SCHeMA

Integrated in Situ CHEmical MApping probes

FP7-OCEAN 2013.2: GA-614002 October 2013 - September 2017
www.schema-ocean.eu
Content

3 SCHeMA project: objective, motivation, main achievements
5 Target hazardous chemical and biological compounds
6 Species related to the Carbon cycle sensing module
8 Nutrient sensing module
10 Trace metal sensing module
12 Portable VOCs sensing system
14 Mini Algae sensing module
16 Autonomous modular integrated observation system
17 Web-based system interface and data information system
19 Field biogeochemical processes observation
21 Summary and outlook

Photography, images and Figures have been kindly provided by members of the project and may not be copied, printed or otherwise disseminated without express written permission of SCHeMA
The SCHeMA Project

The SCHeMA multi-disciplinary collaborative project aimed at providing an open and modular sensing solution for in situ high resolution mapping of a range of anthropogenic and natural hazardous compounds. Key targets were species relevant to the carbon cycle, macro-nutrients, micro-nutrients/pollutants, hazardous algae species and volatile organic compounds. All these compounds may adversely affect marine ecosystems, living resources and ultimately human health. The long-term objective is to provide innovative tools to enhance ocean observing system capabilities to rapidly localise problems and alert targeted groups.

Motivation

The World’s oceans and seas, and especially coastal areas have a huge impact on our daily lives. They play an integral role in the Earth's climate and weather. The marine ecosystems are also vital to the livelihood and food security of billions of people around the world, and to the economic prosperity of most countries. However, sea- and land-based human activities are increasingly impacting the health of our marine ecosystems. No economy can sustain its prosperity if the natural resource upon which this prosperity depends is systematically being degraded. **Ocean sustainability is today recognized as one of the major challenges of the 21st century.**

Marine environments, including organisms, are vulnerable and influenced by a wide diversity of anthropogenic and natural substances that may have adverse effects on the ecosystem equilibrium, living resources and, ultimately human health. Identification of relevant types of hazards at the appropriate temporal and spatial scale is thus crucial to detect their sources, to understand the processes governing their magnitude and distribution, and ultimately to evaluate and manage their risks and consequences to maintain marine biodiversity and prevent economic losses.

The traditional monitoring approach, based on field campaign sampling followed by analysis of the collected samples after return to the laboratory, is not appropriate for this purpose as it can only harvest data for a limited time-space window. It is also is very costly and time consuming.
Ocean monitoring: present and future

Nowadays, monitoring approaches involve the use of submersible sensing devices providing capability for in situ, long-term and frequent analysis. However, the commercial availability of field deployable sensors and sensing devices is still limited, and most of these tools tend to be too large, expensive, and power-hungry, thus preventing their widespread use.

Current research and developments focus on more robust, easily usable, cost effective multifunctional autonomous sensing tools that provide reliable in-situ measurements of key parameters. Design and production of cost-effective sensors suitable for large-scale production is a key requirement. The sensing probes should also be compact enabling deployment from several types of platforms like free floating devices, moored buoys, platforms, or ships. Sensor probes by themselves are pointless if they cannot be installed on hosts capable of transmitting the information. Data flow issues, storage, transmission, standardization and accessibility are therefore key features to their integration as part of an end-to-end system.

The partners of SCHeMA have successfully developed an array of miniaturized devices combining various innovative analytical and technical solutions, namely: on-chip sensor arrays; antifouling membranes; solid state ion-selective membrane electrodes; in-line desalination device; passive acidification modules; multispectral optical sensing devices. These devices were assembled into four compact, low power consumption, multichannel submersible probes based on advanced green technology. A Network Controller, dedicated wired/wireless communication interfaces, and web-based front-end system were also developed. These devices enable plug-and-play connection of a specific suite of sensing probes; remote control of the sensing network; data transfer, storage, standardization, modelling and user-friendly accessibility by public authorities, scientists and existing observation/monitoring systems.

The SCHeMA open and modular sensing solution for in situ autonomous high resolution mapping of a broad range of biogeochemical parameters

Interfacing of the SCHeMA submersible devices and a commercial multiparameter probe provides a fully integrated autonomous marine water quality observation system with capability for high-resolution simultaneous quantification of species relevant to the carbon cycle; macro-nutrients; micro-nutrients/pollutants; hazardous algae species; master bio-physicochemical parameters. Portable systems, based on promising analytical approaches, allowing the detection of the biotoxin saxitoxin and a range of volatile organic compounds were also developed. The SCHeMA integrated multifunctional marine water quality observation system has been successfully field evaluated, validated and applied in Atlantic and Mediterranean coastal areas and its capability demonstrated to potential end-users.

This brochure gives an overview of the main achievements made over the last four years of the SCHeMA Project.
Target hazardous chemicals and biological compounds

- Bioavailable trace metal species
- Species relevant to the carbon cycle
- Nutrients
- Volatile organic compounds
- Potential harmful algae

SCHEMA focused on the quantification of compounds that may harm the equilibrium of marine ecosystems, potentially impacting human health, the fishing industry, coastal tourism, and the long-term sustainability of our seas and oceans.

Trace elements are ubiquitous elements influenced by diverse components of the Earth’s geochemistry, and playing critical roles in ecosystem function. Some metals (e.g. Hg, Cd, Pb) and metalloids (e.g. As) have high toxicity even at very low concentrations, while others are either essential or toxic (e.g. Cu, Zn), depending on their concentrations, chemical form, and the nature of the organisms exposed. Metal compounds, due to their intrinsic properties of toxicity, persistence, and/or tendency to bioaccumulate, may have a long-term impact on the biomass composition, activity and health, even a long time after a significant decrease in their release. Bioaccumulation of specific trace metal species may also induce the endogenic production of organic compounds or biotoxins related to biological detoxification processes.

Problems with man-made organic pollutants are mainly related to their toxicity, long degradation period and/or liability to bioaccumulate. The impact of organic compounds is largely determined by the form in which they enter the environmental compartment and by the kinetics of any subsequent degradation processes. Anthropogenic release of nutrients as well as of CO2 lead to significant perturbation of the water quality of the estuaries and coastal zones, e.g.: (harmful) algal bloom and concomitant eutrophication; oxygen depletion and phycotoxin release; change in water carbonate saturation; transition of coral reef ecosystems dominated by corals and coralline to sytems being dominated by seaweeds and fleshy macro algae. Potential changes to the climate due to global warming may also impact the water resources in unforeseen ways. For example, increase in temperature may increase bacteria activities which may enhance solubility and/or toxicity of pollutants (e.g. reduction of As(V) to As(III) which is 60 times more toxic and more soluble; methylation of Hg(II)). Increase in rainfall and intense floods may in turn induce additional release of hazardous species from both natural and anthropogenic sources through fresh-water run-off or erosion of contaminated sediments/soils.

Combining rugged, reliable submersible sensing probes enabling the simultaneous spatial and temporal observation of all these compounds are required to obtain a more complete picture on their behavior and fate as well as a better prediction of their synergic impact.
Carbon Cycle Sensing Module: CSM

- 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 urgent importance to study ocean acidification caused by the absorption of anthropogenically emitted CO₂. Since the concentrations of the associated chemical species (CO₂, 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.

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 membranes¹ for pH, carbonate and calcium together with a reference electrode.

(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. The detection cell is placed together with the algae module into a water- and pressure-proof cylindrical housing, which is connected to the electronics part (hardware for pump and valve control, potentiometric 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 it into the titanium cage together with the rest of SChEEMA probes.

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 drifts 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 Harbor (Italy) deployed at 4.3 m depth.

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. Thereby, interesting biochemical trends has been found, such as day/night cycles and temperature dependence of carbonate and calcium levels in Genoa Harbor (Italy) as well as tidal-dependence in Arcachon Bay (France).

\[\begin{align*}
\text{pH} & \\
\text{Carbonate (nM)} & \\
\text{Calcium (nM)} & \\
\end{align*}\]

\[\begin{align*}
\text{pH} & \\
\text{Carbonate (nM)} & \\
\text{Calcium (nM)} & \\
\end{align*}\]

2. In situ temporal variation of pH, carbonate and calcium during a deployment in Genoa Harbor (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.
Nutrient Sensing Module: NSM

- Accurate detection of nitrate in seawater
- Inline coupling of needed pretreatments
- 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 specially suitable for this purpose\(^2\) 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\(^2\) and passive acidification modules\(^3\) are coupled to the detection cell. Thus, the desalination module reduces the amount of chloride in seawater down to milimolar 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.

\[\text{NSM image and fluidics design. 1: desalination unit, 2: valve, 3: acidification unit, 4: potentiometric flow cell, 5: submersible housing.}\]

The Desalination unit\(^2\)

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 \(\sim 5 \text{ mM}\). The desalinator operates by the exhaustive electrochemical plating of the halides from the thin layer sample onto a silver element as silver chloride (E\(_{\text{app}}\) = 800 mV, t=300 s), which is coupled to the transfer of the counter cations across a permselective ion exchange 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 detection of salinity without the need of changing the probe, as in the case of conductivity measurements.

The Acidification unit

The working principle of the developed acidification unite relies on the cation-exchange process between the sample and an ionic-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 (Figure 2) clearly show tidal-dependence of chloride and nitrate levels.

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.
Trace Metal Sensing Module: TMSM

- 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

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). Only some specific metal species are potentially available for bio-uptake. Bioavailability is therefore of primary concern when considering if a trace metal serves as micronutrient 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 allowing direct, simultaneous measurements of the bioavailable fraction of cadmium, lead, copper, zinc, arsenite and inorganic mercury (Cd(II), Pb(II), Cu(II), Zn(II) As(III), Hg(II)) with sensitivity at sub-nanomolar (ng/L) level using antifouling Gel Integrated MicroElectrode arrays (GIME).

![Diagram of TMSM](image)

*Details of the key components of the TMSM (a). TMSM ready for operational deployment (b).*

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. When a GIME sensor is interrogated using anodic stripping voltammetry, the output recorded signals are directly proportional to the concentration of the dynamic metal species (sum of free metal ions and small labile complexes). The dynamic fraction of trace metals correspond to the maximum concentration of metals potentially available for bio-uptake, and therefore represents the metal fraction with the highest risk of toxicity.  

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 incorporate three potentiostats and pre-amplifiers, a 3.4V power supply as well as all required hardware and firmware for measurements of the target trace metals, pressure and temperature; background subtraction; automatic peak current measurements and their conversion into concentrations; data storing; and data transmission via wired or wireless interface.

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 hours time interval. A life time of typically one month were observed for the GIMEs used. During their one-month operational deployment, up to 350 simultaneous measurements of the four metals were successfully achieved.

The TMSM was also successfully applied for the simultaneous detection of all the target metals 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). The results recorded revealed that, in dynamic tidal coastal ecosystems, the concentration of the bioavailable fraction of the targeted trace metals may double within few hours (Arcachon Bay) and varies, following different trends depending on their complexation properties, by up to one order of magnitude in the salinity / turbidity gradients of the Gironde Estuary.

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 the Gironde Estuary (June 2017).
Portable VOCs sensing module: VOCs-SM

- Accurate and reliable measurements
- Direct chemical sensing and continuous monitoring of dissolved volatile organic compounds
- Easy maintenance

The importance of detecting volatile organic compounds (VOCs) such as benzene, toluene, and the xylene isomers (BTX) along with other hazardous pollutants is based on their toxicity, mutagenicity, and carcinogenicity having a potential risk to humans, animals, and the marine ecosystem.

Until now, detection of VOCs is conventionally performed using chromatographic methods, e.g., gas chromatography and high-performance liquid chromatography combined with a variety of detection schemes. However, such methods are time- and cost-extensive, and largely limited to laboratory-based measurements. Therefore, real-time monitoring directly in-field is not possible.

The infrared fiber-optic evanescent wave/field spectroscopy has been increasingly used for direct measurements of VOCs dissolved in aqueous matrices (e.g., drinking water, surface water, seawater, etc.)\(^1\)\(^4\) This method holds promise for detection of hazardous VOCs pollutants directly either on-site and in situ in the marine environment\(^3\)\(^4\) since it is time-saving, and cost-effective due to the redundancy of taking samples to a well-equipped laboratory. Moreover, sensing in the mid-infrared (mid-IR) spectral region (4000 - 400 cm\(^{-1}\)) provides inherent molecular selectivity. It is possible to evaluate single- or multi-component systems due to highly characteristic absorption bands of organic molecules in the so-called fingerprint region.

UULM, as part of SCHeMA, developed a portable optochemical sensor based on mid-IR fiber-optic evanescent field spectroscopy capable of simultaneously detecting multiple VOCs. The sensing element (i.e., transducer) is a silver halide (AgX) fiber covered by a hydrophobic polymer membrane and located inside a µ-flow cell build by microtechnolgy. The AgX fiber acts as an internal total reflection waveguide. It has a flattened section actually transducing the absorption signatures of VOCs enriched from aqueous solution into hydrophobic polymer membrane coated onto this sensing segment. The analyte molecules are enriched into the membrane, and probed by the evanescent field, while water is effectively excluded due to the hydrophobic nature of the polymer.

By the use of a pump, the seawater to be investigated can be directly transported from the depth or from surface waters inside the microfluidic platform (i.e., flow cell) for analyte enrichment. Evaluation of the obtained IR spectra is readily performed via univariate methods (i.e., evaluation of peak area) due to well separated spectroscopic signatures, and may be further advanced using data evaluation strategies.

The portable VOCs-SM was evaluated during a field measurement campaign in Arcachon Bay providing excellent accurate and reliable results (high \(R^2\)-values for the established calibration functions; detection limits at around 800 µg/L were achieved) for the simultaneous detection of ten analytes.
The hydrophobic polymer coating not only enriches the analytes, but also protects the silver halide fiber (i.e., sensing element) from degradation in seawater. The sensing fiber is considered as a consumable that is regularly exchanged during extended application periods (approx. 6 months). Further required maintenance is the regular exchange of tubes connected to the flow cell ensuring minimal losses due to evaporation (approx. 6-12 months).

The VOC-SM can readily be transported for on-ship, on-shore, or moored buoy applications enabling on-site monitoring of contaminated coastal areas, harbor areas, and industrial sites. Remaining challenges are further improvement of the achievable detection limits towards the environmental limits recommended by the European Union. Currently, the VOCs-SM may serve as a real-time alarm system in case of accidental emissions or release providing a high molecular selectivity.

Mini Algae Sensing Module: ASM

- 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 energy absorbed 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. 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. 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.

Picture of the algae detection module (left and right) and the modular LED modules used as excitation sources (middle).
In the detection module, 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 reference data and a multivariate pattern recognition algorithm allows identification of the taxonomic affiliation of the sample.

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. This approach allows the measurement of changes in the biomass concentration that indicate the onset and deterioration of an algal bloom.

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.

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.

The fluorescence signal intensity 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 (see zoom plot).
Autonomous modular integrated observation system

- Network controller
- Plug-and-play connection of SCHeMAS' and commercial sensing probes
- Simultaneous measurements of a range of hazardous chemical and biological compounds

The simultaneous measurement of a large number of parameters at appropriate spatial and temporal scale is of urgent importance to go deeper insight into the potential toxic effects of compound mixtures. Aquatic ecosystems are indeed continually exposed to a very complex mixture of chemical and biological substances, the composition of which is always changing. However, in the great majority of risk assessments, only single compounds are considered and there are no generally applicable guidelines as to when and how assessment of combinations of hazardous compounds should be carried. One of the main concerns is whether some compounds can enhance the toxic effect of other ones, so that they jointly exert a larger effect than predicted (referred to as “cocktail-effects”). The acquisition of detailed data bank is also required to deeper understand the complex bio-physicochemical processes insuring the proper functioning of the marine ecosystems and assess any dysfunctionning related to anthropogenic pressure as quickly as possible. Both aspects are crucial for sustainable management of the oceans, and especially the coastal area.

Integration of the submersible chemical sensing probes developed (CSM, NSM, TMSM, ASM) into an autonomous modular observation system for simultaneous mapping of the target chemical and biological compounds was therefore one of the specific objectives of SCHeMA.

To achieve this, a Network Controller were developed. This module is based on a Linux operating system and up-to-date networking technologies used for localization and long distance data transmission. The Network Controller allows plug-and-play connection of a selected suite or all SCHeMA submersible sensing probes as well as other commercial available probes (e.g. CTD probes), thus providing an open and modular sensor network whose the configuration can be adapted to the requirements of specific environmental studies or pollution controls.

The Network Controller acts as gateway between the mapping probe network and the SCHeMA web-based information system facilitating wireless sensing module registration and data transfer using international Open Geospatial Consortium Sensor Web Enablement (OGC-SWE) standards.
Web-based system interface and data information system

- Sensor probe registration
- Real-time visualization of the data recorded by all the probes deployed
- Sensor probe reconfiguration
- Data standardization and access

Access to marine data is of crucial importance for marine research and a key issue for various studies, from climate change prediction to offshore engineering. Sharing observed data benefits everyone: changes in one country’s waters affect those of its neighbors. National data alone are therefore not sufficient to improve our knowledge on the sea as a European and global system connected by shifting winds, seasonal currents, etc.

A web-based data information system, based on implemented and enhanced international standards, was developed as part of SCHeMA. This system is a chain of devices, hardware and software modules, and communication interfaces that cover the entire communication process from sensing modules to web application for data standardization, stamping, storage, processes, distribution and sharing.

The Network Controller is the transducer of the information sent by the in situ integrated mapping probes to a Land Station. The land station provides a web-based system interface for accessing sensor information (metadata registries) and measured sensor observation (data files). The hardware/software modules allows encoding and standardization of the sensor information and data send under different formats by the various SCHeMA and commercial sensing probes. The resulting machine readable formats enable automatic management and processing of all the recorded information as well as open access to measured sensor observations – through Observation and Measurements (O&M) standard – as well as sensor descriptions – encoded in Sensor Model Language (SensorML).

The web-based data information system architecture is composed of four main modules:

**Sensor Observation System (SOS) Interface:** web service interface enabling (i) the Data producers (the SCHeMA submersible probes) to register themselves to the system and to send its collected observation, and (ii) the Data consumers (users, client applications) to discover and retrieve data and metadata on SCHeMA probes and observations. This interface is based on the Open Geospatial Consortium Sensor Observation System (OGC-SOS) standard (one standard in the OGC Sensor Web Enablement (SWE) suite of standards)

**Database (DB):** the relational database management system (RDBMS) where the metadata (information on the sensor and sensing probes) and data are stored. It is based on a Microsoft server built on top of Structured Query Language (SQL), a standardized programming language that database
administrators and other information and technology professionals use to manage databases and query the data they contain.

**Notification Manager:** application managing the alarms notification to the users; an alarm will be send when e.g. a sudden increase in concentration of one or several hazardous compounds or a failure of one sensing probe is detected.

**Web Interface:** user front-end system to access from the web all the information stored in the SCHeMA system. The web user interface (WUI) allows the user to manage the probes/sensors, view the stored observations and metadata, handle alarms and access remotely the sensors configuration features. Moreover, The SCHeMA WUI offers different means to discover, access and download available data, more specifically the system integrated WMS (Web Map Feature), SOS Web Interface and manual discovery and download features. The SCHeMA WUI is running a specific module to manage user authentication and user rights. Some of the features are restricted to SCHeMA partners.

---

**The SCHeMA web data portal**

The SCHeMA data portal has been online since April 2016 at the address [http://dataportal.schema-ocean.eu](http://dataportal.schema-ocean.eu) and, at the time of writing this report (November 2017) have more than 90K page hits.
Field biogeochemical processes observation and system demonstration

- Sensor validation and application in various European coastal key areas with high socio-economic impacts (tourism, oyster farming...)
- Accurate detection at high resolution and under drastic conditions (turbidity, salinity gradients...)
- Observation of relevant biogeochemical processes improving scientific knowledge on target pollutants behaviour in coastal marine waters
- End-users demonstration

A range of hazardous compounds were detected and quantified in situ by the SCHeMA autonomous integrated system allowing continuous monitoring of diverse coastal aquatic environments, reflecting both natural and anthropogenically modified conditions. Performances of the developed system were tested in real conditions during numerous field tests held in European coastal key areas. To evaluate the reliability of the in situ data, samples were collected in parallel to the in situ measurements during each field campaign and analysed after return to the laboratory using a panel of traditional techniques. In the different field tests, sensors were either moored to an observation platform or deployed on-board Research Vessels.

Among the various relevant environmental observations, some examples are presented.

1. Pollution gradient in an industrial harbor: TMSM detection of bioavailable trace metals supposedly freshly released into the environment by human activities.

2. NSM detection of increasing agricultural inputs from anthropogenized watersheds at ebb tide; sensor functioning over a tidal/diurnal cycle

![In situ dynamic Cu TMSM](image1)

![In situ nitrates NSM](image2)
3. ASM determination of relative abundance of different algal groups, sensor functioning in a highly turbid estuary over a diurnal cycle

Overall, the field application campaigns of the SCHeMA multifunctional observation system in European coastal key areas were successful. All the results proved the efficiency of both the individual probes and the integrated system in providing relevant high resolution in situ data. The rich data sets provided new insights in various biogeochemical processes through high spatial and temporal resolution data, obtained for the first time. These original results will be disseminated to the scientific communities via publications in peer reviewed scientific journals. The field data also demonstrated the capability of the individual probes and integrated multifunctional system in tracking sources of hazardous chemical and biological compounds, and in acting as an alert system for the surveillance of these substances. For example, in the Arcachon Bay, South-West France, the SCHeMA integrated multifunctional sensing system detected (i) a diffuse source of zinc and copper, under their most bioavailable forms, from industrial origin; (ii) nutrient inputs issued from agriculture and carried to the bay by freshwater effluents; and (iii) identified the presence of Dinoflagellates, phytoplankton group producing a neurotoxin. These data will help researchers to advance monitoring strategies, boost the ability to predict the impact of target compounds on the local ecosystem, and give clues for the sustainable management of the bay’s ecosystem.

Potential end-users were invited at various occasions, including during the SCHeMA field application in the coastal Atlantic Ocean and Lugurian Sea. More than 60 persons from different institutions and SMEs working in various sectors (water management field, environment protection policy, National or European environmental monitoring and marine environmental protection programs) have participated to the SCHeMA demonstration activities. Overall, the collected feedbacks were fully positive. The project and its outcomes stimulated interest in its innovative aspect, interdisciplinary developments, and applications. The multi-element analysis capability of each individual probes for specific group of hazardous compounds was regarded as of special interest, and in line with the needs of on-going scientific environmental programs and water quality monitoring activities.
Summary and outlooks

The SCHeMA partners have developed miniature sensors that can map in situ and at high resolution a number of variables relevant to several descriptors of the Marine Strategy Framework Directive and the United Nations Sustainable Development Goals, namely: ocean acidification, biological diversity, marine food webs, non-indigenous species, human-induced eutrophication, concentration of contaminants, hydrographical conditions.

These sensors were assembled into miniature low power consumption submersible probes based on advanced green and EnOcean technology. A network controller and Web-based information system, based on OGC-SWE interfaces and GSM transceivers, were also developed. Interfacing of all the devices provide a fully integrated autonomous modular sensing network to identify and quantify substances that are harming the equilibrium of marine ecosystems, potentially impacting human health, the fishing industry, coastal tourism and the long-term sustainability of our seas and oceans.

The SCHeMA individual sensing probes and the autonomous marine water quality observation system have been successfully field evaluated, validated and applied in contrasting areas of the Atlantic and Mediterranean coastal zones. Their capabilities, when operating in real conditions, were demonstrated to potential end-users as part of several field applications and demonstrations.

SCHeMA did promote new skills, jobs and collaborations as well as new business opportunities in the world market of marine sensors and autonomous monitoring platforms. Sixteen early stage researchers (PhDs and PostDocs) have contributed to the successful development and validation of the SCHeMA sensors, sensing probes and integrated system. SCHeMA has collaborated with other EU funded Ocean of Tomorrow projects in the enhancement and development of international standards and platforms for the dissemination of marine data. This is expected to push not only European programs in Ocean observations, but also Europe’s role as a global leader in data interoperability and improved data access. SME partners have foreseen the commercialisation of several SCHeMA R&D solutions.

SCHEMA partners are now working on bringing their field validated prototypes to the market, as well as improving the ability of the probes to detect other detrimental chemical compounds.