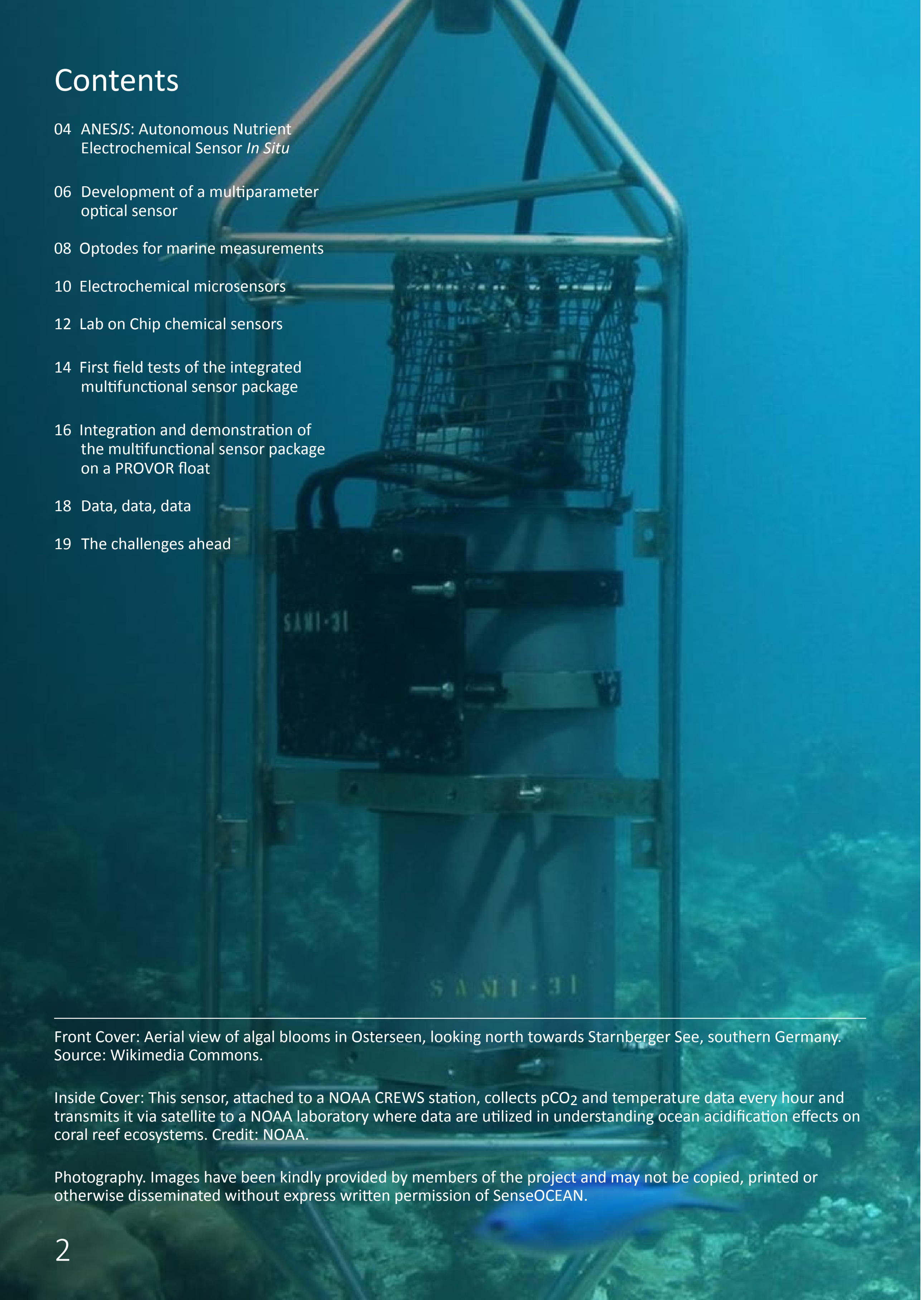
Sense OCEAN

Marine Sensors for the 21st Century

2017



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Front Cover: Aerial view of algal blooms in Osterseen, looking north towards Starnberger See, southern Germany. Source: Wikimedia Commons.

Inside Cover: This sensor, attached to a NOAA CREWS station, collects pCO_2 and temperature data every hour and transmits it via satellite to a NOAA laboratory where data are utilized in understanding ocean acidification effects on coral reef ecosystems. Credit: NOAA.

The SenseOCEAN Project

The main aim of the SenseOCEAN project was to develop new chemical sensors for in situ measurements of the marine environment and to combine these to produce an integrated multifunctional sensor package.

The ocean covers 70% of the earth's surface and plays a key role in the earth's climate as well as providing food and minerals, recreational opportunities and vital transportation routes. Pressures on the ocean related to climate change and pollution from an increasing coastal population are threatening ocean health. The oceans are also valuable as a cultural heritage, for many house highly diverse life forms (many are not yet known) and are simply beautiful. Warming, acidification, deoxygenation, overexploitation and pollution (agriculture, erosion, mining etc.) are all threatening ocean health.

For the sustainable management of our ocean, detailed and continuous monitoring of ocean health is required. Traditionally water samples from the ocean are collected and analysed in land-based laboratories. Such a strategy provides only snapshots and is very expensive; unlike personal activity trackers such as 'fitbit' which track our health on a minute-by-minute basis, we have no way of taking the pulse of the ocean. Hence, continuous monitoring is preferable, ideally with direct data transfer via cable or satellite.

Recent developments

Exciting recent developments involve the use of in situ chemical sensors in the oceans. They are deployed on fixed moorings, water column profilers (autonomous floaters) or on frames in the deep sea. The use of sensors on gliders allows us to cover large areas of the ocean. With autonomous sensor platforms we can perform long-term and frequent analyses. Such long-term monitoring of several parameters in parallel allows us to correlate different phenomena and provide insight into controlling mechanisms. For example, variations in water chemistry (nutrients, pH, O_2) can, when linked to either tides, illumination or pollution, point to natural phenomena or destructive human action. The limited availability and high costs of sensors and sensing platforms has so far prevented their widespread use.

The partners of SenseOCEAN have developed low cost novel chemical sensors that can be mass produced and will be used in extensive monitoring of our oceans. In demonstration missions we have mounted these sensors on platforms for combined water chemistry studies. The operation of the developed sensors has been harmonized to function with common interfaces, plugs and connectors. Data formats were standardized. All the developed sensors can be used on various frames and gliders, in combination with commercially available sensors. We have built a multifunctional control unit to which a specific suite of sensors can be connected, the selection depending on the specific measurements required.

The SenseOCEAN sensors have been miniaturized, and therefore they can be mounted easily on underwater vehicles, moorings and floats. Our sensors use little power and need few or no reagents. Special protection systems are used to reduce biofouling on the sensors, to warrant stable functioning. Therefore, they can be deployed over long periods of time. Observations of the many different chemical and physical variables in the ocean will provide a more complete picture than we currently have. Combining many sensors will lead to new insights into how the oceans and our world function.

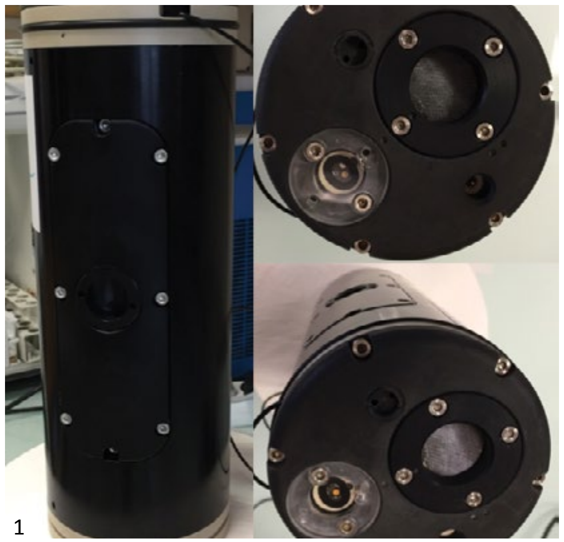
This brochure highlights some of the exciting progress that has been made over the last four years of the SenseOCEAN project.

ANES*IS*: Autonomous Nutrient Electrochemical Sensor *In Situ*

- **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. Infact the nutrient must first be converted into a complex that will react with an electrode. The SenseOCEAN silicate and phosphate electrochemical sensors use 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 right, 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.

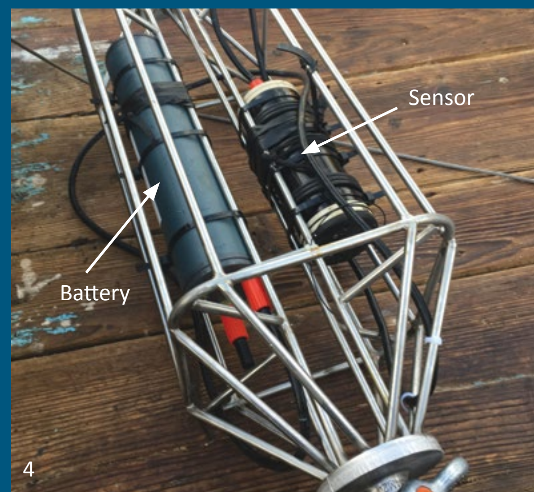
The sensors are 25 cm long (without connector) and 9 cm diameter, weighing 2.2 kg in air.

The silicate sensor was deployed for two weeks on a mooring at 55 metres depth in the upwelling zone off Chile at Talcaruca Point in April 2017.

The silicate concentration was measured every hour, ~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 (an oceanographic instrument platform used for making subsurface measurements in the ocean, the most well known are probably the Argo floats) 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 (see later article in this brochure).

The deployment was very successful. Around 40 measurements were obtained and sent back to the lab by satellite where they will be analysed.



As silicate and phosphate are non-electroactive species, their conversion to electroactive molybdate complexes in acidic medium is required[1-3].

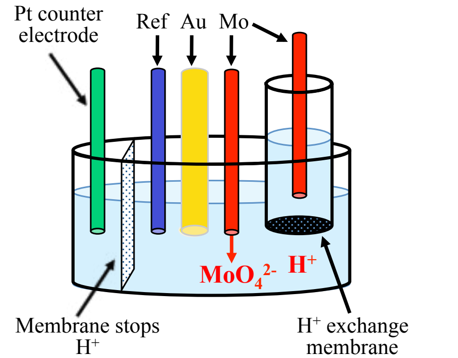
$Si(OH)_4 + 12\ MoO_4^{2-} + 24\ H^+ \rightarrow H_4Si(Mo_{12}O_{40}) + 12\ H_2O$

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

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 required acidic pH, the reduction of H^+ on the counter-electrode is prevented by isolating the counter-electrode behind a membrane limiting proton diffusion.



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

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

1 Sensor shown in the housing that is required to protect it from pressure when deployed in the ocean.

2 Sensor deployment on a profiling float in the Mediterranean Sea.

3 Sensor deployed.

4 Sensor and power supply mounted on a frame ready for deployment on a mooring off the coast of Chile.

Development of a multiparameter optical sensor

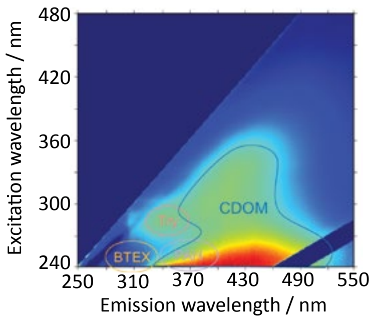
- One design, several variants – Measures CDOM, Chlorophyll a, PAHs
- Pollution detection for oil, sewage, agricultural run-off – Detects onset of harmful algal blooms

The measurement of fluorescence is a very sensitive technique for monitoring various compounds in the environment. This is particularly useful for the measurement of Coloured Dissolved Organic Matter (CDOM), chlorophyll and polycyclic aromatic hydrocarbons (PAHs). CDOM originates from riverine or terrestrial sources (e.g. agriculture, sewage discharge, drainage). It can significantly affect biological activity in natural waters because it reduces the available light. Photosynthesis, the process required for the growth of phytoplankton (microalgae), which form the basis of oceanic food chains, depends on sunlight. CDOM also absorbs UVA/B radiation, which can be harmful to organisms. Chlorophyll is present is plant matter, such as phytoplankton. Measurements of chlorophyll in aquatic systems can be used to estimate the amount of phytoplankton. PAHs are environmental pollutants mainly generated during the burning and processing of organic materials such as coal, oil and wood.

The multi-parameter optical sensor

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 characteristics of different compounds

UV fluorescence typically targets compounds associated with CDOM. Visible fluorescence is typically used for dye tracing and chlorophyll detection.

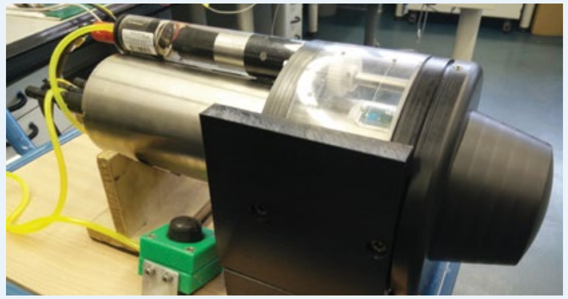
To date, fluorometers have combined a single excitation and emission wavelength to target specific compound groups. However, as can be seen in the figure below, there can be significant overlap in the spectral characteristics of different fluorescence compounds, making it difficult to measure just one type of compound. Further, environmental interferences, e.g. turbidity or 'colour' in the sample, can reduce the fluorescence signal.

To overcome the problems outlined above, a multi-parameter sensor has been developed as part of the SenseOCEAN project. 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. Three variants of the UV sensor have been developed: the 'BTEX' sensor targets 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.

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 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 the algal composition in the sample, e.g. to detect the onset of an algal bloom.

Demonstration: long-term Arctic deployment of FRRf



Left: The instrument was deployed at 15m depth in an Arctic fjord to establish a long-term time series of in situ measurements of algal photophysiology. Right: Autonomous acquisitions were performed every 30 minutes, with the possibility to control the system remotely through the internet to modify parameters or download data.

Fast repetition rate fluorometry is an optical technique that can be used to study the health and physiological status of phytoplankton communities. Through the application of microsecond flashes of light, the reaction centres of the photosystem can be progressively closed and their subsequent relaxation studied. Through a modelled understanding of the photo-physiology of algal cells, it is possible to non-destructively estimate their photosynthetic productivity, activity and community structure.

For a SenseOCEAN demonstration, an FRRf system was adapted with a rotating front-cap, which could be used to repeatedly collect and hold samples of water in a dark environment during measurements. This system was deployed on a cabled observatory at 15m depth in an Arctic fjord in Svalbard to collect a long-term time-series from Aug 2015 – May 2016.

The remote and harsh conditions of the site generated several challenges to maintaining continuous measurements (loss of network, power etc.). However, several thousand acquisitions were made and successfully downloaded over the internet during the periods when the remote node was functional.

The resulting data showed a variable fluorescence response from the phytoplankton, which clearly indicates seasonal variations in the photo-productivity of algal cells. Summer values were in the expected range, the values then dropped as the fjord entered the polar winter and increased during the following spring.

Without in situ measurements, such variations are very difficult to detect, Samples collected e.g. once a month do not provide sufficient evidence and in hostile regions like the Arctic, even monthly sample collection is not always possible due to weather conditions. This demonstration highlights the value of in situ sensor technology.

Optodes for marine measurements

- A palette of novel optical sensing materials
- Two types of read-out devices
- 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 is still hindered by a lack of high-performance sensing materials and the necessity to have dedicated devices for signal read-out.

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 which includes a logger and a battery. It has a very low power consumption. 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.

Fully assembled optodes with copper biofouling protection guards.

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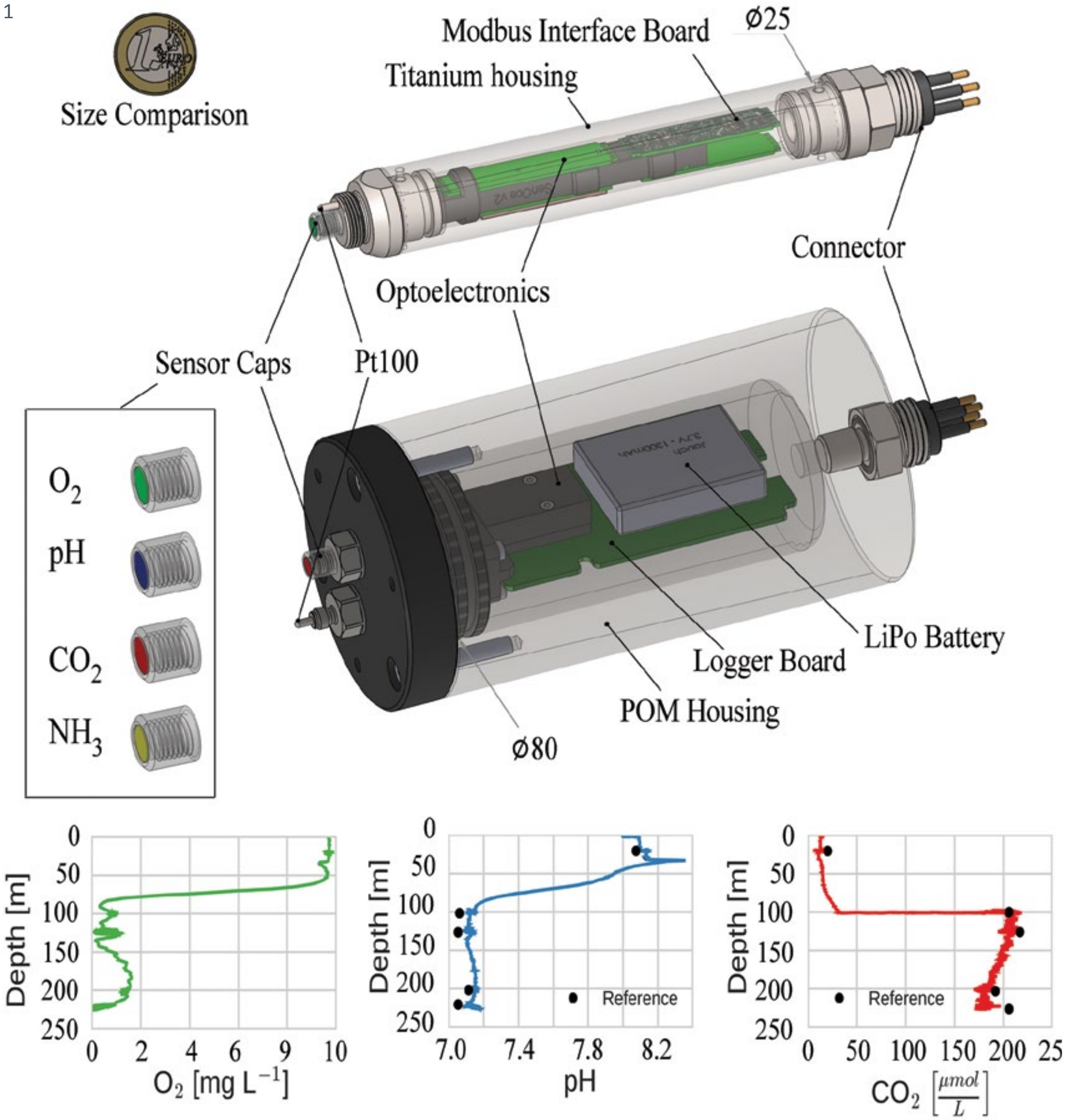

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1 Deep water optode with Modbus interface (top), shallow water stand-alone optode (middle), exchangeable sensor caps for different analytes (left) and experimental results for profiles measured at the Gotland basin in the Baltic Sea (bottom).

2 Stand-alone optode with internal battery and data logger, suitable for shallow water operations (<200m).

Electrochemical microsensors

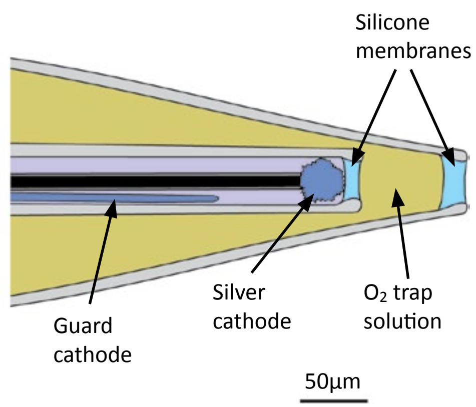
– Accurate and rapid measurements – Non-destructive – Can be used for sediment-water interface measurements – Wide range of applications - waste water plants through to open ocean

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 (which can be present in high concentrations) will also give a signal.



Structure of the CO_2 microsensor

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.

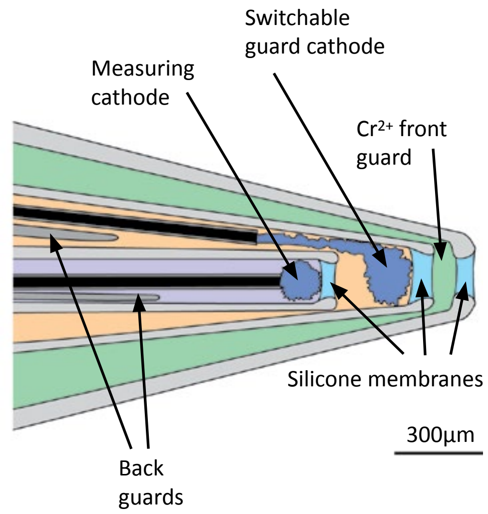
The N_2O microsensor

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 analyzing 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)

At very low concentrations, it can be difficult to distinguish the N_2O signal from the background. 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 with the normal N_2O sensor there is also an oxygen scavenging compartment based on O_2 reduction by chromium (II) ions or ascorbate.

See the later article in this brochure about the first field tests for some interesting results from this sensor.



Structure of the STOX type N_2O microsensor

Field DataLogger Mini from Unisense

Field DataLogger Mini with a microsensor attached. 2 or 4 channel versions are available.

As part of the SenseOCEAN project, one of our partners, Unisense has developed and brought a product to market. The Field DataLogger Mini enables the use of all Unisense sensors in situ and it can be integrated with many external platforms.

Sensors are easily connected and it is easy to set up, data is stored for export after the deployment. A customised version of the DataLogger has already been deployed in the Mariana Trench.

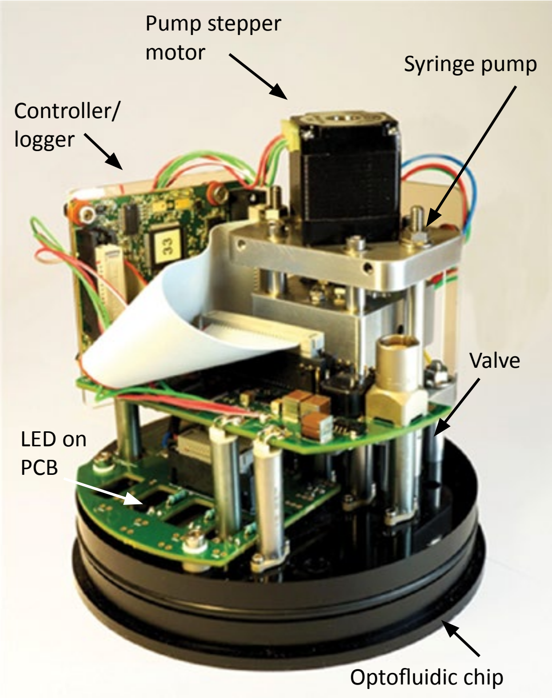
Lab on chip chemical sensors

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

Imagine shrinking the tools and skills of a routine chemical analysis laboratory into a small plastic chip. This is exactly what the "Lab on Chip" sensor does. It works by mixing a small sample of water (for example seawater) with a chemical reagent to create a chemical reaction. This reaction causes the water sample to change colour, for example from clear to blue. The degree of colour change is measured by the sensor and processed to determine the amount of a particular chemical species in the water sample. Different compounds produce different colours; for example the amount of nitrate (N) in water can be measured from the pink colour of the solution. The pH (acid or alkaline) of the sample can also be read from a change in the colour of the solution. The lab on chip sensor automatically takes a water sample, mixes the correct chemicals and measures the colour, all in a few minutes. These sensors are small ~1 litre in volume, very accurate, and can measure tiny amounts of many different chemicals. They take the complicated methods usually found in state of the art laboratories and shrink these down into a single device that works remotely in the field for long periods of time. Any drift in the senor performance is compensated for by occasionally measuring clean reference solutions (without the chemical present) or solutions of know concentration.

A Family of Sensors

We have developed a family of lab on chip sensors that measure important chemicals in natural waters (e.g. oceans, rivers and lakes) using different reagents. These chemicals include nutrients that are used by plants when they grow such as nitrate, ammonia, phosphate and silicate. The sensors also measure the effect of carbon dioxide (a greenhouse gas produced by burning fuels) as it dissolves in water by measuring the pH (how acid the water is), Total Alkalinity (TA: the ability of the water to absorb acid) and Dissolved Inorganic Carbon (DIC: the total amount of carbon dioxide and products of dissolved carbon dioxide). We also measure trace metals such as iron that are essential for plant growth. The family can be expanded to explore other elements or even to measure bacteria or plankton in the future.



Common lab on chip sensor design

Sensors have been attached to a robotic submarine like the one shown here and used in the Celtic Sea and at an offshore carbon dioxide storage site.
Credit: National Oceanography Centre

A unique feature of the sensors is that they all use similar components with a common overall design. This common design consists of a "chip": a plastic disc containing lots of small channels about the size of a human hair. Here the seawater is mixed with different reagents to produce the colour change that is then measured. They also have a custom pump; small valves to direct fluid around the chip; and electronics that control the pumps and valves and measure the colour changes. These are all housed in a low-cost plastic casing which is filled with oil. This serves to protect the electronics from seawater and ensures that the inside and outside pressure is the same - this can be 1000 times higher than atmospheric pressure in the deep sea. The chip takes in a sample of seawater through a filter, and the various chemical reagents are stored in plastic bags. The chip is made using microfabrication (the accurate manufacture of small features) to create a network of very narrow channels in which the fluid is processed and measured. Because these are so small the sensor only needs tiny volumes of water to operate. The volume of waste is also small and captured in a small bag for safe disposal rather than being ejected into the environment.

Each sensor (for different chemicals) in the family has a different level of technical maturity. Some (such as ammonia and DIC) are at the prototype stage and work well in the laboratory, whereas others (nitrate, phosphate, pH) have been successfully tested many times in the sea. In one example, a sensor has been deployed continuously in Christchurch Harbour to monitor how much, when and why nitrate and phosphate is brought into this enclosed Estuary from the land. It also measures when and where these chemicals are stored or flushed into the sea. Data from the sensors has shown that storms are important in these processes. The nitrate sensor has also been attached to a robotic submarine that glides (like an airplane glider but in water) in the Celtic sea (southwest of the UK) to measure changes in nutrients. Recently sensors that measure nitrate, phosphate and pH were deployed on the NOC submarine "*Boaty McBoatface*" (#boatymcboatface) and also on a nearby "lander" - a frame attached to the seabed, to test for a possible leak of carbon dioxide from an offshore store. This shows how the sensors could be used to monitor off-shore carbon dioxide stores e.g. CO_2 generated by power stations, or steel and cement manufacture. This gas can be trapped for long periods of time in exhausted oil reserves or in subsurface water bodies (Aquifers).

The sensors have world beating performance, and deliver new capabilities to scientists, companies and government bodies who need to measure chemicals in water. To make the best use of these new technologies they need to be manufactured in volume and sold to companies or government agencies that are responsible for measuring and monitoring chemicals in the environment.

First field tests of the integrated multifunctional sensor package

One of the key aims of SenseOCEAN was to integrate the developed sensors into a multi functional package to measure a broad set of biogeochemical parameters. To achieve this a plug-and-play interface module was designed, to which multiple sensors can be connected. The module, which provides the interface is a Modbus-EMAP iridium board designed by SenseOCEAN partners CTG and nke. Its role is to power each sensor, enable automatic data logging, and facilitate data transfer to the end user via satellite (iridium network).

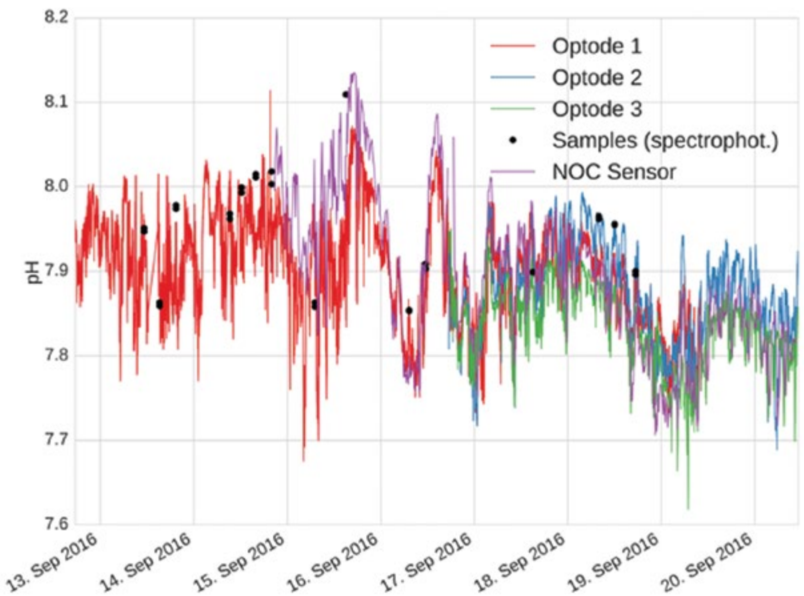
Single sensors were integrated into one multi sensor unit, controlled by the Modbus-EMAP interface, for the first time in Kiel (Germany) in the autumn of 2016. Two multi sensor units were equipped with optode sensors (O_2, CO_2, NH_3, Na^+), lab on chip (LOC) sensors (NO_3^-, NO_2^-, PO_4^{3-}, Fe^{2+}, pH) and electrochemical sensors (silicate, N_2O).

One multi sensor unit was submerged for a week at ~2m depth in Kiel Fjord. The other was secured to a CTD Rosette in order to make measurements throughout the water column for five days in the Baltic Sea. To allow comparisons of the results obtained from the sensors with measurements made in the laboratory using state of the art techniques, samples were also collected at each location for later analysis back on shore.

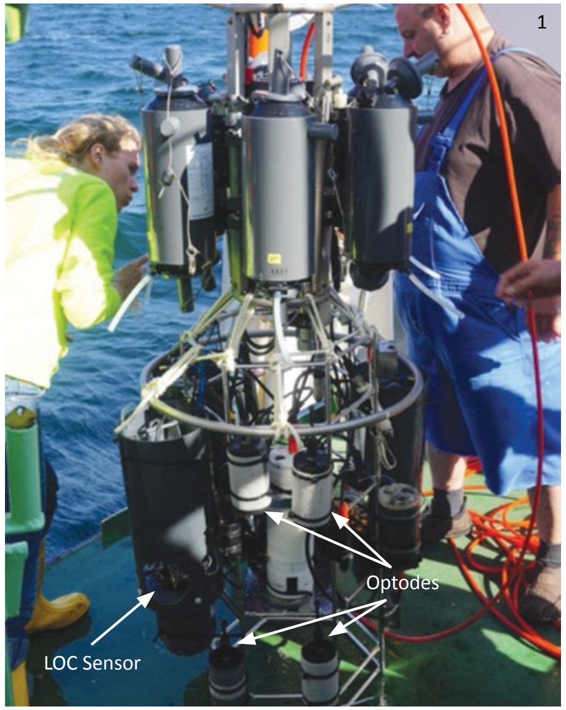
Up to seven sensors were interfaced with the Modbus module and successfully operated in Kiel Fjord and down to 25m depth in the Baltic Sea. In Kiel Fjord, the LOC sensors and optodes operated continuously for up to seven days while regularly transmitting data to the Modbus module. The Kiel tests were also an opportunity to compare and contrast data from different instruments measuring the same parameter. In Kiel Fjord, the LOC and optode pH data showed consistent trends and were in good agreement with the laboratory measurements.

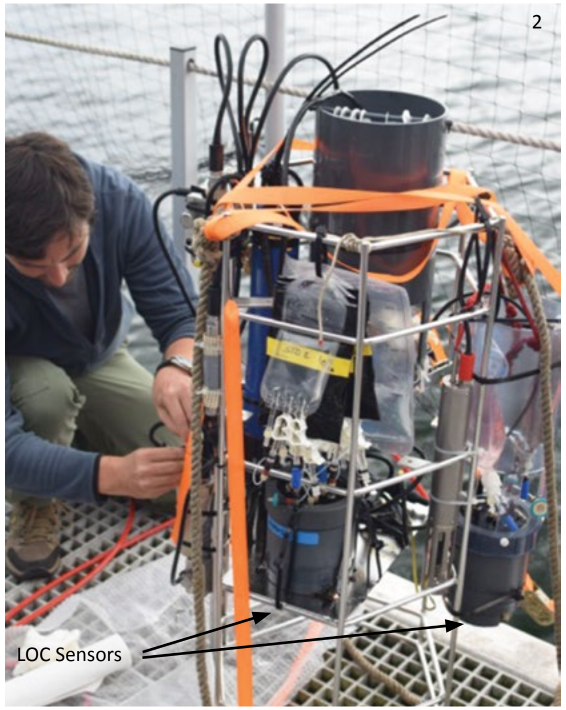
Some sensors were also tested as stand alone devices. In Kiel Fjord, the Aarhus University team deployed an electrochemical nitrous oxide (N_2O) sensor equipped with a new in situ amplifier and data logger developed by Unisense. N_2O is a potent greenhouse gas. It is released in the atmosphere as a result of human activities and also produced in oxygen deficient zones of the ocean. The continuous, 2.5 day N_2O electrochemical sensor data from Kiel Fjord ranged from 75 to 150 nM with a peak near midday on 17th September. Higher frequency fluctuations on the order of 25 nM are also evident throughout the record. Normal concentrations of N_2O in surface waters are ~10 nM, hence these results indicate there are additional processes contributing to the N_2O concentration and that these processes could be highly variable throughout the day.

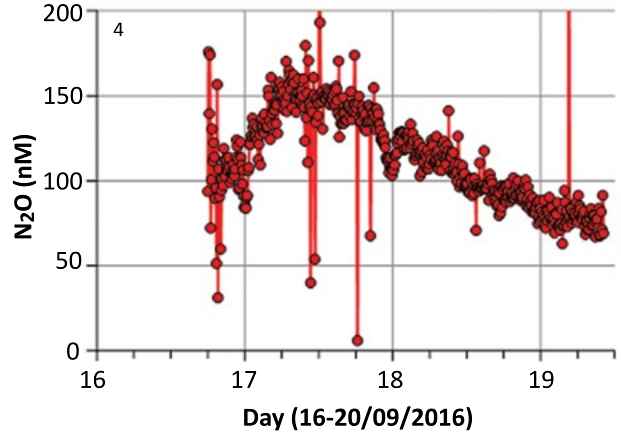
The Kiel tests were a resounding success for SenseOCEAN. Once further testing and rigorous validation has been carried out, a truly integrated and easy to use multi parameter sensor system will be available to scientists, industry and regulatory bodies throughout the world.



Data from the deployment in Kiel Fjord. Optodes (TU Graz) and LOC pH (NOC) sensor data are overlaid with laboratory measurements of samples. Data courtesy of Tianya Yin (NOC), Christoph Staudinger and Sergey Borisov (TU Graz).







1 SenseOCEAN biogeochemical multi sensor unit prior to deployment at an offshore station in the Baltic Sea.

2 Deployment from a floating pontoon in Kiel Fjord.

3 Electrochemical STOX-N_2O sensor ready for deployment in Kiel Fjord.

4 The resulting data courtesy of Emilio Garcia-Robledo and Niels Peter Revsbech (Aarhus University).

Integration and demonstration of the multifunctional sensor package on a PROVOR float

Profiling floats are oceanographic instruments that spend most of their time drifting below the ocean surface, returning to the surface periodically to transmit data that has been collected. The most well-known are the ARGO floats deployed to make temperature and salinity measurements throughout the oceans; there are currently ~3000 deployed. These profiling floats provide an ideal platform to increase our understanding of the oceans by using them to deploy in situ sensors such as those developed in the SenseOCEAN project. Hence, the nke PROVOR profiling float was chosen as one of the platforms on which to demonstrate the integrated sensor package. Trials of the newly developed SenseOCEAN integrated sensor package on the PROVOR float were conducted in Spring 2017 in the Mediterranean Sea.

One PROVOR CTS5 profiling float including a standard CTD probe, was equipped with a lab on chip sensor, an electrochemical sensor and two optode sensors for monitoring nitrate, silicate, O_2 and pH in the seawater column.

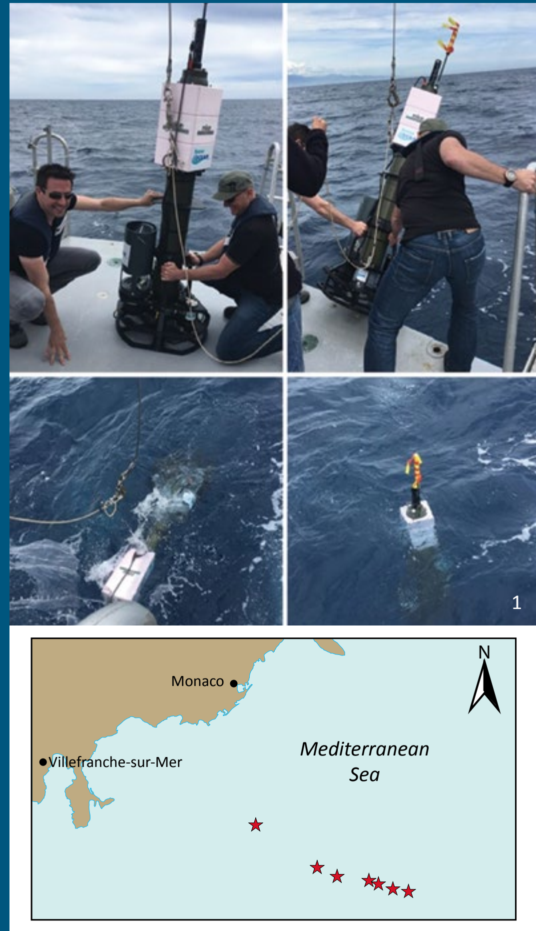
The O_2 optode operated as expected throughout the deployment. Preliminary data are shown in the figure to the right.

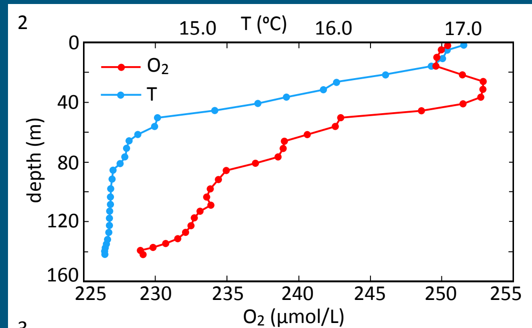
The nitrate concentrations in the Mediterranean Sea are typically reported as having a maximum value of ~10 µM at depth and near-zero values towards the surface. The nitrate sensor returned processed values which are consistent with these general expectations. Although post processing and a thorough quality analysis of the data is still to be done, the overall consistency of the sensor data and agreement with expected values suggests that the sensor performed well during the deployment.

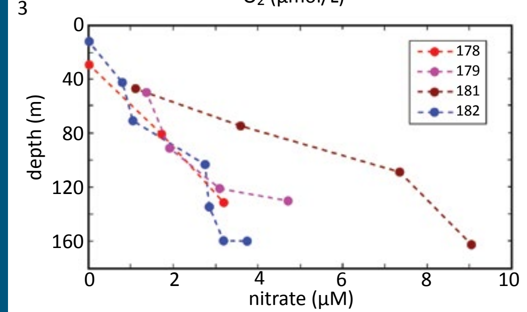
The silicate sensor made more than 40 measurements and successfully transmitted the data. The processed values returned by the sensor were typical of those usually found in Spring in the Mediterranean Sea.

Overall the deployment was considered successful with all sensors making measurements and recording data, and the data being transmitted, without any corruption, via satellite back to land.

Preparation of the profiling float on the CNRS boat.







Preparations for the demonstration

Prior to deployment, the complete chain, with sensors (O_2, pH, NO_3 and SiO_2) Modbus module and Iridium communication was validated in the laboratory. This enabled checking and optimization of sensor measurement rates, float configuration and navigation settings.

Nke designed a custom bracket system (based on other SenseOCEAN work done by CTG) to attach each sensor to the float. The sensor suite is placed at the bottom of the float to improve its stability and buoyancy in seawater. Each sensor is positioned to ensure minimal disturbance during the descent/ascent phase of the float and to ensure that all sensors measure the same water layer. NO_3, pH and O_2 sensors were connected to the platform via the Modbus module.

The buoyancy and stability characteristics of the float were checked and adjusted during a test deployment in a 50m deep freshwater quarry prior to the main deployment. This trial also allowed a final check that data file acquisition (via Modbus) and data transmission (via EMAP to secured RUDICS server) were operating correctly.

For the main trial in the Mediterranean Sea, the float was programmed to conduct one profile each day to a depth of 600 metres for 4 days. To ensure the data files were not too large for transmission, the frequency of the sensor measurements were set as follows: O_2 and pH data, once per minute and NO_3, once every ten minutes during the ascent phase of the profile. The silicate sensor measured at a lower frequency of once per hour when the float was at parking depth. This is necessary to allow sufficient time for the complexation reaction to take place (see article on ANES*IS* p.4).

1 Deployment of the profiling float (PROVOR CTS5) in the Northwestern Mediterranean and map showing location of profiles.

2 Preliminary data obtained with the O_2 optode implemented on the float during May 2017. Data are consistent with expected values. The maximum observed at ~30m is most likely due to photosynthesis.

3 Uncorrected preliminary nitrate concentrations measured on the float at various locations offshore from Villefranche-sur-Mer. The legend refers to profile numbers that were performed over three days in May 2017. Values are within the expected range.

Data, data, data....

The production of low cost, low energy miniaturised sensors will increase the number of sensors deployed and the amount of data collected by sensors. Once this happens, how do we ensure that people can access and use this data?

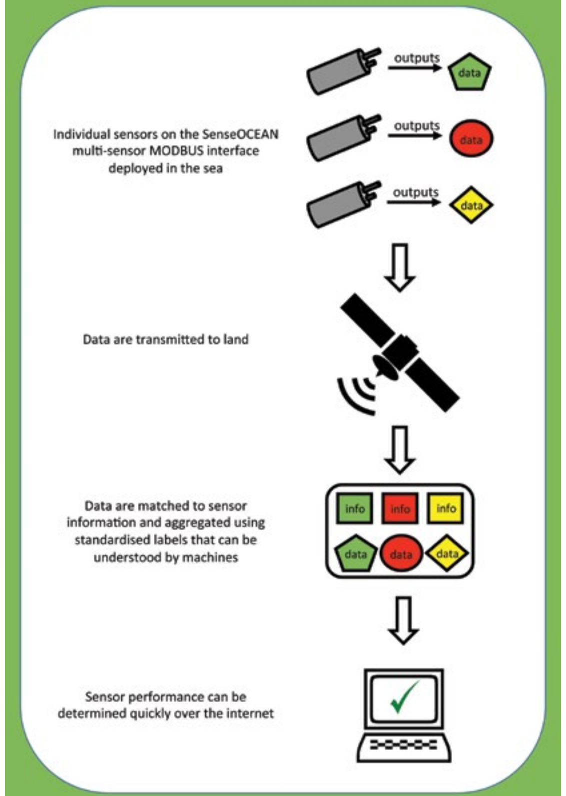
To enable data processing and dissemination to be automated, opening data up to the 'Internet of Things', and to maximise the scientific and societal impact of data collected, the SenseOCEAN project has enhanced and implemented data standardisation based on open internationally agreed standards. Namely the World Wide Web Consortium Linked Data and Open Geospatial Consortium Sensor Web Enablement. The SenseOCEAN project has worked with international partners to develop common marine templates for the dissemination of marine data.

Individual sensors output data in different ways when the SenseOCEAN multifunctional sensor package is deployed in the environment. To help us quickly examine how well the sensors are performing, the data from each sensor is transmitted to land where they are matched with detailed information about the sensor which produced it, such as its outputs, specification and calibration history. The data and information are then tagged with state-of-the-art non-proprietary standardised labels so that they can be understood by machines. This helps us to automatically align and combine all of the data sent. It also makes it easy to access data and sensor metadata (information describing the data) over the internet.

The impact of this standardisation and machine readable data formats is that it becomes possible to automatically process and combine data. This enables ready creation of data products for industry, academia, government and the public. The use of standards also makes data processing more efficient by reducing complexity and ensuring the increased data volumes are manageable.

Standardisation enables freely available open software to be used to access and interact with the data, and the use of standard terminology to describe data ensures unambiguous data utilisation.

State-of-the-art standardised sensor output



The challenges ahead

SenseOCEAN has given us a suite of tools for marine sensing applications that can directly address key parts of the United Nations Sustainable Development Goal (UN SDG) 14. We have new and exciting technologies for measuring and monitoring the progression of ocean acidification, eutrophication of coastal waters, biodiversity in our oceans, ocean deoxygenation and oceanic greenhouse gases levels. The sensor devices can be used on a range of platforms including floats, autonomous underwater vehicles, moorings, benthic landers and ships from the open ocean to the coast.

In coming years we can anticipate the development of autonomous marine sensor systems to detect and monitor microplastics, noise of human derived activities (shipping, oil exploration, coastal windfarm development) and emissions from shipping activities. Sensors are required that address emerging environmental issues, such as those that can determine community structure and function (phytoplankton, zooplankton and bacteria). Improved in situ sensor monitoring approaches are required to facilitate offshore industrial operations, including hydrocarbon exploration and extraction, windfarms, carbon capture and storage.

Looking forward, the devices can be used for monitoring fish farms, sewage outfalls and industrial discharges to ensure that ecosystem services are not harmed. The sensors will allow us to monitor ocean acidification and oceanic greenhouse gas (e.g. CO_2, N_2O) levels in view of the emission reduction measures related to the Paris Agreement. The diminishing role of the ocean taking up greenhouse gases, and thereby mitigating climate change, will form an important future application of sensors. A widespread future application of sensors will increase our confidence that the seas around us are clean and safe for all. As the costs of sensor systems are reduced, we can see a time when we will have a network providing real-time data that allows us to respond and provide input to forecasting models, and deliver information to decision support systems for process control and disaster mitigation.

SenseOCEAN Partners:

Natural Environment Research Council, UK (Coordinator)

Aarhus University, Denmark

Alfred Wegener Institut Helmholtz Zentrum für Polar und Meeresforschung, Germany

Chelsea Technologies Group, UK

CNRS-LEGOS, France

Graz University of Technology, Austria

Max Planck Institute of Marine Microbiology, Germany

nke Instrumentation, France

Pyro Science GmbH, Germany

TE Laboratories, Ireland

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