameter sensor has been developed as part of the SenseOCEAN project where multiple fluorescence channels are used in combination with turbidity, absorbance and temperature measurements to provide robust monitoring in the presence of a range of environmental interferences. Two main variants of the sensor have been developed: one for UV fluorescence applications and the other for algal studies, monitoring chlorophyll fluorescence.

In the UV variants, a single excitation wavelength is used to excite fluorescence in the sample. The sensor then isolates three different fluorescence emission wavelengths. In addition, absorbance, turbidity and temperature are monitored and algorithms developed during the project are applied to linearize the fluorescence response and correct for these interferences. This has the added benefit of significantly extending the dynamic range of the fluorescence measurement by a factor of 20. Three variants of the UV sensor have been developed: the 'BTEX' sensor targets single ring aromatic compounds associated with fuel contamination; the 'Crude' sensor targets polycyclic aromatic hydrocarbons (PAHs); while the third targets the amino acid Tryptophan, which is associated with bacterial contamination in the environment, e.g. due to sewage or agricultural run-off. All three monitor CDOM and chlorophyll-a fluorescence to identify potential signal interferences from background environmental fluorescence and/or algae.

Figure 15 Multiparameter optical sensor

The algal version of the multi-parameter sensor operates in a different manner to the UV variants. In this sensor, four different excitation wavelengths are used to excite specific pigment groups associated with the light harvesting complexes in algae. Energy absorbed by these pigments is rapidly transferred to chlorophyll-a in Photosystem II and the resulting fluorescence is then detected. By monitoring the changing contributions to chlorophyll-a fluorescence from the different excitation wavelengths, it is possible to detect shifts in algal composition of a sample, e.g. to detect the onset of an algal bloom. The four variants of the multi-parameter optical sensor are summarised in Table 2

Parameter	BTEX	Crude	Tryptophan	Algae
BTEX	✓			
PAH		✓		
CDOM	✓	✓	✓	
Tryptophan			✓	
Chlorophyll-a & -c	✓		✓	✓
Chlorophyll-b & -c				✓
Phycocyanin				✓
Phycoerythrin				✓
Turbidity	✓	✓	✓	✓
Absorbance	✓	✓	✓	✓
Temperature	✓	✓	✓	✓

Table 2. Parameters measured by the four variants of the optical sensors

In addition to the sensor development, work has also focussed on developing traceable standardized calibration for the fluorometer. To date, it has been difficult to compare the output from different manufacturers' sensors, because their responses will be highly dependent on sensor geometry, the excitation and emission wavelengths used, the spectral characteristics of the light source and detector and the compound used for calibration. This lack of standardization has inhibited the wider use of fluorescence for routine environmental monitoring. A standardization method has been developed during the project that allows the sensor to report fluorescence in standardized and traceable 'relative fluorescence units'. This enables the detected fluorescence to be compared directly between measurement channels and across different sensor types. Careful management and internal referencing of the excitation light source also ensures long term calibration stability.

2.10. Optical Sensor O1

NeXOS O1 Fluorescence Sensors are new compact, low-power multifunctional optical sensor systems based on multi-wavelength fluorescent technology. Their aim is to provide detailed information on both water constituents and other relevant contaminants that are optically active in either UV or optical spectral regions. In NeXOS, three different fluorescence sensor types have been constructed. Two of them, the MatrixFlu-UV and the MatrixFlu-VIS are based on a similar system design with different inner optical designs and complementary capabilities. The two use different combinations of three or four narrow band excitation and emission wavelengths. The third O1 system, the MiniFluo, consists of two separate single channel fluorescence detectors within a single housing. It detects two distinct parameters in the water column related to the wavelength combination of fluorescence signals from hydrocarbons in the water.

2.10.1. Optical Sensor O1 MatrixFlu-UV and MatrixFlu-VIS

Highlights:

- **Four detection channels in an ultracompact seawater-resistant housing (available in stainless steel and titanium, depth rated for 300 or 6,000 m)**
- **Includes an excitation light source of three or four LEDs surrounded by semiconductor detectors collecting fluorescence signals that pass through adaptable, selectable narrow bandwidth filters**
- **Power consumption is below 1.8 W at 12 to 24 Vdc and weight is less than 600 g in air**
- **OGC PUCK and Sensor Web Enablement (SWE) enabled**
- **Validated on wave-glider and buoy**

Both MatrixFlu sensors (fig. 16) include an excitation light source of three or four LEDs surrounded by semiconductor detectors collecting fluorescence signals that pass through adaptable, selectable narrow bandwidth filters. The light source provides excitation of a sample volume in front of the sensor. The detectors are aligned in an angle of 170° compared to emitted light in order to sample the same volume. The combinations of wavelengths can be found in Table 3.

Table 3. Wavelength matrix for MatrixFlu UV (violet) and VIS (green)

Emission / Excitation	280 nm	360 nm	460 nm	540 nm	655 nm	682 nm	850 nm
254 nm	FDOM	PAH	FDOM	FDOM			
280 nm	Scat280	PAH	FDOM	FDOM			
320 nm			FDOM	FDOM			
375 nm			FDOM		FDOM	FDOM	
470 nm			Scat460			CHLa	
590 nm					PC	PC via CHLa	
850 nm							Scat850

Scat850 indicates the scattering signal at 850 nm. PAH = polycyclic aromatic hydrocarbon, PC = Phycocyanin, CHLa = Chlorophyll a and FDOM = fluorescent dissolved organic matter components.

Figure 16. O1 Matrixflu sensors

Both versions have four detection channels in an ultracompact seawater-resistant housing (available in stainless steel and titanium, depth rated for 300 or 6,000 m). In both versions, measurements are performed with all possible excitation emission combinations, thus unfolding a matrix of fluorescent and backscattering signals. Power consumption is below 1.8 W at 12 to 24 Vdc and weight is less than 600 g in air. When combining both sensors, e.g., using a compliant fitting for glider applications, an unchallenged range across the UV-VIS electromagnetic spectrum is available. This allows observing not only established parameters but also has the potential of observing previously unknown substances that may be encountered in multipurpose applications. Matrix sensing obviously produces more data than single-channel fluorometers. Therefore, onboard processing and storage capacities were included to make use of higher-level operations, such as characterizing substances from multisensory information or performing data quality checking from redundant information. Onboard computational power additionally enabled the easy integration of standard protocols such as MODBUS-RTU and OGC-PUCK on Ethernet, RS-232 and RS-485 interfaces. Sensor operation can be controlled either from outside via the above protocols or as a response to power up, a simple solution for less sophisticated platforms. Finally, cost-efficiency is achieved from factors such as integrating multiple sensors into one, supporting flexibility in the mission's target parameters, ease of integration due to open standard protocols and enhanced data access based on embedding processing capacities and an open standard compliant software architecture.

2.10.2. Optical Sensor O1 Minifluo

Highlights:

- **Can detect and quantify four polycyclic aromatic hydrocarbons (PAH): naphtalene (NAPH), phenanthrene (PHE), fluorene (FLU), and pyrene (PYR) together with tryptophan aromatic amino acid**
- **Single-band bandpass filters allow for detection through a quartz double-convex lens**
- **OGC PUCK and Sensor Web Enablement (SWE) enabled**
- **Validated on deep glider**

Figure 17. O1 MiniFluo sensor

The third optical fluorescence sensor, the MiniFluo (fig. 17), was developed and built with two single channels which enable the detection and quantification of four different polycyclic aromatic (PAH) as indicated in Table 4: naphtalene (NAPH), phenanthrene (PHE), fluorene (FLU), and pyrene (PYR) together with tryptophan (TRY, an aromatic aminoacid). The design has single-band bandpass filters that allow for detection of fluorescence signals through a quartz double-convex lens (UV grade fused silica) by a Si- photodiode. The mechanical design is made of a very compact housing (Ø x L: 75 x 60 mm) anodized aluminium for the upper part and a copper plate for the bottom part. The main advantages of MiniFluo are the simultaneous measurement of two petroleum components with a miniaturized design having low power consumption of 0.36 Watt at 12 VDC. This enables the integration on underwater platforms such as gliders. A standardized I2C protocol is used to also support sensorML and NeXOS compliant connectivity to SOS data storage.

Table 4. Wavelength matrix for MiniFluo

	Excitation (nm)	**Emission (nm)**
NAPHTALENE	275	340
TRYPTOPHANE	275	340
PHENANTHRENE	255	360
PYRENE	270	380
FLUORENE	260	315

2.11. Miniaturized, multi-channel Algae Sensing Module: ASM

Highlights:

- **Flexible and modular design**
- **No sample preparation**
- **Early stage detection of arising algal blooms**
- **Identification of harmful algal groups from among an algal assemblage**

Fluorometric measurements are sensitive methodologies that have been used extensively for monitoring of diverse compounds in the marine environment, as they are more sensitive than conventional absorbance measurements. Phytoplankton absorb light at very specific wavelengths and re-emit part of the absorbed energy as fluorescent light at longer wavelengths. Fluorescence can therefore be used as selective technique to identify relevant algal groups in an algal assemblage of mixed composition. In addition, distinct emission windows reduce interferences from other marine compounds.

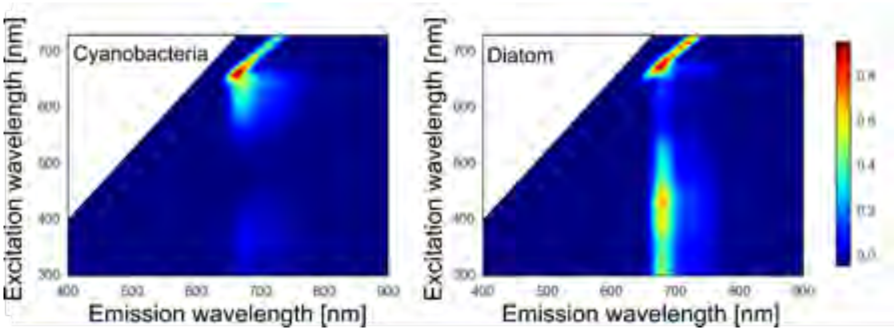


Figure 18 Spectral characteristics of cyanobacteria compared to other algal groups, using diatoms as an example.

Conventional algae fluorometers compare the fluorescence emitted upon excitation at two different wavelengths aiming to separate cyanobacteria and algae according to their major spectral differences as shown in figure 18. However, there can be significant overlap in the spectral characteristics of different algae making it difficult to discriminate further groups. In addition, various biological and chemical interference, e.g. from colored dissolved organic matter (CDOM), yellow substances such as humic matter or suspended particles in the sample can lead to alterations in the fluorescence signal and have to be taken into account for data evaluation procedures.

To address these problems, TU Graz, as part of the SCHeMA project, has developed a miniaturized, multi-channel detection module. This in-situ device enables the early stage detection of phytoplankton species in algal blooms and the real-time identification of their taxonomic affiliation. The appliance has a modular design to allow easy replacement of optical components. Although the ASM is able to identify various algal groups, the system was optimized for reliable identification of toxin producing cyanobacteria and dinoflagellates from among other algae in an algal assemblage of mixed composition. In addition, the ASM is able to track the biomass concentration in order to determine the onset and deterioration of algal blooms.

Figure 19 Rendered picture of the algae detection module (left and right) and the modular LED modules used as excitation sources (middle). The picture on the right illustrates the arrangement of optical and electronical components. Photodetectors are aligned with 90° angle to the excitation source and covered with emission filters to minimize cross-talk between excitation and emission channels.

In the detection module (fig. 19), up to eight different wavelengths are used to excite specific pigments in the photosystems of the phytoplankton sample. Upon excitation, the energy absorbed is rapidly transmitted throughout the light-harvesting complex of the photosystems to chlorophyll-a in the reaction center. Part of the energy is used to maintain the photosynthesis of the algae and surplus energy is emitted as fluorescent light. The resulting fluorescence and the contribution of certain excitation wavelengths to the fluorescence signal is detected by the miniaturized ASM. Algorithms are then applied to standardize and correct the fluorescence signal aiming at greater inter-comparability within the detection system and between experiments. Subsequently, the recorded fluorescence pattern is compared to a set of reference data and a multivariate pattern recognition algorithm allows the identification of the taxonomic affiliation of the sample (fig. 20).

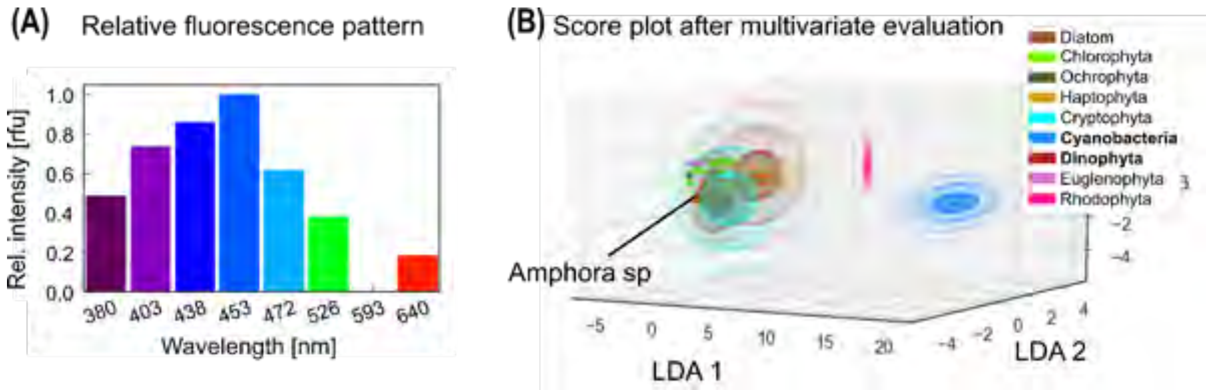


*Figure 20 (**A**) Relative fluorescence intensity upon excitation at different excitation wavelengths for amphora sp, a diatom sample. (**B**) Resulting score plot after applying the multivariate pattern recognition algorithm aiming at the comparison of the unknown sample to a set of reference data.*

For semi-quantification of the phytoplankton biomass, the detection unit counts cell events passing through the system and correlates the number of events with the average fluorescence intensity at certain wavelengths. Up to a certain cell density limit, signal spikes can be resolved and the detected spikes can be counted as cell events (see zoom-in plot of fig. 21). This approach allows the measurement of changes in the biomass concentration that indicate the onset and deterioration of an algal bloom.

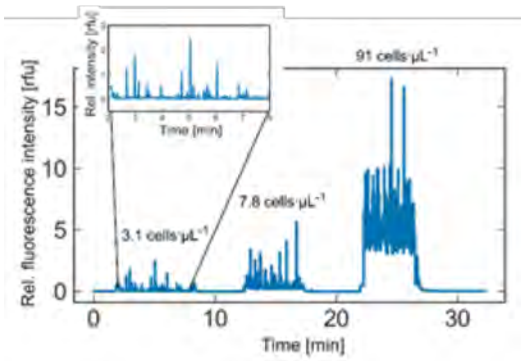


Figure 21 The intensity of the fluorescence signal emitted from the photosystems strongly depends on the biomass in the measurement chamber. If the cell density is low enough, the cell events, passing through the measurement chamber, can be resolved and counted.

Signal responses are highly dependent on various instrument parameters, e.g. spectral characteristics of the excitation sources and detector and absolute intensity of the light sources, among other things. The current deficit in inter-calibration strategies has compromised the utilization of fluorometers in environmental science. Therefore, an internal calibration and standardization strategy was developed allowing direct comparison within the multi-channel detector system and between different measurement instruments. In addition, work has also focused on developing a software interface for external and detailed data evaluation of individual cell events. The software combines the acquired knowledge of standardization procedures and data evaluation methodologies using a multivariate pattern recognition algorithm. This facilitates the application of the device for various scientific issues, for example the investigation how the relative fluorescence pattern of a phytoplankton sample varies along its growth phase.

2.12. Optical Sensor O2 – Phytoplankton identification sensor

Highlights:

- **Integrating cavity providing reliable identification of at least 7 phytoplankton groups**
- **a) OSCAR-G2: Compact, submersible, and commercially available. Operate as bench-top or profiling instrument**
- **b) HyAbs: Completely automated absorption sensor dedicated for long term usage as bench top instrument in location with no restriction of power consumption**
- **OGC Sensor Web Enablement (SWE) enabled**
- **Validated on ferrybox**

Based on the integrating cavity approach of the PSICAM, the NeXOS project developed two automated sensors capable of the continuous, hyperspectral measurement of the absorption coefficients of water, OSCAR-G2 (fig.5) and the HyAbS (fig. 6). Both take advantage of the use of an integrating cavity, since this avoids errors introduced by light scattering on particles present in the sample and it increases the sensitivity of the measurements. From the hyperspectral (2 nm resolution) absorption coefficient data, which is the primary output of the sensors, phytoplankton-related information can be derived. Certain coefficients can be used as optical proxies for important bulk parameters like chlorophyll-a and total suspended matter (TSM), which are a quantitative measure of phytoplankton in the water. Furthermore, the shape of the spectrum can be evaluated with respect to taxonomical information, since it is determined by the presence of accessory pigments, which are often specific for certain types of phytoplankton. This phytoplankton identification is done by comparison of the measured spectrum to a database of spectra with known phytoplankton compositions. The algorithms for this approach have also been developed in the course of the project.

Figure 22. O2 sensor – OSCAR G2

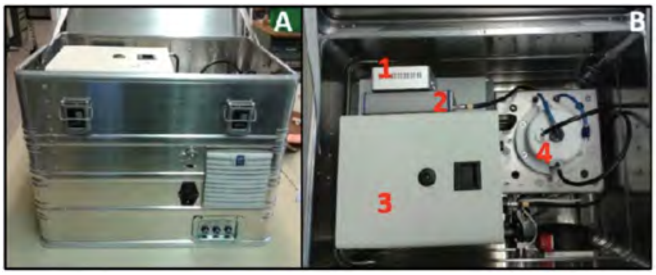


Figure 23. O2 sensor - HyAbS

2.13. Acoustic Sensors

Highlights:

- **Compact, low power consumption digital hydrophone with embedded pre-processing of acoustic data, including MSFD descriptor 11 and Bioacoustics**
- **Open-hardware for user programming of new processing routines (ANSI C)**
- **High dynamic range, down to Sea-State 0**
- **Array configuration tested with Precision Time Protocol (IEEE 1588)**
- **Bench tested down to 445 bar pressure**
- **XP X 10-800 standard tested for cold, hot storage, moisture, vibration and mechanical shocks**
- **Ethernet and RS232 communication, SCPI protocol**
- **OGC PUCK and Sensor Web Enablement (SWE) enabled**
- **Validated on glider, profiling floats and fixed platforms (cabled and moored)**

Figure 24. NeXOS A1 - Passive Acoustics

A1 is a compact, low power consumption digital hydrophone (fig. 24) with embedded pre-processing of acoustic data, using the Open Geospatial Consortium (OGC) Programmable Underwater Connector with Knowledge (PUCK) and Sensor Web Enablement (SWE) interoperability standards. The embedded processing reduces the communication bandwidth requirements for real time data access.

A1 consists of one transducer and two A/D converters, simultaneously sampled, with different gain, to measure and detect a broader range of acoustic source levels from 50 dB to 180 dB with reference to 1µPa and includes selectable analog gain settings or traceable automated gain control, in the frequency range from 1Hz to 50kHz.

The architecture of A1 sensor is composed of five elements: Transducers (HYD) of different types depending on depth requirements and cost (Neptune Sonar D/70, Technology Limited SQ26-01, JS-B100-C4DP), a Signal Conditioning Unit (SCU) which includes 2 channels of amplifier stage with selectable whitening equalizer, anti-aliasing filter, selectable gain, sampling frequency; a micro-power SAR Analog to Digital Converters 16 bit ADS8867; a microcontroller Unit (MCU) LPC4370; and an Underwater connector 12-pin male MCBH12M. During operation, the transducer signal is pre-amplified with an input stage of 20 dB gain, common for both channels. The first channel (CHA) has a post-amplifier stage with selectable gain (20 or 40 dB) that can be preceded by an “equalizer” filter in order to optimize the signal to ocean noise ratio at low frequency. The equalizer circuit is a one-pole high pass filter with a cut-off frequency of 3200 Hz and it can be enabled or disabled through the MCU.

The second channel (CHB) does not alter the hydrophone pre-amplified signal. Both channels have a low pass antialiasing filter. The operator, through the MCU, can set the cut off frequency of the anti-aliasing filter depending on the application and on the sampling frequency. The hydrophone signal is sampled by two 16-bit SAR converters controlled by an ARM microcontroller. The working sampling frequency (up to 100 kS/s for a 1Hz to near 50kHz acoustic bandwidth) is controlled by the MCU timer. The MCU processes the sampled data and transmits the results on an EIA RS-232 serial port. A1 is equipped with a real-time clock that tags sampled data and a Pulse Per Second (PPS) input for the GPS link. Frequency range may be selected by the MCU, changing the frequency clock of the antialiasing filter. Three types (see Table I) of transducers are available for A1, depending on their sensitivity, shape and maximum operating depth. Within NeXOS, a prototype of A1 for each of these transducers was manufactured. There are a number of significant technological innovations included in the A1 implementations. These include the adjustable dynamic range that can cover 50 to 180dB re 1µPa, either manually or automated. There is a programmable gain amplifier stage to configure the analogue signal conditioning stage for both low and high sound level monitoring. For interface with platforms, the A1 has a PUCK automated management element which enables flexibility for controlling sensor operations and data flow to the users. Finally, there is an option for the raw data to be converted to reduce communication overloads. Power consumption in operation is about 0.9 W at 12 to 24 Vdc.

Figure 25. A2 - Passive acoustic array

A2 is a compact hydrophone system for observing the volumetric environment, enabling real-time measurement of underwater noise and of several soundscape sources. It consists of an array of four digital hydrophones (A2hyd) with Ethernet interface and one Master Unit for data processing. (fig. 25). A2hyd sensors have the same characteristics as the A1 sensor regarding the Signal Conditioning Unit (SCU), the A/D Converter (ADC) and the Micro Controller Unit (MCU), with the difference of a smaller internal memory (32 GB) and no internal battery. A JS-B100 hydrophone transducer has been selected for deep underwater application. Each of the four digital A2hyd hydrophones transmits the digitized acoustic data to the Master Unit through Ethernet. The Master Unit manages the timing synchronization of the four A2hyd sensor signals for simultaneous sampling. The time synchronization of the Master Unit and the slave units (A2hyd) is performed using the IEEE1588 Precision Time Protocol (PTP) standard. The Master Unit processes the acoustic data.

Table 5. Transducer Characteristics For A1 And A2 Sensors

	Hydrophone Type		
	Neptune Sonar mod. D/70	***Technology Limited mod. SQ26-01***	***JS-B100-C4DP Acoustic Sensor***
Sensitivity CHA	-138/-158 dBV re 1μPa	-133.5/-153.5 dBV re 1μPa	-141/-161 dBV re 1μPa
Sensitivity CHB	-178 dBV re 1μPa	-173 dBV re 1μPa	-181 dBV re 1μPa
Frequency range (±1.5dB)	From 1 Hz to 50 kHz	From .151 Hz to 28 kHz	From 1 Hz to 50 kHz
Sea noise equalizer	HP filter one pole 3.2 kHz	HP filter one pole 3.2 kHz	HP filter one pole 3.2 kHz
Beam pattern	Omni-directional		
Input equivalent noise (@5kHz G=60dB	27 dB re 1μPa/√Hz	22.5 dB re 1μPa/√Hz	30 dB re 1μPa/√Hz
Working depth	Up to 1500 m	Up to 2000 m	Up to 3600 m
Weight	333 g	317 g	480 g
Size	Φ 34 x 255 mm	Φ 34 x 255 mm	Φ 34 x 255 mm

The signals from the four A2hyd are transferred to the Master Unit through four underwater cables, 10 m long (allowing diverse geometric configurations) that are connected to the cap of an underwater housing containing the Master Unit. Another underwater cable connects the housing to the user interface for transmitting the data processed by the Master Unit. The A2 receives relevant oceanographic parameters (sound velocity, temperature, depth, time) via Ethernet, in order to optimize the algorithms. The acoustic array A2 can also be equipped with positioning sensors (pan, tilt, compass) to allow the measurement of its geo-referenced position on request. Thus, it has a capability of providing directional sound source information giving real-time waveform streaming when used on platforms with medium-high power and communication capabilities. Consistent with the open source philosophy of NeXOS, A2 offers programmable, open source construction and software with RS232 or Ethernet connectivity. The embedded functions developed for these innovative sensors are noise statistics (including EU MSFD indicators), mammal detection (PAMGUARD), and relevant raw data storage in internal memory for recovery beyond internally processed observations. These features make the digital NeXOS hydrophones unique for ocean monitoring applications. NeXOS A1 and A2 allow both industrial and research applications from diverse platforms (e.g., Gliders / AUVs/ larger platforms including deep fixed observing systems) for environmental measurements such as noise from human activities (air guns, shipping noise, etc.), ambient noise and bioacoustics, and seismic events.

2.14. EAF-RECOPESCA sensor system

Highlights:

- **Multifunctional cost efficient sensor system that builds upon the RECOPESCA concept and technologies**
- **Measures Dissolved oxygen (STPO2) and Fluorescence (STPFluo)**
- **Includes sensor for temperature measurement during fishing**
- **Robust enough to be placed on fishing gear, self-powered and autonomous**
- **Modular and scalable.**
- **OGC Sensor Web Enablement (SWE) enabled (data layer)**

The EAF multi-functional sensor system builds upon the RECOPESCA concept and technologies by adding new observations relevant to fisheries management. The challenge in NeXOS was to develop cost efficient sensors that do not require any efforts by the fishermen and thus are self-powered and autonomous. Also, the sensors must be tough enough to be placed on commercial fishing gear. The existing RECOPESCA measures pressure, temperature, salinity and turbidity. It includes a hauler counter, specifically based on the ship weighting scale. A data concentrator is used to store and transmit the data to a shore management centre in near-real-time. For the EAF application, NeXOS created two additional sensors, one for oxygen and the other for fluorescence, which is a proxy for chlorophyll. These have application for both fish population assessments and as Essential Ocean Variables for the operational oceanographic community. To achieve low cost, existing sensor components were evaluated and inexpensive components offering adequate accuracy were selected.

The OEM transducer selected for the oxygen measures (gas or dissolved oxygen in liquids) is the Pico2 by Pyro Science Company. The module utilizes a measuring principle based on red light excitation and lifetime detection in the near infrared using unique luminescent oxygen indicators (REDFLASH technology). The measuring principle is based on the quenching of the REDFLASH indicator luminescence caused by collision between oxygen molecules and the REDFLASH indicators immobilized on the sensor tip of surface. The REDFLASH indicators are excitable with red light (more precisely: orange-red at a wavelength of 610-630 nm) and show an oxygen-dependent luminescence in the near infrared (NIR, 760-790 nm). The measuring principle is based on a sinusoidally modulated red excitation light. This results in a phase-shifted sinusoidally modulated emission in the NIR. The “Piccolo2” (a.k.a by the manufacturer and hereafter Pico2) measures this phase shift. The phase shift is then converted into oxygen units based on the Stern-Vollmer-Theory.

Figure 26. EAF sensor

The OEM transducer selected as fluorometer is made by Turner Designs. It is a single-channel, mini-fluorometer designed for monitoring fluorophores in water, as for example chlorophyll a. It is designed to be integrated into a multi- parameter system from which it receives power and delivers a voltage output proportional to fluorescence to the system data logger. The excitation wavelength is 460 nm and the emission wavelength is 620 – 715 nm. This OEM transducer provides a wide measurement dynamic range of 0.03 to 500 µg. L-1 for Chlorophyll a that can be scaled down by user-selectable gain.

Voltage output can be correlated to concentration values by calibrating with a standard of known concentration.

Both sensors have been integrated in the RECOPESCA system and the housing contains the electronic board and the battery, able to power the sensors for several months (variable, depending on environmental conditions) without batteries replacement. Both sensors systems have been tested and qualified for pressure of 30 bar according to the French standard AFNOR NF X10-812.

3. Data Management and Standards

With increasing data size and the need to operate on remote platforms with multiple sensors, there are tremendous benefits to streamlining data management. This is an end to end issue progressing from data creation by a sensor to the sensor platform interface to the communication of data into the hands of users. Another issue is standardization to facilitate the use of sensors across platforms and the application of multiple sensors in a single platform. The Ocean of Tomorrow (OoT) projects have all investigated and implemented solutions for data and metadata standardisation following international standards produced by the open geospatial consortium (OGC) and/or the World Wide Web Consortium (W3C). The four 2013 Topic 2 projects had requirements that differed slightly because, in some cases, the DoW / technical Annex included development of platforms or information systems in addition to sensors. As such, the OoT projects covered a broad range of data technologies that are reflected in this consolidated recommendation. The overarching requirements from each project are summarised in Table 6.

Table 6. Summary of overarching requirements for data for each OoT project.

OoT project	**Requirements**
COMMON SENSE	Interoperability within devices and hardware aggregator (Smart Sensor Unit (SSU)) by implementing **NMEA 2000** protocol. Interoperability-focused data and information flow from sensor to user based on OGC standards including **SOS**, **SensorML** and **O&M** In the gateway, the NMEA data is automatically processed and transformed into the O&M data format Open source **52°North** implementation of SOS 2.0 was deployed 3 different connection types: A) real-time data stream; B) offline data upload; C) Devices not connected to the SSU and who do not support the NMEA format: a transformation tool was developed in Python User interface to visualize data. This is built using OpenLayers and GeoServer, and also uses the Web Map Service (WMS) standard
NeXOS	Interoperability-focused data and information flow from sensor to user based on OGC standards including SOS, SensorML and O&M Integration of multiple sensors on a platform Remote sensor management **(OGC SPS)** User notification capability for data (**OGC SAS)** Plug'n'play operations with embedded **SensorML** (**OGC PUCK and SEISI**) Protocols to reduce data transmission volume through efficient data compression **(EXI)** SensorML editor for facilitating use of SensorML (**Smle**) User interface to visualize data
SCHeMA	Interoperability-focused data and information flow from sensor to user based on OGC standards including SOS 1.0, SensorML and O&M

	Integration of multiple plug&play sensors on a platform (**OGC SWE**) Sensor command editor and remote sensor management and planning **(SensorML and SPS)** Notification service for system errors and warnings **(SAS)** User interface to visualize data User interface to qualify and flag data (quality check/quality flag)
SenseOCEAN	Exposure of metadata & data via OGC SWE standards (SOS, SensorML, O&M) INSPIRE compliant data and metadata exposure W3C Linked data compliant metadata exposure The capability to uniquely identify a sensor enabling plug and play operation on low bandwidth systems and legacy observation platforms

The OoT projects have made a significant contribution to data standardisation and services across Europe producing "success stories". Highlights are:

- The formation of and contribution to the SWE Marine Profiles community. This community includes European, Australian and USA membership and is forming common data templates and standards for use within the marine community.
- Semantic enrichment of SensorML and O&M making these standards truely machine readable in the marine domain
- The development of common SWE software solutions by 52North
- The creation of tools to facilitate the use of SensorML and SOS such as Smle Published controlled vocabularies.

These success stories exemplify the impacts that the OoT have not only on European programs in ocean observations, but on Europe's role as a global leader in data interoperability and improved data access. The impacts are in reducing the costs and complexity of observing operations because the developments allow ready interfaces between sensors and platforms (reducing labor and improving reliability). They also facilitate access by researchers to both data and information (improving the outcomes of investment in observations). The use of OGC and W3C standards along with the innovations of the OoT projects address critical bottlenecks in the flow of information from sensors to users such as the limitations of communication bandwidths for Iridium satellite services. Ultimately, the ability to have data interoperable enhances the comparison of observations of diverse character and discipline, creating an environment for new research outcomes. These benefits come from widespread adoption of the OoT outcomes along with continued advances in the technology and its adaptation to observation applications. The data recommendations reflect the next steps.

The following text describes the data recommendations for different aspects covered by the OoT projects and is divided into the following sections:

- A summary of standards implemented by the OoT projects with joint recommendations and lessons learned
- A summary of standards that emerged during the OoT project with recommendations
- A closing section on research priorities beyond the end of the OoT projects

3.1. Standards implemented by the Ocean of Tomorrow projects

3.1.1. Standards implemented by OoT projects

The implemented OGC Standards by the OoT projects in the OGC Sensor Web Enablement SWE framework (http://www.opengeospatial.org/ogc/markets-technologies/swe) were:

- Observations & Measurements (O&M) –The general models and XML encodings for observations and measurements.
- PUCK Protocol Standard – Defines a protocol to retrieve a SensorML description, sensor "driver" code, and other information from the device itself, thus enabling automatic sensor installation, configuration and operation.
- Sensor Model Language (SensorML) – Standard models and XML Schema for describing the processes within sensor and observation processing systems.
- Sensor Observation Service (SOS) – Open interface for a web service to obtain observations and sensor and platform descriptions from one or more sensors attached to a platform.
- Sensor Planning Service (SPS) – An open interface for a web service by which a client can 1) determine the feasibility of collecting data from one or more sensors and 2) submit collection requests.
- Sensor Alert Service (SAS) provide notification of events such as measurements, sensor anomalies, observation actions
- Smart Sensor Interface for Sensors and Instruments (SEISI) - SEISI Sensor Systems support both a pull-based data access interface (i.e. based on the SOS standard) as well as a push-mechanism for delivering data into observation databases on near real time.
- Efficient XML Interchange (EXI) – Binary encoding and compression of XML for efficient exchange.

The implemented W3C standards by the OoT projects were:

- Semantic Sensor Network (SSN) – Ontology for describing sensors and their observations.
- Resource Description Framework (RDF) - Standard model for data interchange on the Web.
- SPARQL Protocol and RDF Query Language (SPARQL) - An RDF query language, that is, a semantic query language for databases, able to retrieve and manipulate data stored in RDF format.

The implementation of these standards by OoT projects are described in Table 7.

Table 7. Summary of the standards implemented by the OoT projects

	OGC								W3C		
OoT project	**O&M**	**PUCK**	**SensorML**	**SOS**	**SPS**	**SAS**	**SEISI**	**EXI**	**SSN**	**RDF**	**SPARQL**
COMMON SENSE	✓		✓	✓							
NeXOS	✓	✓	✓	✓	✓	✓	✓	✓			
SCHeMA	✓		✓	✓	✓	✓				✓	
SenseOCEAN	✓		✓	✓					✓	✓	✓

3.1.2. Recommendations on implemented standards

Marine SWE profiles

Several of the OoT projects made significant contributions to the development of marine SWE profiles group (originally initiated by EU projects ODIP and ODIP2) that can harmonize how OGC SWE standards are applied in marine applications. The high level of interest in achieving this is reflected by the number of subscribers to the mailing list coordinating these efforts (ca. 100 users). Evolution of Marine SWE profiles has resulted in a broad set of recommendations for further SWE development:

- Further promote the application of interoperable Sensor Web standards among sensor manufacturers, operators and data consumer (a project such as a dedicated H2020 CSA would be the ideal platform for this work)
- Create a repository for best practices that allows easy discovery and access.
- Evaluate the current state of Marine SWE Profiles through first implementations (e.g. interoperability demonstrations between projects). These results should serve as input for important updates and evolution of profiles
- Decide on a collaborative platform to allow the distributed edition and publication of the Marine SWE Profiles documentation
- Maintain the use of vocabularies and allow users to create their own terms
- Implement integration tests for discoverability, interoperability and presentation of the sensor/observation descriptions originating from different SOS servers implementing the SWE Marine profiles
- Profiles specific to a discipline or application are required at the syntaxical and semantic levels of interoperability. It is recommended that work continues to coordinate and support the creation of a marine community profile for SOS, O&M and SensorML to facilitate better interoperability.
- Produce evaluation tools that will take into consideration the common profiles and the SWE Vocabularies
- Consider the Marine SWE Profiles in editors (generation of standardised content), servers, and client applications (ensuring consistent interpretations)
- Investigate the usage of REST/JSON binding for current standards
- Official extension of the INSPIRE Directive to support the OGC Sensor Observation Service 2.0. The fine details of sensor data harmonisation and interoperability are of a very technical nature, which in the long term facilitates more cost-effective monitoring programmes, data access, and data preservation. The continued implementation of the INSPIRE Directive to support interoperable data discovery, data visualisation, data delivery, and data processing is a very important policy initiative to underpin this. Consideration should be given to the official extension of the INSPIRE Directive to support the OGC Sensor Observation Service 2.0 (SOS) as a data download service option with clear implementation guidelines.

SensorML

The OoT projects have identified specific recommendations for SensorML

- Enable semantic interoperability of SensorML via the adoption of controlled vocabularies to define terms and values in SensorML; Integrate the use of vocabulary servers for selecting definitions and values of SensorML elements
- Continue the work on refining SensorML descriptions as part of the Marine SWE Profiles Working Group
- Improve the currently available tools for editing SensorML by optimizing their usability
- Enhance the support of SensorML templates for sensor type descriptions (i.e. SensorML typeOf element)
- Add more comfortable graphical elements to model part-of relationships
- Investigate interoperable solutions for storing and managing SensorML-based metadata (i.e. going beyond the metadata query functionality of the OGC SOS interface)

Linked data

The recommendations below originate from the experiences of the SenseOCEAN project.

- Standardized ontologies should be reused as much as possible to facilitate inclusion and expansion of the web of data. There are several well-known ontologies, many published by W3C, that provide the artefacts needed to essentially describe sensor data and metadata
- Reuse controlled vocabularies per domain and community
- Publish more working examples, success stories and applications of Linked Data to demonstrate the power of Linked data.
- Create a list of proposed commonly used and approved ontologies and controlled vocabularies to be used by the Linked data community.
- Use standardised vocabularies for standard terms e.g. use NERC Vocabulary Server v.2.0 (NVS2.0) for the marine domain. Unit of measure and observable properties are domains where users tend to get confused or dissatisfied. We chose the P01 and P06 vocabularies of NVS2.0
- To model sensor models and instances in SSN use W3C good relations ontology and schema.org. Schema.org vocabulary is best used though through RDFa, Microdata or JSON-LD formats

Access control of data and cyber security

Significant gaps were identified in both access control when focusing on open data and the cyber security of web services implemented by the OoT projects (using OGC and W3C standards). To further this work there are some overarching recommendations:

- Draft requirements on Sensor Web access control mechanisms
- Enhance the Marine Sensor Web Profiles activities with recommendations on how access control within Sensor Web infrastructures shall be enabled. For this purpose, we recommend investigation of possible approaches to enhance the OGC SOS interface with fine-grained access control mechanisms at multiple points in the data flow.

Persistent Identifiers (PIDs) for instruments, platforms and deployments

The need to assign globally unique and resolvable persistent identifiers to instruments, platforms and deployments was identified and is being pursued with in a new Research Data Alliance working group (https://www.rd-alliance.org/groups/persistent-identification-instruments). Their overarching recommendations are:

- Develop the use of a universal persistent identifier schema for active devices
- Recommend a metadata profile to describe active devices that harmonises existing identification standards and complements existing metadata schemas
- Explore methodology/technology to register and resolve the new PID
- Operationalise the solution, engaging instrument developers and manufacturers in the process

3.2. Emerging standards

Over the course of the OoT projects, new standards and services emerged. These standards are closely related to or built on those implemented within the OoT projects. Consequently, the OoT projects are well placed to identify gaps in knowledge and recommend elements that need pursuing further. As an example, a major development is the introduction of the Internet of Things (IoT). This refers to the use of intelligently connected devices and systems to leverage data gathered by embedded sensors and actuators in machines and other physical objects. Adding intelligence to sensors (such as with the PUCK capability mentioned earlier) is a process that has been started and should continue.

Emerging OGC standards and protocols considered in the context of the OoT projects:

- SWE Common Data Model – Defines low-level data models for exchanging sensor related data between nodes of the OGC Sensor Web Enablement (SWE) framework.
- SWE Service Model -– Defines data types for common use across OGC Sensor Web Enablement (SWE) services including operation request and response types.
- SensorThings API - OGC standard specification for providing an open and unified way to interconnect IoT devices, data, and applications over the Web.

Other emerging standards and protocols considered in the context of the OoT projects:

- MQ Telemetry Transport (MQTT) - It is a publish/subscribe, extremely simple and lightweight messaging protocol, designed for constrained devices and low-bandwidth, high-latency or unreliable networks.

3.2.1. Recommendations on Applicable standards that emerged during the OoT projects

Linking to IoT technologies

There are currently several activities in the Internet of Things community which may be considered as complementary enhancements of the established Sensor Web architectures. The OoT projects recommend that these are pursued in addition to the OGC and linked data technologies already investigated. Specifically:

- Evaluate the applicability of IoT protocols (e.g. MQTT, AMQP, COAP, LoRaWAN, etc.) to marine applications: Although first evaluations are performed as part of ongoing projects (e.g. ODIP II), the complexity of this topic requires dedicated work items/work packages as part of new research projects.
- Evaluate the OGC SensorThingsAPI (http://ogc-iot.github.io/ogc-iot-api/): This work should be performed on a short-term basis. A recommendation is to enhance existing Sensor Web implementations (e.g. those using OGC Sensor Observation Service) with additional SensorThings API support as well as support of regular REST- and JSON-bindings of the OGC Sensor Observation Service and ISO/OGC Observations and Measurements standards. The availability of both types of implementation would be the basis for a scientifically sound comparison and implementation.
- Evaluate the Web of Things for IoT (https://www.w3.org/WoT/)
- Enhance the guidance on Marine Sensor Web Profiles with recommendations on Internet of Things technology: The results of the previously explained evaluation activities should be reflected as dedicated chapters of the Marine Sensor Web Profiles Best Practice documentation.

Sensor plug and play

The NeXOS project made progress with Plug and play using PUCK based standards while SenseOCEAN used Globally Unique Identifiers (GUID) to implement plug and play. Significant work is needed to align these efforts with the IoT and enable web resolvable unique identification of sensors. This work would be consistent with the PID directions mentioned above,

- Investigate mechanisms for tasking sensors from the sensor web based on the transportation of a SensorML file from the user to the sensor in order to modify sensor parameters.
- Investigate how to track and implement changes in sensor characteristics (settings for gain or timing) on the SensorML as a function of time. If the instrument configuration is stored inside a sensorML file, when this sensorML file changes due to a change on the instrument configuration, it has to be reflected on the data. Modifications of the instrument configuration have to be available as metadata with the instrument data. Define a process and sustainable repository to maintain history of SensorML files.

Push based communication flows

Push technology, or server push, is a style of Internet-based communication where the request for a given transaction is initiated by the publisher or central server as opposed to pull/get, where the request for the transmission of information is initiated by the receiver or client such as the SOS protocol used in the IoT projects.

- Investigate a profile for the OGC Publish/Subscribe standard that is tailored to the needs of marine Sensor Web applications. The results of this work should be published as a new topic within the Marine Sensor Web Profiles best practice documentation. Due to the complexity of this task, this activity can be initiated as part of current projects (e.g. BRIDGES). However, this question should be a significant topic in future research projects.
- Address the expansion and further implementation of the SEISI developed in NeXOS.
- Evaluate the use of push based communication patterns through bandwidth constrained links
- Evaluate the applicability of event stream processing tools to marine application scenarios and develop exemplary implementations for selected used cases.
- Develop Publish/Subscribe extensions for existing OGC SOS servers.

Web processing services

The IoT projects have produced OGC endpoints. Communities such as EMODnet need to be able to aggregate results of these services in order to produce data products. The SWE service model, common data model provides a framework for such aggregation.

- Investigate the coupling of marine Sensor Web services (e.g. SOS servers complying to the Marine SWE Profiles recommendations) to OGC Web Processing Service instance. This should be realised as a set of demonstrators showing the dynamic integration of different observation data sources and process types.

Discovery of Sensor Web Resources

A natural extension to the exposure of data and metadata to web via OGC standards is to enable cross-disciplinary discovery via search engines. Long terms, with standardised data, would enable the generic aggregation and production of data products. There is significant development needed to move the work from OoT projects into broader use by the marine domain:

- Demonstrate the harvesting of marine Sensor Web metadata by traditional (google) and specialized search engines by building dedicated tools that make use of the Marine Sensor Web profiles as metadata foundation.
- Explore the use of Linked Data to discover Sensor Web resources (e.g. Linked Data layer on top of Sensor Web infrastructures)
- Integrate discovery functionality into Sensor Web viewers to enable a dynamic binding of services and client applications.
- Link Sensor Web metadata harvesters to marine data infrastructures and portals.
- Investigate light-weight discovery tools for the Sensor Web that offer a low complexity in their user interface (comparable to a Google search for the Sensor Web).

3.3. Priorities for future research identified by the OoT projects

The OoT projects have made a significant contribution to the standardisation of metadata and data on the web and there are key activities that we believe should be sustained. The Marine SWE profiles group should continue to support formal and broader adoption of the progress made in the Marine domain to reduce the likelihood of duplication of these efforts (a project such as a dedicated H2020 CSA would be the ideal platform for this work). Formulation and publication of best practice documents through activities such as ODIP or AtlantOS are a mechanism to achieve this but not a long-term solution.

The standards developed need formalisation and maintenance to be applied on their constituent elements: maintenance and enhancement of controlled vocabularies as a base for continued evolution; and creation and maintenance of an easily searchable ontology-based repository of marine data best practices for broader access and increased adoption of these practices by the marine community. This work has begun and was announced on at the Plenary meeting of the Research Data Alliance (https://www.rd-alliance.org) last week and the objective is a semantic look up service of ontologies on diverse domains (https://bsceudatwp8.bsc.es/).

To date there has been little uptake of OGC and W3C standards by sensor manufacturers for several reasons. The data and protocol standards have been in constant flux for a decade, development of standards is not widely known in the community that purchase equipment. Hence, standardised data has not been a requirement in calls for tenders, and common tools for standard format (e.g. SensorML) editors have been missing. Once best practices are published, common tools exist and standards produce success stories, sensor manufacturers can be invited to provide information about the sensor models they produce/sell, that will be identified by unique identifiers and resolved in standard metadata formats.

There are also several gaps clearly identified by the OoT projects that need research and development activity before best practice can be defined: developing persistent identifiers for sensors/platforms/deployments to enable their unambiguous and web resolvable identification with connections to digital object identifiers DOIs, that are being used to identify datasets and publications; working towards common data and service levels policy (service level agreement, users rights, data citation, data use, security etc.); and improving data availability into major EU infrastructures and repositories (e.g. EMODnet, CMEMS, SDN).

The emerging standards such as IoT are at a level of maturity similar to that of the OGC and W3C standards prior to their enhancement by the OoT projects. Further research and development is needed to assess these standards against the requirements within the marine domain and this should be the priority for these standards. This would determine their applicability in the marine domain and the enhancements that would be required to enable their broader adoption.

The OoT projects have rightly focused on the marine domain and their recent developments need sharing to expand the data discovery to broader communities such as the atmospheric community or the public. One approach may be to invite search engine experts like google to align marine standard developments with work planned in this domain, this would require new major research projects

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4. Contributions to MSFD and SDGs

The four projects address a number of variables relevant to several descriptors of the Marine Strategy Framework Directive and indicators of the United Nations Sustainable Development Goals (SDG 14). SDG 14 refers to the conservation and sustainable use of the oceans, seas and marine resources. The Goal defines a number of targets and indicators. These indicators link targets to quantitative values, establishing clear means of progress evaluation. The contributions of the four projects are summarized in the following tables.

Projects vs SDG14 Indicators	COMMON SENSE	NeXOS	SCHeMA	SenseOCEAN
14.a.1 Budget allocation to research in the field of marine technology as a percentage of total budget for research	4,7M€ budget[11] (incl. 3,4 M€ EC contr.)	8,1M€ budget (incl. 5,9M€ EC contr.)	6,7M€ budget (incl 5,2 M€ contr.)	8M€ budget (incl 5,9M€ EC contr.)
14.2.1* Percentage of coastal and marine development with formulated or implemented integrated coastal management/maritime spatial planning plans (…), based on an ecosystem approach (…)	Water quality (incl. MSFD GES) Environmental impact monitoring[12]			
14.3.1 Average marine acidity (pH) measured at agreed suite of representative sampling stations		Carbon Cycle	Carbon Cycle	Carbon cycle
14.5.1 Coverage of protected areas in relation to marine areas	Cost effective sensors[13] and platforms			

Projects vs MSFD GES Descriptors	COMMON SENSE	NeXOS	SCHeMA	SenseOCEAN
Descriptor 1 Biological diversity is maintained. The quality and occurrence of habitats and the distribution and abundance (…)		Bioacoustics Phytoplankton Fisheries (EAF)	Phytoplankton	Phytoplankton
Descriptor 3 Populations of all commercially exploited fish and shellfish are within safe biological limits, exhibiting a (…)		Fisheries (EAF)		
Descriptor 4 All elements of the marine food webs, to the extent that they are known, occur at normal abundance and diversity (…)	Nutrients	Phytoplankton Carbon cycle	Phytoplankton Nutrients Carbon cycle	Phytoplankton Nutrients Carbon cycle
Descriptor 5 Human-induced eutrophication is minimised, especially adverse effects thereof, such as losses in biodiversity, (…)		CDOM Oxygen Phytoplankton	Oxygen Nutrients Phytoplankton	Oxygen Nutrients Phytoplankton CDOM
Descriptor 7 Permanent alteration of hydrographical conditions does not adversely affect marine ecosystems.	Pressure, Temperature Nutrients	Pressure, temperature Phytoplankton Oxygen	Temperature Turbidity Nutrients Phytoplankton	Temperature Nutrients Phytoplankton
Descriptor 8 Concentrations of contaminants are at levels not giving rise to pollution effects.	Heavy metals/trace metals	Dissolved hydrocarbons	Heavy metals/trace metals	Hydrocarbons
Descriptor 11 Introduction of energy, including underwater noise, is at levels that do not adversely affect the marine environment.	Underwater noise	Underwater noise Bioacoustics		

[11] European Commission and Member States, percentage of total contribution not provided.
[12] Spatial planning involves observing. Projects contribute to the availability of technological solutions for the monitoring of areas before activities take place, and to control the activity once it is in place.
[13] The provision of cost-effective sensors is expected to contribute increase coverage and resolution through the scaling up of observing system presence in the ocean, including protected areas.